

Lithium in the aragonite skeletons of massive *Porites* corals: A new tool to reconstruct tropical sea surface temperatures

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[1] Previous studies have demonstrated the potential for the Li content of coral aragonite to record information about environmental conditions, but no detailed study of tropical corals exists. Here we present the Li and Mg to Ca ratios at a bimonthly to monthly resolution over 25 years in two modern *Porites* corals, the genus most often used for paleoclimate reconstructions in the tropical Indo-Pacific. A strong relationship exists between coral Li/Ca and locally measured SST, indicating that coral Li/Ca can be used to reconstruct tropical SST variations. However, Li/Ca ratios of the skeleton deposited during 1979–1980 do not track local SST well and are anomalously high in places. The Mg/Ca ratios of this interval are also anomalously high, and we suggest Li/Ca can be used to reconstruct tropical SST only when Mg/Ca data are used to carefully screen for relatively rare biological effects. Mg/Li or Li/Mg ratios provide little advantage over Li/Ca ratios, except that the slope of the Li/Mg temperature relationship is more similar between the two corals. The Mg/Li temperature relationship for the coral that experienced a large temperature range is similar to that found for cold water corals and aragonitic benthic foraminifera in previous studies. The comparison with data from other biogenic aragonites suggests the relationship between Li/Mg and water temperature can be described by a single exponential relationship. Despite this hint at an overarching control, it is clear that biological processes strongly influence coral Li/Ca, and more calibration work is required before widely applying the proxy.

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1. Introduction

[2] The possibility to extend the instrumental record of sea surface temperatures (SSTs) by analyzing the chemistry of the aragonite skeletons of tropical corals has been explored and utilized in recent decades [Beck *et al.*, 1992; Shen *et al.*, 1992; McCulloch *et al.*, 1994; Tudhope *et al.*, 2001; Quinn and Sampson, 2002; Corrège *et al.*, 2004; Felis *et al.*, 2004; Kilbourne *et al.*, 2004; Ayling *et al.*, 2006]. The proxies that have been developed and widely

applied for SST are $\delta^{18}\text{O}$ [e.g., Tudhope *et al.*, 2001], Sr/Ca [e.g., Gagan *et al.*, 1998], and U/Ca [e.g., Min *et al.*, 1995]. The $\delta^{18}\text{O}$ composition of corals is also a function of the $\delta^{18}\text{O}$ of seawater (which is correlated with salinity regionally) and therefore compliments a true SST proxy by enabling paleo- $\delta^{18}\text{O}$ water (salinity) estimates [e.g., Ren *et al.*, 2003]. Although U/Ca has been observed to correlate well with SST in various locations [e.g., Min *et al.*, 1995; Felis *et al.*, 2009, 2010] the pH dependence of U speciation in seawater [e.g., Raitzsch *et al.*, 2011] suggests coral U/Ca should also be affected by seawater carbonate chemistry (salinity), as recently confirmed by culturing experiments [Inoue *et al.*, 2011]. Coral Sr/Ca has been shown to be a robust SST proxy under various conditions [e.g., Gagan *et al.*, 1998], but concerns have been raised about variability in surface water Sr/Ca ratios [e.g., Brass and Turekian, 1974; de Villiers, 1999] and the possibility of changes in global seawater Sr/Ca ratios over glacial–interglacial cycles [Stoll and Schrag, 1998]. Therefore, the development of other proxies for SST in tropical corals is desirable.

[3] Calcium carbonate has two major polymorphs in nature, trigonal calcite with six-fold coordination and orthorhombic aragonite with ninefold coordination. Although tropical corals build their skeletons from aragonite, it is nonetheless informative to consider trace element incorporation into calcite

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and aragonite. The lithium content of inorganic calcite was observed to be negatively correlated with temperature in laboratory precipitation experiments conducted with low-salinity solutions [Marriott *et al.*, 2004a]. The same study also analyzed lithium in the aragonite skeleton of a *Porites* coral from Jarvis Island at a sampling resolution of approximately four samples per year. Over two to three seasonal SST and coral $\delta^{18}\text{O}$ cycles, the Li/Ca values suggested an inverse relationship with temperature where coral Li/Ca decreased by 5% for every degree of temperature increase [Marriott *et al.*, 2004a]. This temperature dependence is large compared to that of only around 0.7% per degree for Sr/Ca [e.g., Corrège, 2006]. This makes coral Li/Ca a very promising tool for SST reconstructions, even when considering the lower concentration of Li in coral aragonite ($\mu\text{mol/mol}$ versus mmol/mol) and the poorer measurement precision likely to be obtained as a result. A further study found no influence of salinity on the Li/Ca ratio of inorganically precipitated aragonite [Marriott *et al.*, 2004b]. This is more evidence that the Li/Ca ratio of aragonite could be a robust proxy for SST, but unfortunately these authors did not perform inorganic aragonite precipitation experiments at different temperatures.

[4] Studies of the Li/Ca ratio of calcite foraminifera shells have generally not reproduced the clear temperature dependence displayed by inorganic calcite but instead suggest Li/Ca is influenced by growth rate and therefore seawater carbonate ion concentration [Delaney *et al.*, 1985; Hall and Chan, 2004; Hathorne and James, 2006; Lear and Rosenthal, 2006]. More recently, the combination of Li/Ca with the known temperature proxy of foraminiferal Mg/Ca, as Mg/Li ratios has been shown to correlate better with deep sea temperatures than Mg/Ca ratios alone [Bryan and Marchitto, 2008]. Interestingly, the largest improvement found by using Mg/Li instead of Mg/Ca ratios in benthic foraminifera was for the aragonitic species *H. elegans* [Bryan and Marchitto, 2008]. This work inspired others to investigate Li/Ca and Mg/Li ratios, and clear relationships with deep sea temperature have been observed in various species of aragonitic cold water corals [Case *et al.*, 2010; J. Raddatz *et al.*, Temperature dependence of stable Sr isotopes, Sr/Ca and Mg/Li in the scleractinian cold water coral *Lophelia pertusa*, submitted to *Chemical Geology*, 2012; hereinafter referred to as Raddatz *et al.*, submitted manuscript, 2012].

