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Skeletal P/Ca tracks upwelling in Gulf of Panamá coral: Evidence for a new seawater phosphate proxy

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[1] The supply of limiting nutrients to the low latitude ocean is controlled by physical processes linked to climate variations, but methods for reconstructing past nutrient concentrations in the surface ocean are few and indirect. Here, we present laser ablation mass spectrometry results that reveal annual cycles of P/Ca in a 4-year record from the scleractinian coral *Pavona gigantea* (mean P/Ca = 118 μmol mol^{-1}). The P/Ca cycles track variations in past seawater phosphate concentration synchronously with skeletal Sr/Ca-derived temperature variations associated with seasonal upwelling in the Gulf of Panamá. Skeletal P/Ca varies seasonally by 2–3 fold, reflecting the timing and magnitude of dissolved phosphate variations. Solution cleaning experiments on drilled coral powders show that over 60% of skeletal P occurs in intracrystalline organic phases. Coral skeleton P/Ca holds promise as a proxy record of nutrient availability on time scales of decades to millennia. **Citation:** LaVigne, M., M. P. Field, E. Anagnostou, A. G. Grottoli, G. M. Wellington, and R. M. Sherrell (2008), Skeletal P/Ca tracks upwelling in Gulf of Panamá coral: Evidence for a new seawater phosphate proxy, *Geophys. Res. Lett.*, *35*, L05604, doi:10.1029/2007GL031926.

1. Introduction

[2] A direct paleo-proxy for surface water nutrient concentrations has not yet been discovered. Although climate-driven changes in physical mixing of the upper ocean exert a fundamental control on open ocean primary production by governing nutrient supply in the present ocean [*Behrenfeld et al.*, 2006], there is currently no reliable method for reconstructing past surface water nutrient dynamics for comparison to records of variations in global climate or local vertical mixing. Sedimentary proxies for surface nutrient supply and utilization (i.e. foraminiferal Cd/Ca, δ^{13}C, diatom δ^{30}Si and organic matter δ^{15}N) are related to nutrient concentrations indirectly, and cannot provide the temporal resolution that coral proxies offer [*De La Rocha et al.*, 1998; *Elderfield and Rickaby*, 2000; *Kohfeld et al.*, 2000; *Mortlock et al.*, 1991; *Rickaby and Elderfield*, 1999; *Sigman et al.*, 1999]. Coralline Cd/Ca, Ba/Ca and δ^{13}C have been explored as tracers of upwelled nutrient supply based on modern relationships between the vertical distributions of Cd, Ba, δ^{13}C, and nutrients [*Lea et al.*, 1989; *Shen et al.*, 1987, 1992; *Tudhope et al.*, 1996]. Quantitative relationships between these proxies and surface water nutrient concentrations, with respect to both sub-surface supply and subsequent biological utilization, are too variable for these indirect proxies to provide well-constrained phosphate or nitrate concentration histories [*Grottoli*, 2002; *Grottoli and Wellington*, 1999; *Shen et al.*, 1992; *Takesue and van Geen*, 2002]. Thus there is a valuable role for a new, more direct, proxy of surface ocean nutrient concentration.

[3] A deep water phosphate proxy calibration was published recently for the solitary deep sea coral *Desmophyllum dianthus* [*Montagna et al.*, 2006]. A small number of studies have suggested that *Porites, Montastrea,* and *Diploria* surface corals record coastal phosphorus runoff and pollution as increased P/Ca, incorporated in both inorganic and organic P phases (auxiliary Table S1[1]) [*Alibert et al.*, 2003; *Dodge et al.*, 1984; *Kumarsingh et al.*, 1998; *Shotyk et al.*, 1995]. These authors provided qualitative interpretations of skeletal P/Ca variations and speculated on the P incorporation mechanism, encouraging further quantitative development of this proxy and application to open water oceanic environments.

[4] In this study, we analyzed P/Ca ratios by laser ablation high resolution inductively coupled plasma mass spectrometry (LA-HR-ICP-MS) and Sr/Ca by LA-ICP-Optical Emission Spectroscopy (OES) in a *Pavona gigantea* coral from the Gulf of Panamá, a region where regular annual upwelling causes ~3 fold variations in surface water phosphate concentration, and continental runoff has little effect on overall nutrient input [*D'Croz and O'Dea*, 2007; *D'Croz and Robertson*, 1997]. This rapid in situ laser ablation technique allowed us to test whether the pronounced annual cycle in surface water phosphate at this site was recorded in the fine-scale geochemical variations across the coral growth bands. In addition, we explored the mechanism of incorporation and chemical form of phosphorus present in the skeleton, using chemical leaching procedures and analysis of inorganic and total phosphorus. This study lays the initial groundwork for investigating ocean phosphate coral records hundreds to thousands of years long, potentially providing a means of linking past nutrient dynamics in the subtropical and tropical ocean to global climate shifts.

