Geophysical Research Letters

RESEARCH LETTER
10.1029/2018GL079529

Key Points:
- This study reports that the mortality of modern coral reefs could be exacerbated by volcanic eruptions
- The anomalies of rare earth contents and Al/Ca ratios associated with microdomain images indicate an external impact from the 1991 Pinatubo
- Our results highlight amplified responses of vulnerable coral reefs to environmental changes under global warming

Supporting Information:
- Supporting Information S1
- Data Set S1

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Citation:
Wu, C.-C., Shen, C.-C., Lo, L., Hsin, Y.-C., Yu, K., Chang, C.-C., et al. (2018). Pinatubo volcanic eruption exacerbated an abrupt coral mortality event in 1991 summer. *Geophysical Research Letters*, *45*. https://doi.org/10.1029/2018GL079529

Received 11 JUL 2018
Accepted 1 NOV 2018
Accepted article online 8 NOV 2018

Pinatubo Volcanic Eruption Exacerbated an Abrupt Coral Mortality Event in 1991 Summer

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Abstract Widespread coral bleaching and mortality associated with global warming have occurred frequently since the phenomenon was first documented in the early 1980s. One such episode that occurred in 1991 over the tropical Pacific-Indian Ocean region has been attributed to high summer sea surface temperatures. However, we found that sea surface temperature values from the South China Sea region do not provide a comprehensive explanation for the event. Our results, based on time series records of rare earth elements, trace element Al/Ca ratios, and microdomain images from corals in the South China Sea, suggest that this coral mortality event was exacerbated by heavy ash fallout from the cataclysmic 1991 volcanic eruption of Mount Pinatubo. Our findings highlight the profound impact of a volcanic eruption on the modern vulnerable coral reef ecosystems, already under the stress of global warming.

Plain Language Summary Intensive and frequent coral bleaching events have occurred under global warming conditions in recent decades. However, abrupt and extensive mortality episodes, such as which occurred in the South China Sea in mid-1991, cannot be explained solely on the basis of high summer sea surface temperatures. Here we examine this event in the light of time series of rare earth elements, trace element Al/Ca ratios, and microdomain images for coral samples collected in the South China Sea region. Our results suggest that the second-largest volcanic eruption of the 20th century, the 1991 Mount Pinatubo volcanic eruption, exacerbated this coral mortality event. The sensitive impacts of such a volcanic eruption on modern vulnerable coral reefs, associated with the stress of thermal conditions, are demonstrated.

1. Introduction

Coral reefs are one of the integral components of the biosphere (e.g., Veron, 1995), hydrosphere (e.g., Roberts et al., 2002), geosphere (e.g., Reaka-Kudla, 1997), and anthrosphere (e.g., Nyström et al., 2000). They are among the most diverse ecosystems on Earth and offer habitat for copious marine organisms (e.g., Roberts et al., 2002). Food and nutrients from reef-associated organisms are consumed by billions of humans (e.g., Moberg & Folke, 1999). Biodiversity provides reef communities survival options after environmental disturbances, such as tropical storms, cyclones, and tsunamis (Knowlton et al., 2010; Nyström et al., 2000). However, currently, coral reefs worldwide are struggling under the effects of rapid climate change associated with global warming (e.g., Hughes et al., 2017, 2018; Spalding & Brown, 2015).

Coral bleaching events, even severe to mass mortality, can be caused by environmental stresses (e.g., Lough & van Oppen, 2009). When stresses exceed a threshold tolerance, a coral's population of endosymbiotic algae (zooxanthellae) is expelled, and whitening (bleaching) occurs (Glynn, 1996). The first report of mass coral bleaching emerged in 1982–1983 in the eastern tropical Pacific (Glynn, 1983, 1984) and was followed by