[5] Inorganic precipitation experiments suggest that Li^+ is incorporated into aragonite by heterovalent substitution of Ca^{2+} in the CaCO_3 structure [Okumura and Kitano, 1986; Marriott *et al.*, 2004b]. Although there are many studies of Mg incorporation into CaCO_3 [e.g., Morse and Bender, 1990; Rimstidt *et al.*, 1998, and references therein], the mode of incorporation into coral aragonite is not established [e.g., Allison *et al.*, 2011; Gaetani *et al.*, 2011]. The results of X-ray Absorption Near Edge Structure (XANES) studies are difficult to interpret but suggest Mg exists in *Porites* coral samples as magnesite (MgCO_3) [Farges *et al.*, 2009]. In contrast, another XANES study of corals suggests Mg is present as a disordered phase or is associated with organics [Finch and Allison, 2008]. Culturing of *Porites* corals shows little direct temperature control on Mg/Ca ratios but indicates Mg/Ca increases with the extension rate of the coral [Inoue *et al.*, 2007]. However, the lack of a measureable Li isotope fractionation within corals skeletons argues against

a kinetic control on Li incorporation into coral aragonite [Marriott *et al.*, 2004a; Rollion-Bard *et al.*, 2009]. Although the existing data concerning the controls of Li and Mg incorporation into biogenic aragonite are often difficult to reconcile, the similarities (apparent partition coefficients $\ll 1$) and differences (heterovalent 2Li^+ versus homovalent Mg^{2+} incorporation) between these two elements means their combined study can potentially improve the understanding of trace metal incorporation into biogenic aragonite.

[6] Here we investigate the use of Li/Ca ratios, and the combination with Mg/Ca as Mg/Li and Li/Mg ratios, as sea surface temperature proxies in tropical corals. We utilize modern *Porites* corals from locations with exceptional local in situ temperature data to calibrate these promising new proxies while revealing some potential caveats to their use that highlight the complexity of biomineralization processes.

2. Methods

2.1. Coral Samples

[7] The details of the *Porites* coral (OGA-02-1) from the Ogasawara Islands (Japan) located at $\sim 27^\circ$ N in the western subtropical North Pacific (hereafter OGA coral) are given in Felis *et al.* [2009]. Local SST was measured during the calibration period ~ 1200 m from the OGA coral site (Tokyo Metropolitan Ogasawara Fisheries Center). A *Porites* coral (TAH-95) was drilled at a water depth of 4–5 m on the north side of Tahiti (French Polynesia) located at $\sim 17.5^\circ$ S in the central tropical South Pacific (hereafter Tahiti coral) [Felis *et al.*, 2012]. Local SST was measured during the calibration period ~ 850 m from the Tahiti coral site [Gerard, 1992]. Coral samples were slabbed, X-rayed, and microsampled following established methods [Felis *et al.*, 2000, 2004], with an average temporal resolution of >7 samples/yr for the OGA coral and of >17 samples/yr for the Tahiti coral. Aliquots of this powder were analyzed for stable isotopes as well as Sr/Ca and U/Ca ratios [Felis *et al.*, 2009, 2012], and the same powder was used for the ICP-MS analyses reported here. Growth rates for the OGA coral during the studied period were 1.0–1.7 cm/yr with an average of 1.3 cm/yr [Felis *et al.*, 2009] and were about 1.2–1.6 cm/yr with an average of 1.4 cm/yr for the Tahiti coral [Felis *et al.*, 2012].

2.2. ICP-MS Analysis

[8] For ICP-MS analysis, ~ 300 μg of coral powder was weighed and placed into a small (8–30 mL) acid-cleaned HDPE bottle. The powder was dissolved by adding 5–25 mL of 0.3M HNO_3 made from thermally distilled HNO_3 diluted with 18.2 M Ω cm H_2O (Milli-Q). After equilibration for at least 12 h, 100–1000 μL of sample solution was removed and diluted with 0.3M HNO_3 to have a Ca concentration of 10 ppm in an acid-cleaned PE centrifuge tube. Analyses were performed using either an Element 2 (Thermo Scientific) sector field ICP-MS at the University of Bremen or the Agilent 7500cs ICP-MS at the GEOMAR, Kiel. The majority of the data were measured in Bremen, with only the additional sampling transect of the OGA coral measured in Kiel. The isotopes monitored during this study were ^7Li , ^{24}Mg , ^{25}Mg , ^{27}Al , ^{43}Ca , ^{48}Ca , ^{55}Mn , ^{88}Sr , ^{137}Ba , and ^{238}U . Raw intensities were blank corrected and normalized to ^{43}Ca before element/Ca ratios were calculated using

the technique of *Rosenthal et al.* [1999]. A standard solution was prepared from single-element solutions to have known element/Ca ratios similar to the samples and a Ca concentration of 10 ppm. All samples with Ca intensities >15% larger or smaller than the standard were rediluted accordingly and run again. Aliquots of the JCP-1 *Porites* coral powder reference material [*Okai et al.*, 2002] were analyzed as unknowns to ensure consistency between measurement sessions and the two laboratories. The average JCP-1 value and standard deviation ($n = 25$) during the course of this study was $6.29 \pm 0.13 \mu\text{mol/mol}$ for Li/Ca, $4.17 \pm 0.05 \text{ mmol/mol}$ for Mg/Ca, $1.51 \pm 0.04 \text{ mmol/mol}$ for Li/Mg, $0.66 \pm 0.02 \text{ mol/mmol}$ for Mg/Li, and $1.18 \pm 0.01 \mu\text{mol/mol}$ for U/Ca. Based on these analyses the external precision at the 95% confidence level (2σ) is estimated to be 4% for Li/Ca, 2.7% for Mg/Ca, 5.1% for Li/Mg and Mg/Li, and 2% for U/Ca.