1.1. Coral Sample

[5] The *Pavona gigantea* coral fragment used in this study was reared under ambient conditions for one year at 1 m

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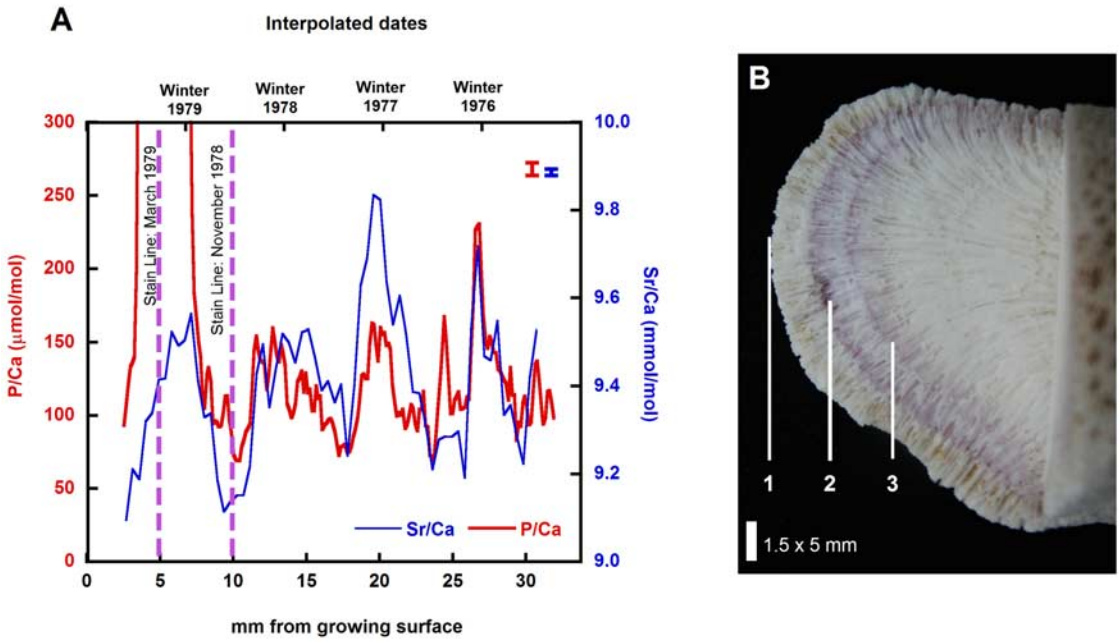

Figure 1. (a) P/Ca (μmol/mol; red) and Sr/Ca (mmol/mol; blue) ratios measured by LA-HR-ICP-MS and -ICP-OES through the upper 31 mm (~4years) of *Pavona gigantea* skeleton from the Gulf of Panamá upwelling region. Locations of dated stain lines (dashed purple) are marked for comparison with Sr/Ca, a SST proxy used as an indicator of seasonality (peaks are maximum upwelling and minimum temperature). Elevated P/Ca ratios in the upper portion of coral are dominated by the organic tissue layer from ~0–7 mm below the growing surface. Inset Y-error bars represent 0.2% Sr/Ca and 7% P/Ca ratio precision (see text). (b) Photograph of a cross section of the *Pavona gigantea* coral analyzed by laser ablation, and by solution phase of drilled powders. Scale bar represents approximate size of drilled pits. 1) Growing surface of coral collected November 1979; 2) March 1979 stain line; 3) November 1978 stain line.

below mean low tide on a fringing reef on the southeastern corner of Isla Contadora (8°37′23″N; 79°02′31″W), Perlas Archipélago in the Gulf of Panamá as part of a larger study [*Grottoli and Wellington*, 1999; *Wellington*, 1982]. Two dates (20 November 1978; 17 March 1979) were marked with Alizarin Red staining in situ (Figure 1). The 30 mm of skeleton subsampled for the current study represented ~4 years of growth including the phosphorus rich tissue layer that penetrates 7 mm below the growing surface of the coral. The slab was cut with a clean dry band saw and analyzed without solution cleaning.