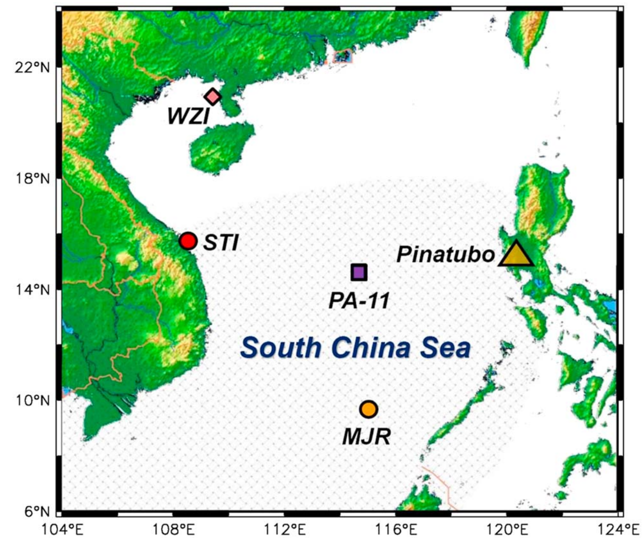

Figure 1. Map of the South China Sea region. The symbols denote locations of Son Tra Island (STI) coral (red circle), Meiji Reef (MJR) coral (orange circle), Weizhou Island (WZI) coral (pink diamond), open South China Sea seawater (purple square, station PA-11; Alibo & Nozaki, 2000), and Mount Pinatubo (yellow triangle). The shaded area represents the fallout distribution territory of the Pinatubo volcanic eruption in mid-June 1991 (modified from Paladio-Melosantos et al., 1996).

severe and global-scale events affecting many of the world's reefs in 1998, 2010, and 2015–2016 (Hughes et al., 2017, 2018). These coral bleaching events prompted immediate studies to elucidate the causes and consequences of reef declines.

A particularly intensive coral mortality event occurred in the summer of 1991. It affected vast regions, including the central Pacific (Hoegh-Guldberg & Salvat, 1995), eastern Pacific (Jiménez & Cortés, 2001), eastern Indian Ocean (Brown et al., 1996), and South China Sea (SCS; Yu et al., 2006). Brown et al. (1996) and Yu et al. (2006) suggested that elevated summer sea surface temperatures (SSTs) during an El Niño phase were primarily responsible, under current global warming conditions. The SCS, the largest marginal sea of the Pacific Ocean, is situated in a meteorologically sensitive zone. Its southern extremity is close to the Western Pacific Warm Pool, whose climate dynamics are intimately related to El Niño-Southern Oscillation (ENSO) variability (Picaut et al., 1996). However, summertime SSTs in the SCS (Smith et al., 2008) between 1991 and adjacent years (1987–1996) do not show any significant temperature differences (Figures S1 and S2), indicating that other factors must have fueled the 1991 summer coral mortality event there. Here we show that rare earth element (REE) contents, trace element Al/Ca values, and skeletal textural features all responded to the 1991 Mount Pinatubo eruption.

2. Materials and Methods

2.1. Sample Collection

We collected a live, massive, 35-cm *Porites* coral head, ST0506, from a water depth of 4 m, off the coast of Son Tra Island (16°13′N, 108°12′E), in central Vietnam, and facing the western SCS (Figures 1 and S3a). An additional supplementary *Porites* coral core, MJL01a, was collected from a water depth of 3–4 m in Meiji Reef (MJR, 9°55′N, 115°32′E), central SCS, in an open-ocean environment surrounded by a reef flat with a large central lagoon (Figures 1 and S4a).

2.2. Geochemical Analysis

We analyzed continuous 4-year REE contents with monthly-to-bimonthly resolution from CE 1990 to 1993 for both corals on an inductively coupled plasma-sector field-mass spectrometer, Thermo Electron ELEMENT II (Shen et al., 2011; supporting information). Ba/Ca, Al/Ca, and Sr/Ca of coral ST0506 with clean treatments (Shen et al., 2005) were also analyzed (Lo et al., 2014). The microdomain skeletal textures of three selected depths of coral ST0506 were also analyzed by a field emission scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (FESEM/EDS) (supporting information).

3. Results

3.1. Temporal Variations of REE/Ca Ratios

Measured skeletal REE/Ca ratios for coral ST0506 are plotted in Figure S5. La/Ca and Yb/Ca ratios are highlighted as representative for the changes of the mass fractions of light rare earth elements (LREE, La-Eu) and heavy rare earth elements (HREE, Gd-Lu) to Ca (Figures 2a and 2b). Distinct and coherent abrupt increases of coral skeletal REE/Ca contents can be observed from spring to summer 1991. Different element/Ca ratios at the peak display an anomaly ranging from 3.2 to 57 times higher than baseline values, from adjacent years in spring 1990 to early 1991 (Figures 2a, 2b, and S5). The sudden REE enrichment ended at a hiatus observed in mid-late 1991. After a 2- to 3-month discontinuity (Shen et al., 2012), the coral recovered in early 1992, and the magnitude of REE/Ca values assumed baseline levels again (Figures 2a, 2b, and S5).