2.3. Data Treatment

[9] The proxy calibration followed established methods [*Felis et al.*, 2004, 2009]. The annual Li/Ca maxima and minima for the OGA coral were tied to the corresponding extreme values in a local monthly SST record (1975–1994; Tokyo Metropolitan Ogasawara Fisheries Center) and subsequently interpolated to bimonthly intervals using the AnalySeries software (freely available at <http://www.lsce.ipsl.fr/logiciels/index.php>). The annual Li/Ca maxima and minima for the Tahiti coral were tied to the corresponding extreme values in a local monthly SST record (1987–1991) [*Gerard*, 1992] and subsequently interpolated to monthly intervals in the same manner. A linear least squares regression was then carried out for interpolated Li/Ca, Mg/Ca, Mg/Li, Li/Mg, and SST data with SST as the independent variable. The Li/Ca-based age model occasionally (7 out of 43 tie points) differs by one or two samples from the Sr/Ca- and U/Ca-based age models used in previous calibrations of the OGA coral [*Felis et al.*, 2009]. Similarly, the Li/Ca-based age model for the Tahiti coral differs little from the Sr/Ca-based age model used in a previous calibration [*Felis et al.*, 2012].

3. Results

[10] The original element/Ca data for the OGA and Tahiti corals are presented in Table S1 (auxiliary materials are available at <http://www.pangaea.de>). The Li/Ca ratio of the OGA coral varies from 6.01 to $9.07 \mu\text{mol/mol}$ and displays clear annual cycles that match the SST records well (Figure 1). The amplitude of the Li/Ca cycles follows the interannual variability of local SST better than that of a gridded SST product that represents a $1^\circ \times 1^\circ$ area (HadISST1.1; see *Rayner et al.* [2003]). During the period between 1979 and 1980 the Li/Ca ratio does not track the SST well, and there are two anomalously high Li/Ca values that will be discussed in detail in section 4.2. Mg/Ca ratios of the OGA coral sometimes show clear annual cycles and range from 3.63 to 4.88 mmol/mol , with the exception of the period between 1979 and 1980, where the Mg/Ca ratios are 5 mmol/mol or greater, peaking at over 8 mmol/mol. The Li/Mg and Mg/Li ratios for the OGA coral display clear annual cycles like the Li/Ca ratios and range from 2.07 to

1.32 and 0.5 to 0.7 mol/mmol , respectively. The exception is the period between 1979 and 1980, where values are anomalously low or high (only Li/Mg shown in Figure 1). The measurements of the period between 1979 and 1980 were repeated, and an additional transect through the same density bands of the coral was also sampled and analyzed. These data confirm the presence of anomalously high Li/Ca and Mg/Ca values (Figure 2), while the Mn/Ca and Al/Ca ratios, which are considered indicators of contamination from Mn oxides and clays, are below suspect levels (Table S1).

[11] The Li/Ca ratio of the Tahiti coral displays clear annual cycles ranging from 5.88 to $7.22 \mu\text{mol/mol}$ that track the local SST well (Figure 3). The Mg/Ca ratios of the Tahiti coral sometimes show clear annual cycles and range from 4.71 to 5.18 mmol/mol . The Li/Mg and Mg/Li ratios for the Tahiti coral also display clear annual cycles like the Li/Ca ratios and range from 1.47 to 1.18 and 0.68 to 0.85 mol/mmol , respectively.

4. Discussion

4.1. Calibration of Li/Ca, Mg/Li and Li/Mg Ratios With Local SST

[12] Regression analysis of the OGA coral Li/Ca excluding the data from samples with Mg/Ca ratios $>5 \text{ mmol/mol}$ reveals a strong relationship ($r^2 = 0.73$, $p < 0.0001$) between Li/Ca and SST. A linear least squares regression was also carried out for bimonthly interpolated Mg/Ca, Mg/Li, and Li/Mg ratios with local SST, and the monthly interpolated data for the Tahiti coral were analyzed in the same way (Figure 4). The resulting relationships are detailed in Table 1. The Mg/Ca ratio of the OGA coral was very weakly correlated with SST, while no significant relationship could be found for the Tahiti coral (Table 1). The slopes for the Tahiti coral Li/Ca-SST and Mg/Li-SST relationships are twice as steep as those found for the OGA coral. A similar range of temperature sensitivities is also observed for other coral-based proxies [*Corrège*, 2006; *Gagan et al.*, 2012, and references therein]. It is interesting to note that the Tahiti Li/Ca data fall directly on those for the OGA coral (Figure 4). Therefore, if only the data from above 26°C were regressed, a similar result would be obtained for both corals. This suggests there may be some degree of nonlinearity to the Li/Ca-SST relationship, but calibrations using small temperature ranges may not be representative. The OGA coral Li/Ca-SST relationship decreases by 1.8% per $^\circ\text{C}$ (at 25°C), while the Tahiti coral Li/Ca-SST relationship decreases by 3.9% and is more similar to the 5% per $^\circ\text{C}$ reported for a Jarvis Island *Porites* coral [*Marriott et al.*, 2004a]. Although it is difficult to assign temperatures accurately without the original SST data, the SST estimates derived by applying the Tahiti coral Li/Ca-SST relationship to the Li/Ca ratios from the Jarvis Island coral fit the SST shown in *Marriott et al.* [2004a] well. This suggests the higher slope of the Li/Ca data from temperatures above 26°C may be widely applicable to *Porites* corals across the tropics.

[13] To test that the relationship between Li/Ca and SST is not an artifact of the annual cycle of another variable causing the Li/Ca ratio to fluctuate, we have conducted a regression of the average annual Li/Ca ratios of the OGA coral with local SST [*Crowley et al.*, 1999; *Evans et al.*, 1999; *Felis et al.*, 2009]. Although the seasonal temperature range at