1.2. LA HR-ICP-MS and ICP-OES

[6] The LA HR-ICP-MS/OES configuration consisted of a 193 nm ArF excimer laser (UP-193, New Wave Technologies, CA), an Element XR high resolution ICP-MS (ThermoFinnigan, Bremen, Germany) and a radial ICP-OES (Vista-Pro, Varian, AU). The laser ablation cell output gas (He) stream was split ~50–50, with each fraction mixed with additional Ar before simultaneous injection into the central channels of the MS and OES. The sample was ablated using a fluence of ~4 J/cm^2 in 25 ns pulse widths at a frequency of 10 Hz. Fine scale skeletal variability was averaged by using a 50 μm by 500 μm custom rectangular mask aligned perpendicular to the growth axis and line scanned at 140 μm/sec following pre-ablation laser passes to remove surface contamination [*Sinclair et al.*, 1998].

[7] Phosphorus was analyzed in medium resolution (MR = 4000 m/Δm) to resolve molecular ion interferences (i.e. N-O$^+$ and N-O-H$^+$). The sensitivity of the MS provided detection limits of sub-ppm P levels, whereas simultaneous elemental detection capabilities of OES provided excellent precision for major element (Sr/Ca) ratios. Three second averaged data resulted in elemental ratio precision of ~7% for P/Ca (sequential scan, MS) and ~0.2% for Sr/Ca (simultaneous detection, OES). The combination of scan rate and 3 second data integrations resulted in 420 μm spatial resolution, equivalent to ~3 week temporal resolution in this coral. Ratios were blank corrected (<2.0%) and standardized against bracketing ablation scans of NIST 612 glass. We used P and Ca concentrations determined by solution-phase ICP-MS on separately digested glass fragments of NIST 612. The P and Ca concentrations we measured in the NIST 612 glass (39.9 ppm P and 88,500 ppm Ca) agreed with other published values (39.1–71.21 ppm P; 84,690 and 85,800 ppm Ca [*Jochum et al.*, 2005]). The certified value of 78.4 ppm was used for the Sr content.

1.3. Solution Phase HR-ICP-MS

[8] The skeleton was also sampled using a diamond drill bit to excavate ~1.5 × 5 mm pits parallel to and ~2 mm away from the ablation line (Figure 1b), producing 4–7 mg of calcium carbonate powder that was split into 3 fractions. Soluble reactive phosphate analyses were performed on the first fraction as described below. Solution cleaning was performed on the second fraction, employing the oxidative/reductive technique designed to leave intact only trace metals that are incorporated into coral skeleton lattice by ionic substitution [*Shen and Boyle*, 1988]. Both cleaned

(2^{nd} fraction) and uncleaned (3^{rd} fraction) powder splits were dissolved in 1N HNO_3 and analyzed for P/Ca by HR-ICP-MS to distinguish "uncleanable" intracrystalline and mineral lattice phosphorus from bulk P in the skeleton.

1.4. Soluble Reactive Phosphate (SRP) Analysis

[9] To quantify the inorganic skeletal phosphorus concentration in this coral, ~2–3 mg splits of the powders described above were dissolved in 2mL of 0.2M trace metal grade hydrochloric acid. Analysis of SRP was performed following a micro-scale version of a standard method [*Koroleff*, 1983], modified to accommodate small volumes of dissolved coral, while providing easily measurable SRP signals analyzed against standard curves that were matrix matched to samples for Ca and acid concentration. Phosphorus measured as SRP represents the upper limit inorganic skeletal phosphorus phase since some organic P could be hydrolyzed at low pH during dissolution, potentially releasing orthophosphate groups. The difference between total (ICP-MS) and SRP measurements is assumed to represent the organic P concentration.

2. Results and Discussion

2.1. Timing of Upwelling Derived From Skeletal Sr/Ca

[10] In situ measurements in the Gulf of Panamá from 1994–2000 indicate that sea surface temperatures dip to ~24°C with regular annual upwelling in late winter/early spring, from ~29°C during non-upwelling periods (auxiliary Figure S1). Although our sample predates in situ and satellite sea surface temperature (SST) measurements, the annual SST cycle is well known from later time-series data [*D'Croz et al.*, 1991; *D'Croz and O'Dea*, 2007; *D'Croz and Robertson*, 1997; *Podestá and Glynn*, 1997; *Toscano et al.*, 2002]. We used Sr/Ca as a temperature proxy to determine the timing of annual upwelling for each year in our coral sample (Figure 1). Based on a *Pavona clavus* Sr/Ca calibration [*de Villiers et al.*, 1994], we calculated ~7°C annual SST variation from skeletal Sr/Ca ratios that varied by ~4–6 % in an annual cyclic fashion (Figure 1). Although this Sr/Ca calibration has potential non-temperature dependencies (e.g. extension rate), predicts cooler temperatures than measured in situ, and is calculated for a different site and *Pavona* species, the estimated SST variation is in sufficient agreement with measured variations for the purpose of this study [*de Villiers et al.*, 1994]. The temperature cycle determined from Sr/Ca in the stain line-dated top 10 mm of skeleton indicates that the SST minimum resulting from the upwelling maximum occurs in ~February in 1979, which agrees with long term mean timing of upwelling in the region (Figures 1 and S1). These data show that skeletal Sr/Ca records the timing of SST variations attributed to annual upwelling, and provide the temporal framework for interpreting P/Ca variations.