In coral ST0506, La/Ca values increased from 10 to 20 nmol/mol before 1991 spring and climbed to a peak of 678 nmol/mol in the summer of 1991, where the position is prior to the onset of the hiatus (Figure 2a). This maximum is 30–40 times higher than values observed in other baseline years. For the segment above the

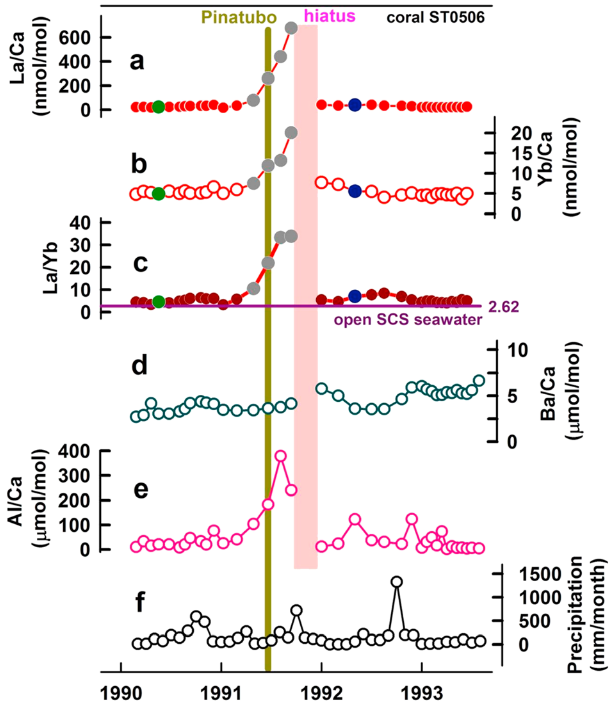

Figure 2. Monthly-to-bimonthly resolved coral ST0506 rare earth element records between CE 1990 and 1993. (a) La/Ca ratios, (b) Yb/Ca ratios, and (c) La/Yb ratios. The purple line shows La/Yb baseline values from an open South China Sea (SCS) seawater station (Alibo & Nozaki, 2000). (d) Ba/Ca ratios, (e) Al/Ca ratios, and (f) monthly instrumental precipitation from 1990 to 1993 (from Da Nang Weather Station). The pink bar indicates the duration of a coral growth hiatus. The dark yellow line denotes the climactic eruption of Pinatubo on 15 June 1991. The green, grey, and blue circles represent the layers corresponding to the rare earth element patterns shown in Figure 3b.

hiatus, La/Ca values dropped to 15–50 nmol/mol in the early 1992. Yb/Ca ratios show a maximum of 20 nmol/mol in the summer of 1991, 4 times higher than values between 1990 and 1993 (Figure 2b).

Similar REE/Ca trends and peaks during the same period in the summer of 1991 are registered in coral MJL01a (Figure S6). La/Ca and Yb/Ca ratios increased from 4.2 to 12 nmol/mol and 1.4 to 2.8 nmol/mol, respectively (Figures S6a and S6b), 2–3 times higher than central SCS baseline values.

3.2. Changes in Coral REE Diagrams

Representative coral ST0506 REE contents for preanomaly, anomaly, and postanomaly, normalized to the post-Archean Australian shale (McLennan, 1989), show a distinct interruption during 1990–1992 (Figure 3b and Table S1). The REE diagram in April 1990 exhibits an increasing trend from Ce to Lu and a negative Ce anomaly, as typical of baseline layers. It represents the characteristics of a no-event coral sample with a symbolic seawater-like REE pattern (Sholkovitz & Shen, 1995; Figure 3c), as observed in a coral from Weizhou Island (21°01′N, 109°04′E; Shen et al., 2011), northwest SCS (Figure 1). From April to August 1991, REE/Ca data display pronounced increases in LREEs and HREEs, and a gradual transformation of the negative Ce anomaly toward more a positive anomaly in the REE diagrams (grey records in Figures 2a, 2b, and 3b). The REE diagrams during June–August 1991 (Figure 3b) with a LREE-enriched and HREE-depleted configuration demonstrate a significant discrepancy from the baseline signatures. These atypical features faded from late 1991 to early 1992. In April 1992, the REE diagram resumes a typical open-ocean seawater pattern with a negative Ce anomaly and HREE enrichment (blue records in Figure 3b).