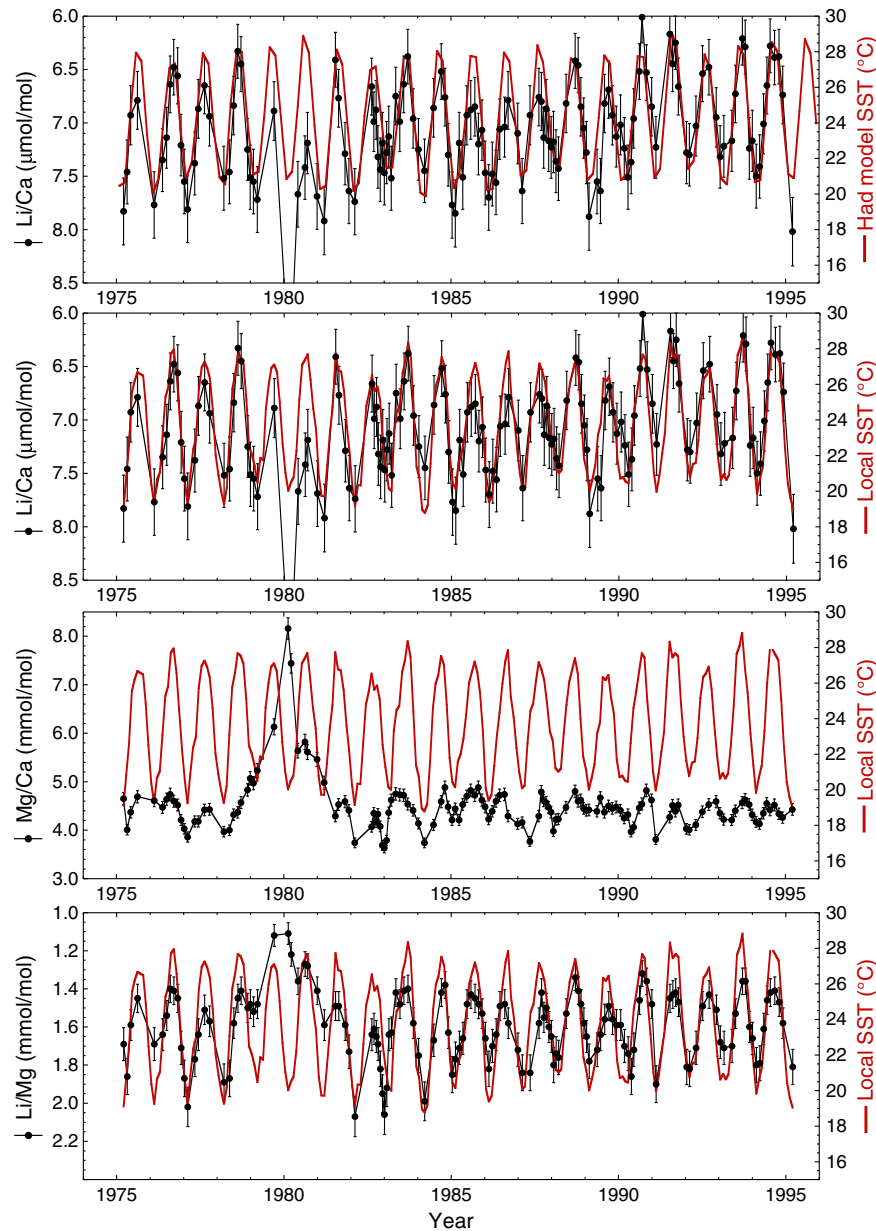


Figure 1. Li/Ca, Mg/Ca, and Li/Mg ratios for a 20 year period of a *Porites* coral from Ogasawara Island (OGA) compared with a gridded SST product that represents a $1^{\circ} \times 1^{\circ}$ area (HadISST1.1) [Rayner *et al.*, 2003] and locally measured SST. Error bars represent the 2σ external uncertainty based on repeated measurement of the JCp-1 reference material (section 2.2).

the OGA location is large, the average annual temperatures vary by only $\sim 1^{\circ}\text{C}$, making the regression with Li/Ca ratios relatively imprecise (Table 1). Even so, the regression of the annual average OGA Li/Ca with SST gives $r^2 = 0.45$ ($p < 0.005$). There is no significant relationship between the annual average OGA Li/Ca ratio and the average annual sea surface salinity [Carton and Giese, 2008], suggesting the variance of Li/Ca ratios is dominated by SST and is relatively insensitive to seawater chemistry. Furthermore, the slope and intercept of the OGA coral average annual Li/Ca-SST relationship are very similar to the seasonal relationship from the Tahiti coral and the OGA coral for temperatures above 26°C . This strongly suggests that the differences between seasonal and average annual Li/Ca-SST

calibrations, also documented for Sr/Ca, U/Ca, and $\delta^{18}\text{O}$ ratios of the OGA coral (see supplementary information of Felis *et al.* [2009]), result from the nonlinearity of the relationship between Li/Ca and SST. Recently it was suggested that two types of calibration are required for coral SST reconstructions using Sr/Ca and $\delta^{18}\text{O}$ ratios, one for seasonal and one for multiannual reconstructions [Gagan *et al.*, 2012]. These authors suggest the differences in proxy sensitivity result from variable “bio-smoothing” attenuating the proxy signal for different coral colonies. However, it seems that variability in the sensitivity of coral Li/Ca potentially occurs within a single colony at different times of the year. The fact that the data from higher temperatures agree points to a lower sensitivity of Li/Ca at lower temperatures. In some *Porites* corals from