2.2. P/Ca as a Seawater Phosphorus Recorder

[11] The key result of this study is the coincident seasonal timing and relative amplitude of skeletal P/Ca variations, compared to the known upwelling cycles in the Gulf of Panamá (Figure 1). Skeletal P/Ca varies seasonally by a factor of 2–3 and is synchronous with Sr/Ca through four annual upwelling cycles. In each cycle, high Sr/Ca ratios indicate low SSTs and correspond to high skeletal P/Ca, suggesting skeletal P reflects seawater phosphate variations driven by seasonal upwelling (Figure 1). The annual P/Ca cycles shown in Figure 1 are evident in replicate analyses of the same laser track and in parallel structural elements (data not shown), but additional work on P/Ca replication and calibration is required before sub-seasonal and interannual variations can be more fully interpreted. These data provide a test of the hypothesis that variations in coral P/Ca record ambient seawater phosphate [*Dodge et al.*, 1984; *Kumarsingh et al.*, 1998; *Shotyk et al.*, 1995].

[12] The Smithsonian Tropical Research Institute (STRI) sampling site is located ~50km inshore from Isla Contadora, and is representative of conditions throughout the Gulf [*D'Croz and O'Dea*, 2007; *D'Croz and Robertson*, 1997]. We use data from the STRI site to represent seawater conditions for the coral site off Islá Contadora [*D'Croz et al.*, 1991; *D'Croz and O'Dea*, 2007; *D'Croz and Robertson*, 1997] and estimate approximate P partition coefficients for *P. gigantea.*

[13] The partition coefficient or 'D' value is frequently used in the biogenic carbonate literature to describe inorganic elemental incorporation from seawater into aragonite ($D = Element/Ca_{coral}/Element/Ca_{SW}$). *Dodge et al.* [1984] estimated a phosphorus D of 1.5 for a Bermuda *Montastrea annularis* coral. Lacking seawater phosphate data corresponding to the period of coral growth for the *P. gigantea* sample analyzed in this study, a D value can only be approximated. We estimated a mean D ~2–3 times higher than reported by *Dodge et al.* [1984]. Vanadium, another oxyanion in seawater, may serve as a comparison element to P. Skeletal vanadium is presumably incorporated as vanadate (HVO_4^{2-}) and has a D ~ 0.03 [*Shen and Boyle*, 1988]. Incorporation of phosphate into the skeletal aragonite lattice by direct anionic substitution would likely proceed through substitution of biphosphate (HPO_4^{2-}) for carbonate ion (CO_3^{2-}), and result in a $D \ll 1.0$ and not >1.0 as we observe. This suggests that P is incorporated into coral skeletons by additional mechanisms, not necessarily in an inorganic form. We conclude that anionic substitution of biphosphate from seawater cannot be the only mechanism of P incorporation.

2.3. Skeletal Phosphorus Incorporation Mechanism

[14] The reliability of coralline P/Ca as a seawater phosphate proxy can be better evaluated if the incorporation mechanism and potential diagenetic effects for both organic and inorganic skeletal phosphorus are better understood. Inorganic skeletal P may occur as a result of direct ionic substitution into the carbonate mineral and/or as discrete particulate phases such as iron phosphates. Organic P phases potentially present in coral skeleton include 1) intracrystalline organic material incorporated during mineral precipitation, 2) adsorbed dissolved organic phosphorus from seawater, and 3) endolithic algae, fungi, or bacteria. To investigate potential phosphorus phases in *P. gigantea* skeleton, we performed solution phase analyses on skeletal powders drilled from a section of the coral parallel to the line analyzed by LA-ICP-MS.