3.3. Ba/Ca, Al/Ca, and Sr/Ca Records of Coral ST0506

Coral ST0506 Ba/Ca and Al/Ca from 1990 to 1993 are presented in Figures 2d and 2e. Seasonal Ba/Ca data vary from 2.8 to 6.5 μmol/mol during CE 1990–1993. A pronounced Al/Ca pulse is found in the summer 1991 with peak values of 378 μmol/mol, 5–50 times higher than the baseline values of 8.0–100 μmol/mol. SST-dependent Sr/Ca data (Figure S5) were combined with ^{230}Th ages (Shen et al., 2012) to establish a detailed chronology (supporting information).

4. Discussion

4.1. Decipher Possible Sources of REE Anomalies

Coral calcification involves not only the extension of the outermost skeletal material but also skeletal thickening of the growth layer to a depth of 0.5- to 1-cm tissue layer (Figure 5 of Barnes & Lough, 1993). The inclusive trace metal records are therefore biased by a few months with growth that preceded the environmental disturbance (Figure 1 of Taylor et al., 1995). Accordingly, the occurrence of this event, manifested in the SCS coral REE records, could occur in June, July, and/or August 1991 (Figures 2 and S6).

The summer 1991 SST anomalies showed no significant difference at Son Tra Island (−0.13 ± 0.34 °C, 1σ) and Meiji Reef (−0.32 ± 0.49 °C, 1σ), compared with seasonal means in adjacent years 1987–1996 (Smith et al., 2008). In addition, the thermal proxy Sr/Ca record of ST0506 (Figure S5) does not reflect an anomalously high SST in the summer of 1991. These minor SST anomalies indicate that the thermal stress alone was not a fatal factor for the coral mortality event described in this study (Figure S2).

Coral skeletal LREE/HREE ratios can be used to identify different REE sources, such as terrestrial runoff discharge, precipitation, bioproductivity, monsoon evolution, and human activities (Jiang et al., 2018; Jupiter, 2008; Nguyen et al., 2013; Wyndham et al., 2004). Here coral ST0506 LREE/HREE ratios, for example, La/Yb ratios, show relatively low values of 3.2–6.3 in 1990, close to a typical low surface seawater value of 2.62 (Figure 2c) in a SCS open-ocean site (Alibo & Nozaki, 2000; station PA-11; Figure 1). An abrupt La/Yb

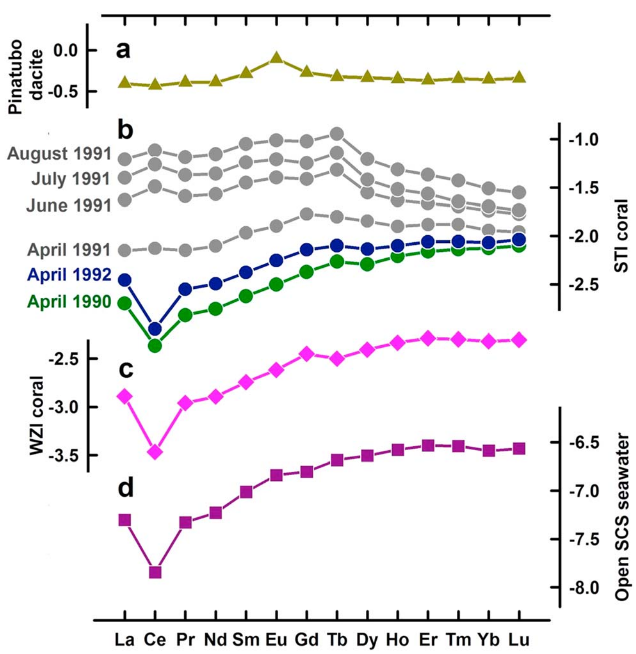

Figure 3. Comparison of shale-normalized rare earth element patterns. (a) Pinatubo dacite. (b) Coral ST0506 rare earth element patterns for period before the 1991 Pinatubo eruption (April 1990, green circle), between-and-after the eruption (June to August 1991, grey circle), and post eruption (June 1992, blue circle). (c) Weizhou Island (WZI) coral (Shen et al., 2011). (d) Open South China Sea seawater (Alibo & Nozaki, 2000).

increase occurred in spring-to-summer 1991, starting with a ratio of 10 and peaking at 34 (Figure 2c). Supplementary coral MJL01a also shows records of about 2–3 times higher La/Yb ratios in mid-1991 (Figure S6c), and the timing of its abrupt increase matches that observed in coral ST0506 (Figure 2c). Pronounced LREE/HREE increases in the summer of 1991 were observed in both corals from the coastal site in central Vietnam (Figure S3a) and the open-ocean atoll in the central SCS (Figure S4a), indicating that local terrestrial runoff (Jupiter, 2008) or pollution (Fallon et al., 2002) cannot be the cause for the REE anomalies.