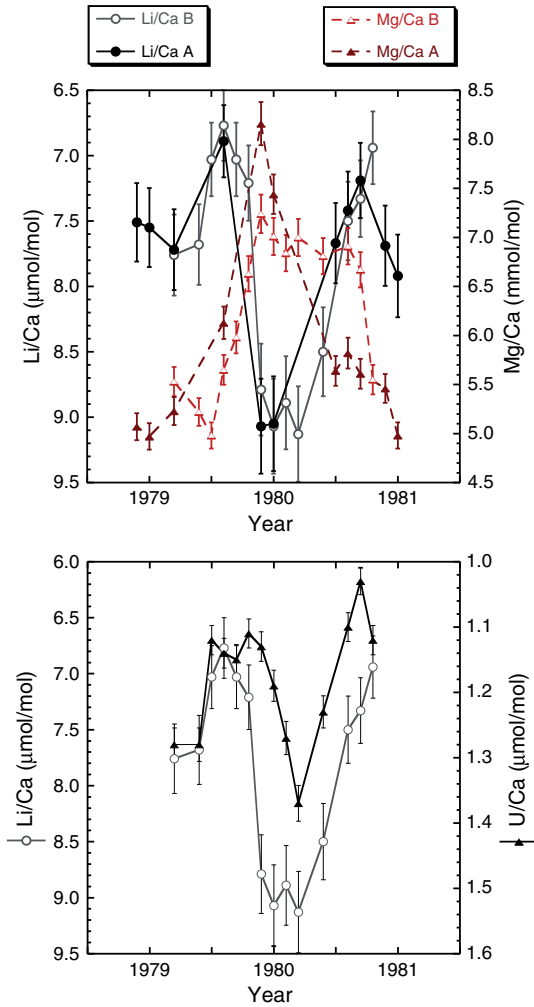


Figure 2. (top) Comparison of Li/Ca and Mg/Ca ratios for two contemporaneous sampling transects of the OGA coral. (bottom) Comparison of Li/Ca and U/Ca ratios from the secondary sampling transect of the OGA coral. Error bars represent the 2σ external uncertainty based on repeated measurement of the JCp-1 reference material (section 2.2).

other Japanese islands, a reduction of extension rate and the formation of a high-density band has been observed during the winter months [Mitsuguchi *et al.*, 2003]. This is not the case for the OGA coral, as the high-density band is precipitated during summer, and the other geochemical records do not indicate reduced growth during winter [Felis *et al.*, 2009].

[14] Interestingly, the slopes and intercepts of the Li/Mg-SST relationships are similar for both OGA and Tahiti corals (Table 1). As the Ca concentration in the coral aragonite varies by <1% [e.g., Gaetani and Cohen, 2006], there should be no induced correlations from comparing Li/Ca with Mg/Ca ratios [Lenahan *et al.*, 2011]. Thus it appears that using Mg/Ca as the denominating ratio accounts for some of the nonlinearity of the Li/Ca-SST relationship above 26°C. More corals from diverse locations should be measured, but it may be that Li/Mg ratios help to overcome some intercoral offsets in paleothermometry.

[15] Using the maximum and minimum slopes from the standard error (Table 1) to calculate the range of element

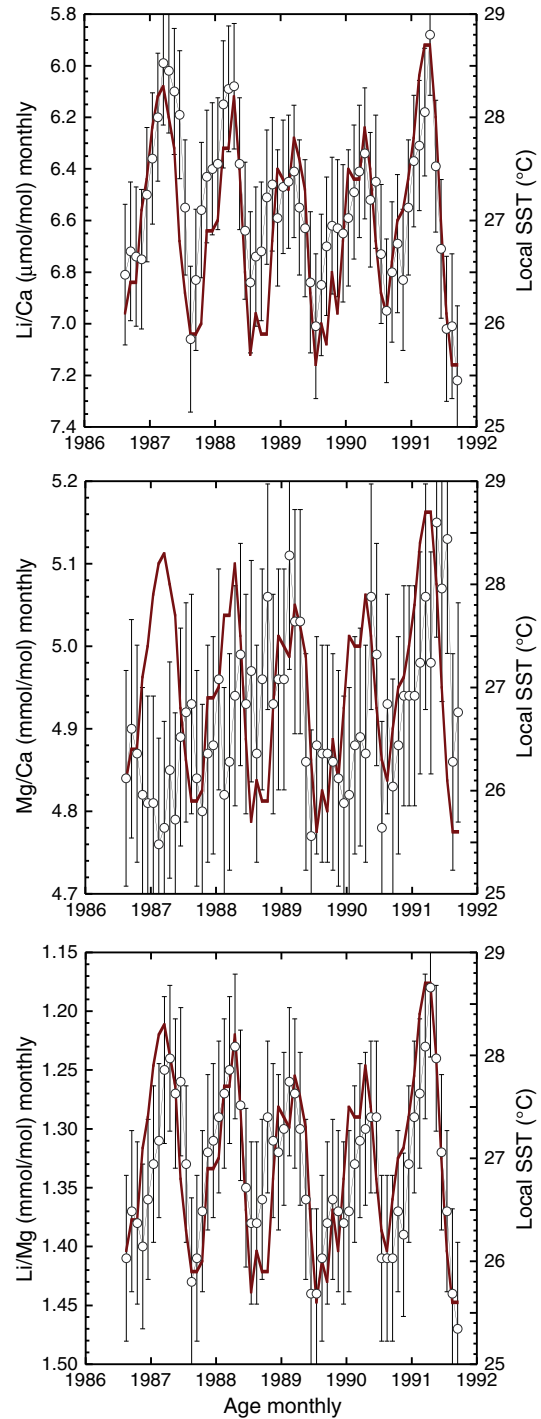


Figure 3. Monthly interpolated Li/Ca, Mg/Ca, and Li/Mg ratios for a *Porites* coral from Tahiti compared to the locally measured SST. Error bars represent the 2σ external uncertainty based on repeated measurement of the JCp-1 reference material (section 2.2).

ratios and the resulting range of estimated SST produces uncertainties of between ±1.0 and 1.7°C for Li/Ca and ±1.1 and 1.9°C for Li/Mg. This is comparable to Sr/Ca slope uncertainties [e.g., Felis *et al.*, 2004, 2009], making Li/Ca and Li/Mg ratios useful additions to the coral paleothermometer arsenal.

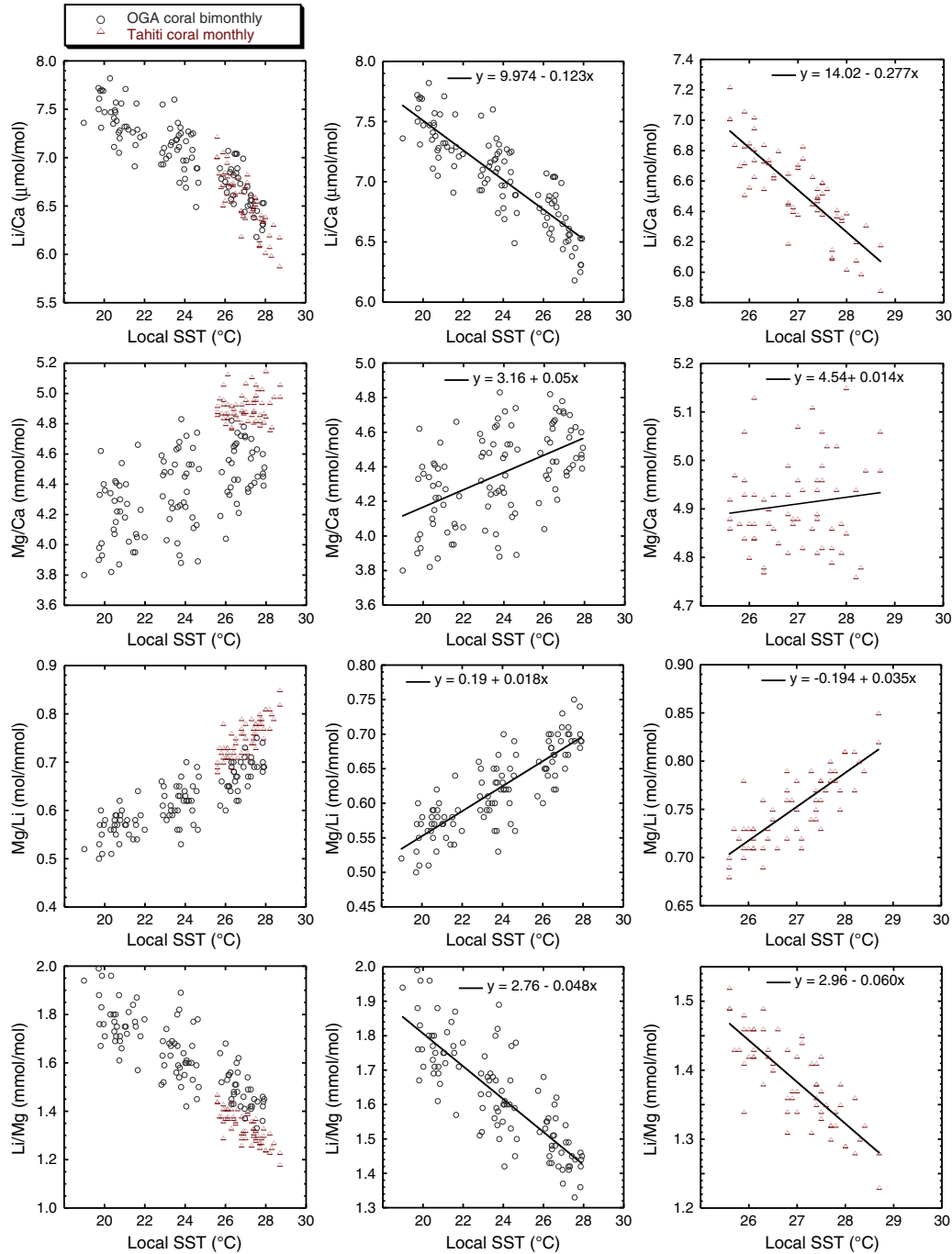


Figure 4. Regression analysis of the Li/Ca, Mg/Ca, Mg/Li, and Li/Mg ratios of OGA and Tahiti corals with locally measured SST. See Table 1 for more details.

4.2. Anomalously High Li/Ca and Mg/Ca Ratios

[16] The anomalously high Li and Mg in the 1979–1980 section of the OGA coral are not the result of contamination by Mn oxides or clays, as confirmed by the analysis of an additional transect through the same density bands. Manganese was below detection in all samples, and Al/Ca ratios were $<100 \mu\text{mol/mol}$ and were often below detectable levels (Table S1). The zone of high Li and Mg is slightly wider in the additional transect than the primary transect, probably the result of a slightly higher growth rate in the additional

transect. The X-ray of the coral looks normal throughout the 1979 and 1980 section, and the Sr/Ca, U/Ca and $\delta^{18}\text{O}$ ratios measured in this section are within normal ranges and follow the SST well [Felis *et al.*, 2009]. This is also the case for the U/Ca (Figure 2) and Sr/Ca ratios (not shown) measured in the additional transect. The $\delta^{13}\text{C}$ through this section of coral [Felis *et al.*, 2009] does not suggest the anomalous Li and Mg could have resulted from biological effects related to symbiont photosynthesis and coral metabolism [e.g., Gagan *et al.*, 1994; Felis *et al.*, 1998; Grottoli, 2002]. Secondary aragonite crystals are known to form in

Table 1. Results for Ordinary Least Squares Regression of Coral Element/Ca Ratios With Local SST^a

	Intercept <i>b</i>	Slope <i>a</i>	Regression Coefficient <i>r</i> ²
OGA Li/Ca	9.97 (±0.18)	-0.123 (±0.007)	0.73
OGA Mg/Ca	3.16 (±0.20)	0.050 (±0.008)	0.26
OGA Mg/Li	0.19 (±0.029)	0.018 (±0.0012)	0.69
OGA Li/Mg	2.76 (±0.08)	-0.048 (±0.003)	0.67
Average annual OGA Li/Ca	14.4 (±2.2)	-0.31 (±0.09)	0.45
Average annual OGA Mg/Li	-0.40 (±0.4)	0.042 (±0.016)	0.32
Average annual OGA Li/Ca	4.30 (±1.0)	-0.11 (±0.04)	0.32
Tahiti Li/Ca	14.0 (±0.7)	-0.277 (±0.025)	0.68
Tahiti Mg/Li	-0.19 (±0.09)	0.035 (±0.003)	0.65
Tahiti Li/Mg	2.96 (±0.16)	-0.060 (±0.006)	0.64

^aUncertainties are the standard error.

modern corals [e.g., Hendy *et al.*, 2007; Sayani *et al.*, 2011], but these have lower Mg/Ca ratios than primary skeleton [e.g., Hathorne *et al.*, 2011]. A thin section from the 1979–1980 section of the OGA coral shows no indication of diagenesis. All this points to the anomalously high Li and Mg occurring in the original coral skeleton. It is interesting to note that the Li/Ca and Mg/Ca ratios are positively correlated with each other in the section where they are anomalously high (Figure 2). This contrasts with the areas of skeleton where Li/Ca ratios closely follow SST and the Li/Ca and Mg/Ca ratios are generally negatively correlated (Figures 1 and 3). High Li and Mg contents have been found associated with centers of calcification (COC) in some cold water corals [Case *et al.*, 2010]. Therefore, the anomalously high Li/Ca and Mg/Ca ratios could potentially have resulted from a higher proportion of COC in this section of the skeleton. Inspection of the current thin sections provides no clear evidence, and different section preparation techniques to highlight COC and image analysis techniques will need to be developed to quantify COC proportion. Even if the underlying mechanism remains elusive, all evidence suggests the anomalously high Li/Ca and Mg/Ca ratios result from a biological effect on the incorporation into the biogenic aragonite.