Skeletal Ba/Ca ratios in nearshore corals reflect precipitation, terrestrial discharge, and flood events (McCulloch et al., 2003; Sinclair & McCulloch, 2004). Coral ST0506 Ba/Ca values of 4.1 μmol/mol in the summer of 1991 are compatible with values of 3.0–6.6 μmol/mol in the adjacent summers. The muted Ba/Ca (Figure 2d) and absence of high precipitation in the summer of 1991 (Figure 2f) suggest that the decoupled high REE contents and La/Yb ratios in coral ST0506 cannot be attributed to regional terrestrial discharge or sediment reworking. These geochemical-based findings are also in good agreement with typhoon track evidence that no coeval typhoons or severe storms swept both coastal central Vietnam and the central SCS in the timing of summer 1991 (Figure S2). Cyclone forcing can thus be excluded.

Aluminum is one of the characteristic and abundant elements in igneous rocks, with a mass fraction range of 10^3–10^4 μg/g (Nockolds, 1954). Al has been used as a trace indicator for volcanic events recorded in carbonates (Siklósy et al., 2009; Wu et al., 2018). Laboratory experiments demonstrated that high amounts of aluminum can be released when tephra enters surface seawater (Frogner Kockum et al., 2006). Our coral ST0506 exhibits extremely high Al/Ca ratios of up to 400 μmol/mol, as compared to the baseline of 10–100 μmol/mol, and displays a distinct pulse in the summer 1991 (Figure 2e). The concurrent increase of Al/Ca and REE contents and ratios in 1991 (Figures 2a–2c) can be explained by the same igneous source.

4.2. REE Anomalies Linked to the 1991 Pinatubo Eruption

The second-largest volcanic eruption of the 20th century, the 1991 Mount Pinatubo in the Philippines (15°14′N, 120°35′E), was coincident with the REE anomalies. The entire duration of these eruptions occurred from 2 April to 2 September. The precursory phreatic eruption of 2 April was small with minor quantities of ash to 500–800 m in height (Global Volcanism Program, 1991). On 15 June, the climactic eruption yielded a maximum altitude of 35- to 40-km ash and spread southwestward, across the SCS and further, to the Bay of Bengal (Holasek et al., 1996; Paladio-Melosantos et al., 1996; shaded area in Figure 1). Large and widespread fallout was collected in sediment traps around the entire SCS region (Wiesner et al., 2004). Hence, this eruption could have been responsible for the regional SCS coral mortality that occurred there in the summer of 1991.

REE diagrams of Pinatubo igneous fallout feature a relative flat pattern with a positive Eu anomaly (Pallister et al., 1996; Figure 3a). The coral ST0506 REE signature following the Pinatubo eruption shows a gradual transformation from a typical seawater-like REE pattern to a peculiar LREE-enriched and HREE-depleted pattern, with a positive Ce anomaly (Figure 3b). This could result from a mixture of tephra and seawater REEs that became incorporated into the coral skeleton (Sholkovitz et al., 1994). The removal of HREEs in mid-1991 can be explained by preferential settling in silts and/or sands, where HREE-enriched minerals are concentrated (Sholkovitz et al., 1999).

The coral REE anomalies in ST0506 and MJL01a are nearly synchronous in mid-1991 (Figures 2a–2c, S5, and S6). The REE peak in ST0506, however, occurs in August (Figures 2a–2c and S5), ~2 months later than the peak in MJL01a (Figure S6). This slight discrepancy is most likely related to the different geographical settings between two sites. In the months following the climactic eruption in June, REEs and Al contents recorded

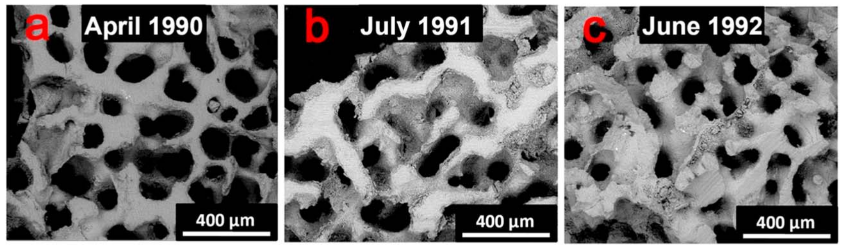

Figure 4. Scanning electron microscope images of three subsamples of coral ST0506. Subsamples were sliced at depths of 15.2, 14.1, and 13.0 cm, corresponding to (a) April 1990, (b) July 1991, and (c) June 1992.

in coral ST0506 were elevated dramatically by direct fallout of Pinatubo ash and from runoff delivery from the catchment area of the Han River to Da Nang Bay (Figure S3a). While over the threshold of environmental tolerance, this coral died in late 1991. The coral recovered in early 1992 and resumed a seawater-like REE pattern (Figure 3b). Between spring and fall 1992, a subdued influx of La/Yb with a range of 4.6–8.3 occurred (Figure 2c), suggesting that residual Pinatubo fallout on land continued to affect the coastal zone by precipitation or storms in the following year.