4.3. Incorporation of Li and Mg Into Biogenic Aragonite

[17] The Li/Mg SST relationship obtained for the OGA coral is similar to those found by previous studies of cold water corals [Case *et al.*, 2010; Raddatz *et al.*, submitted manuscript, 2012] and aragonitic benthic foraminifera *H. elegans* [Bryan and Marchitto, 2008] (Figure 5). The Li/Ca SST relationship is slightly stronger than that for Mg/Li (and Li/Mg), in contrast to previous studies where a stronger relationship was found between Mg/Li ratios and water temperature [Bryan and Marchitto, 2008; Case *et al.*, 2010]. More data from diverse calcifiers are needed, but the comparison of the available Li/Mg (or Mg/Li) data from biogenic aragonite can be explained with a single exponential relationship to water temperature (Figure 6). This hints at the possibility of an overarching mechanism controlling the temperature response of Li and Mg incorporation into aragonite.

[18] As noted in section 1, the incorporation of Li and Mg into biogenic CaCO₃ is poorly understood. Even so, it is important to consider the possible mechanisms for the temperature influence on coral Li/Ca ratios and the anomalously high Li/Ca and Mg/Ca ratios in the 1979–1980 section of the OGA coral. A positive correlation between Mg/Ca ratios and SST has been reported for some *Porites* corals [e.g.,

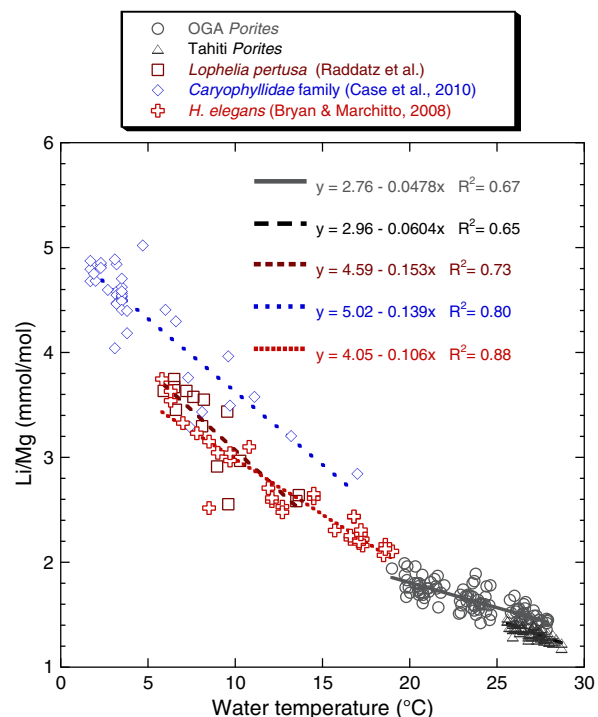


Figure 5. Relationships between Li/Mg ratios with water temperature obtained by this study and from the literature.

Mitsuguchi *et al.*, 1996; Sinclair *et al.*, 1998], but the relationship is often not clear or consistent [e.g., Mitsuguchi *et al.*, 2008]. This is also evident in the poor and insignificant correlation of Mg/Ca with local SST in this study (section 4.1), although some years have clear annual cycles of Mg/Ca. It must be noted that no oxidative cleaning of the coral powder was performed in this study, as is sometimes undertaken before Mg/Ca analysis [e.g., Mitsuguchi *et al.*, 1996, 2003].

[19] Rayleigh fractionation from a closed reservoir combined with a temperature-dependent reservoir depletion has been used to explain the positive relationship between coral Mg/Ca and temperature, as the Mg/Ca ratio of the reservoir would increase as Ca is progressively depleted [Gaetani and Cohen, 2006; Cohen and Gaetani, 2010]. Case *et al.* [2010] attributed the strong positive correlation between Li/Ca and Mg/Ca ratios within the skeletons of cold water corals to the fact that the apparent partition coefficients of both Li and Mg are $\ll 1$,

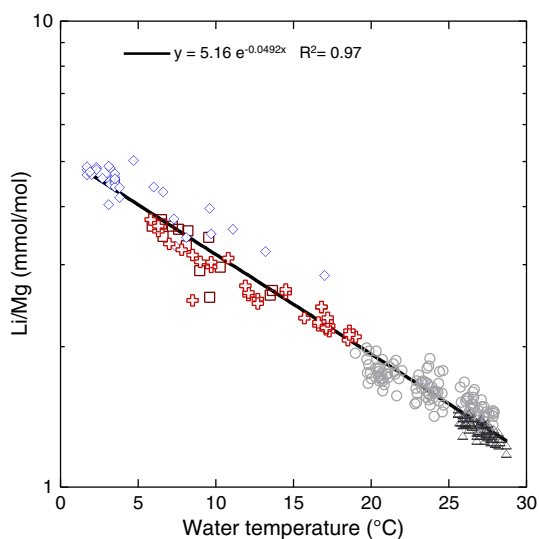


Figure 6. Exponential relationship between Li/Mg ratios and water temperature obtained by this study and others plotted on a log scale. Symbols are the same as in Figure 5.

and they would respond to Rayleigh fractionation similarly. However, within the skeletons of the tropical *Porites* corals examined here the Li/Ca and Mg/Ca ratios are anticorrelated apart from the period of anomalously high Li/Ca and Mg/Ca (Figures 1–3). This difference may simply result from the difference in the sampling scales between the $<100\ \mu\text{m}$ laser ablation sampling of *Case et al.* [2010] and the $<1000\ \mu\text{m}$ drill sampling of this study. Additionally, the large Li/Ca and Mg/Ca variability seen in deep-sea corals, which experience only small changes in temperature, reveals the extent of reservoir depletion and Rayleigh fractionation is not temperature dependent. We suggest that the positively correlated ratios during the period of anomalously high Li/Ca and Mg/Ca of a *Porites* coral resulted from biological effects unrelated to temperature, possibly Rayleigh fractionation during biomineralization. However, under normal circumstances where such effects are minimal, Li/Ca and Mg/Ca ratios are negatively or poorly correlated, and the Li/Ca ratio faithfully reflects SST.