In coral MJL01a, the La/Ca peak coincides with the timing of the Pinatubo climactic eruption in June (Figure S6a), as well as a secondary influx after the spring of 1992 (Figure S6a), indicating that the dominant REE source was direct fallout. The La/Ca maximum is 13 times lower than that found in the ST0506 record (Figures S6a and 2a), that is subject to dilution since it is an open-ocean site (Figure 1). The La/Yb plateau observed in both June and the following 1–2 month(s) (Figure S6c) suggests that the signals lingered in the surface water for a couple of months following the climactic eruption of 15 June. The environmental impact at the open-ocean site was presumably mitigated by dilution as well.

4.3. Microdomain Images

The images of microdomain skeletal structure of coral ST0506 in different transverse sections by FESEM/EDS techniques are given in Figure 4. Selected slices from normal growth layers in 1990 April (Figure 4a) and 1992 June (Figure 4c) contain only fine pristine skeletal carbonate. A slice from the 1991-July anomalous layer (Figure 4b) after cleaning shows that ash was incorporated within the voids of the coral lattice, with enriched matrices including not only C (16%), O (58%), and Ca (9.5%) but also significant amounts of Al (4.7%), Si (8.7%), and K (2.2%), as compared with baseline growth layers with only C (15%), O (50%), and Ca (35%). This microdomain evidence further supports our interpretation of an ash source for the REEs. Hence, evidence from microdomain features, REE and Al/Ca signatures (Figures 4d and 2a–2c and 2e), all suggest that the elevated REEs and Al were at least partly incorporated from particulate phases.

4.4. The Connection Between Volcanism and Coral Mortality

When volcanic ash falls upon the ocean surface, it can release amounts of acids and metals to the environment, leading to acidification and surface water contamination (Frogner et al., 2001). Such factors are among the main contributors to reef degradation and coral mortality (e.g., Anthony et al., 2008; Yu et al., 2004). The image shown in Figure 4b indicates that abundant ash covered the coral surface in the summer of 1991. Such an ash cover would directly interfere with polyp respiration and decreasing photosynthesis by symbiotic zooanthellae. Ash suspended in the water column above would further stress the coral by reducing the amount of available light. Since coral reefs are becoming more and more fragile under the stress of global warming (Hughes et al., 2018), we expect that corals would be especially vulnerable to an abrupt external event, such as the Pinatubo volcanic eruption.

5. Conclusions

This is the first study, to our knowledge, that demonstrates that modern coral reefs were strongly exacerbated by a distant volcanic eruption and yielding sensitive amplified responses under current high global thermal conditions. Contemporary continental nearshore reefs are more susceptible than their open-ocean counterparts. Given that the integrity of the biosphere has reached a high-risk planetary boundary in the Anthropocene (Steffen et al., 2015), threats to reef vulnerability may lead to unprecedented biodiversity loss in the nearer future (Hughes et al., 2018; van Hooidonk et al., 2013). Fully understanding the diverse biogeochemical processes and external impacts on coral reefs are needed for the sustainability of the biosphere.

Acknowledgments
We thank all authors and researchers who participated in this project. We are particularly grateful to K.-Y. Wei, S.-Y. Lee, and Bodo Hattendorf for their insightful discussion and comments on this manuscript. We are thankful for financial support by the Science Vanguard Research Program of the Ministry of Science and Technology, Taiwan ROC (106-2628-M-002-013 to C.-C. S.), the Higher Education Sprout Project of the Ministry of Education, Taiwan ROC (107L901001 to C.-C. S.), and the National Natural Science Foundation of China (91428203 to K. Y.). The details of coral samples, methods, supplementary figures, and original coral skeletal REE concentration data are shown in the supporting information S1. The original coral REE/Ca and trace element Ba/Ca, Al/Ca, and Sr/Ca data can be retrieved from the Data Set S1. The authors have no conflict of interests to declare.

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