[20] Given the clear nonenvironmental controls on tropical coral Mg/Ca ratios observed here and elsewhere [e.g., *Meibom et al.*, 2008], the underpinning use of Mg/Ca ratios in

multielement coral thermometry [*Cohen and Gaetani*, 2010; *Gaetani et al.*, 2011] should be reconsidered. Li/Ca ratios should be very helpful for such multielement techniques, as the apparent partition coefficient of Li is <1 .

4.4. Inorganic Comparisons

[21] The temperature dependent incorporation of various cations into calcite has been predicted using the temperature dependence of the metal carbonate solubility products [e.g., *Rimstidt et al.*, 1998, and references therein]. In contrast to most carbonates the solubility of Li_2CO_3 decreases with increasing temperature [*Smith et al.*, 1971]. The Li_2CO_3 solubility data compiled and determined by *Smith et al.* [1971] gives a solubility product (K_{sp}) of 4.7×10^{-3} at 25°C . This is much larger than the 8.15×10^{-4} calculated from the free energies of formation [e.g., *Chang*, 1989], but to examine the temperature dependence of Li_2CO_3 solubility, the experimental data of *Smith et al.* [1971] was used. The K_{sp} from these data was fitted with a function of the form $\text{Log}K_{sp} = a + b/T + cT$ by nonlinear regression. Then, using equation 18 from *Rimstidt et al.* [1998], the theoretical temperature dependence of Li partitioning into calcite and aragonite was calculated. For both aragonite and calcite the incorporation of Li is predicted to increase with temperature, opposite to the observed negative relationship in *Porites* corals. The use of the correct stoichiometric quotient (ν_c) for Li_2CO_3 incorporation into CaCO_3 , i.e., 2, results in unrealistically low partition coefficients, so the empirically derived term accounting for boundary layer processes [*Rimstidt et al.*, 1998] was used. Simply using the equation for the cations with ionic radii smaller than Ca^{2+} from *Rimstidt et al.* [1998, equation (5)] with the K_{sp} for Li_2CO_3 at 25°C noted above gives an apparent partition coefficient of 5.6×10^{-4} for Li into aragonite. This value is only slightly lower than those found for natural samples and from inorganic precipitation experiments (Table 2), suggesting it is valid as a first-order approximation. These calculations and inorganic precipitation experiments predict the Li content of aragonite should be higher than that of calcite. However, the Li content of biogenic calcite is higher than that of biogenic aragonite (Table 2), suggesting the applicability of the currently available inorganic experimental data to marine biogenic carbonates is limited.

Table 2. Apparent Partition Coefficients^a for Li Incorporation Into Calcium Carbonate From the Literature

Polymorph	Sample	$D_{\text{Li}} \text{ min} \times 10^3$	$D_{\text{Li}} \text{ max} \times 10^3$	Reference
Inorganic aragonite	aragonite: 30 and 40 psu	3.00	3.30	<i>Marriott et al.</i> [2004b]
Aragonite	<i>Porites</i> coral	2.35	3.65	this study
Aragonite	<i>Porites</i> coral	2.20	2.82	<i>Marriott et al.</i> [2004a]
Aragonite	cold water corals various	2.82	6.00	<i>Case et al.</i> [2010]
Aragonite	cold and warm water corals	1.80	3.60	<i>Rollion-Bard et al.</i> [2009]
Aragonite	<i>H. elegans</i>	1.08	1.82	<i>Bryan and Marchitto</i> [2008]
Aragonite	<i>H. elegans</i>	1.48	2.22	<i>Hall and Chan</i> [2004]
Inorganic calcite	calcite: 30 and 40 psu	1.90	2.40	<i>Marriott et al.</i> [2004b]
Calcite	<i>Uvigerina</i>	5.40	7.60	<i>Marriott et al.</i> [2004b]
Calcite	benthic foraminifera	4.53	7.11	<i>Bryan and Marchitto</i> [2008]
Calcite	<i>O. umbonatus</i>	6.00	7.20	<i>Lear and Rosenthal</i> [2006]
Calcite	benthic foraminifera	4.84	7.40	<i>Hall and Chan</i> [2004]
Calcite	planktonic foraminifera	4.16	5.80	<i>Hathorne and James</i> [2006]
Calcite	modern brachiopods	2.28	19.68	<i>Delaney et al.</i> [1989]

^aSee, for example, *Morse and Bender* [1990]. For marine samples, a seawater Li/Ca ratio of 0.0025 mol/mol was assumed.

5. Conclusions

[22] The Li/Ca ratio of coral aragonite is negatively correlated with the SST in which it grew, but the slope appears to be steeper for temperatures $>26^{\circ}\text{C}$. Mg/Li ratios are positively correlated with SST, and the relationship for the OGA coral is similar to that found for cold water corals and the aragonitic benthic foraminifera *H. elegans* in previous studies. Li/Mg ratios are negatively correlated with local SST, and the slopes and intercepts of the Li/Mg-SST relationship are similar for both corals examined. If this Li/Mg-SST relationship is also similar for other corals from diverse locations, then Li/Mg ratios may help overcome the inaccuracies in SST estimation from intercoral variability in proxy relationships. The mechanism behind the temperature dependence of Li/Ca is not known but cannot be simple Rayleigh fractionation, as Li/Ca and Mg/Ca ratios are negatively correlated. More studies of other corals are needed to better understand these proxies, but the empirical calibrations presented here make Li/Ca and Li/Mg ratios useful additions to the coral paleothermometer arsenal.

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