[15] To quantify the proportion of bulk skeletal P in intracrystalline sites, chemically cleaned and uncleaned coral P/Ca values were compared. Uncleaned samples represent total (intracrystalline + non-intracrystalline) P signals and are assumed to be comparable to laser ablation

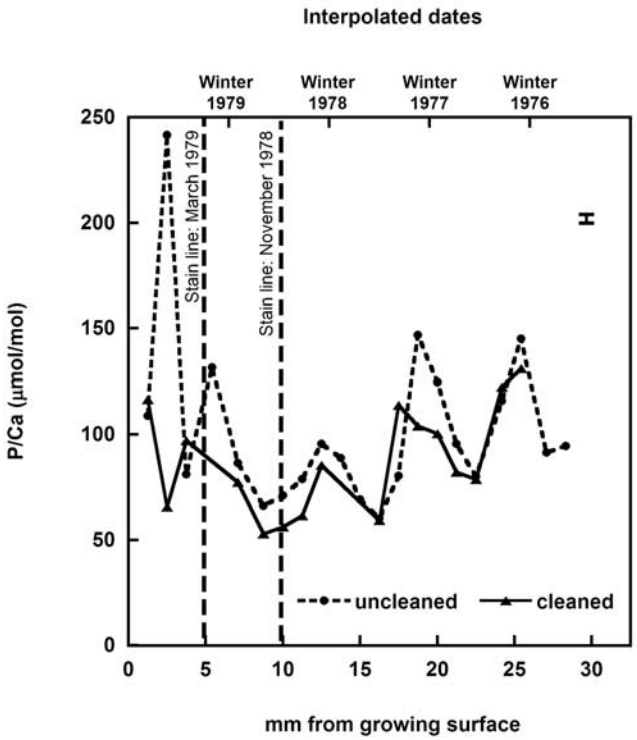

Figure 2. P/Ca (μmol/mol) ratios in cleaned (solid line with triangles) and uncleaned (dashed line with circles) drilled coral powders measured by solution phase HR-ICP-MS. Y-error bar represents 3% precision for solution phase HR-ICP-MS analyses. Dashed lines mark stain lines in coral sample.

data. Laser ablation and drilled solution phase P/Ca results are difficult to compare directly because the two methods have different inherent sampling resolution. The P/Ca ratios in cleaned treatments are interpreted as ''intracrystalline'' (organic plus inorganic P bound between or within individual aragonite crystals) as the cleaning procedure is designed to remove non-intracrystalline material including organic matter, mineral oxides, and surface-sorbed species [*Shen and Boyle*, 1988]. The results show that, below the tissue layer (upper 7 mm) the two treatments give results that differ only slightly; on average, chemical solution cleaning removed 12 ± 10% of the total phosphorus signal (Figure 2). Within the tissue layer, this cleaning procedure removed up to 70% of the total P. This result suggests that, with the exception of this upper layer, ~90% of P in the skeleton is incorporated as an intracrystalline phase uncleanable from the powder particle surfaces (particle dimension ~10 μm).

[16] To determine the fraction of total skeletal P occurring in an inorganic form, we performed SRP analyses on dissolved uncleaned carbonate powder. We found that less than 40% of the total skeletal P signal is inorganic (data not shown) and we assume the remainder is organic P. This result is in agreement with previous studies of other surface corals, which suggested that an organic phosphorus phase could contribute ~25–75% of total skeletal P [*Dodge et al.*, 1984; *Kumarsingh et al.*, 1998; *Shotyk et al.*, 1995]. The P/Ca signal measured by laser ablation is not, therefore, primarily a result of inorganic phosphorus incorporated into coral skeleton by ionic substitution or any other inorganic mechanism. Intracrystalline organic P thus accounts for the majority (over 60%) of *P. gigantea* skeletal phosphorus incorporated during calcification.

[17] The intracrystalline organic matrix of coral skeleton is thought to be dominated by compounds that do not contain phosphorus, primarily amino acids [*Ingalls et al.*, 2003; *Lowenstam and Weiner*, 1989; *Mitterer*, 1978]. Lipids, however, make up a small fraction of intracrystalline organic material, account for 0.003–0.03% of skeletal mass, and may include 12–45 wt% phospholipid [*Ingalls et al.*, 2003; *Isa and Okazaki*, 1987]. Based on these estimates and the molecular weights of common phospholipids, we estimate that intracrystalline phospholipids could contribute roughly ~1–60 μmol P per mol of skeletal Ca, approaching the low range of our P/Ca results for Gulf of Panamá *P. gigantea*. Nucleic acids are another class of phosphorus-rich organic compounds that could contribute to skeletal P/Ca while accounting for only a small fraction of total intracrystalline organic material, but little is known about the nucleic acid content of coral skeleton.

[18] While more work is required to constrain the P incorporation mechanism, it is apparent that variations in total (primarily intracrystalline) P/Ca record cyclical trends in seawater phosphate in the Gulf of Panamá upwelling system. It is uncertain why predominantly organic intracrystalline phosphorus should vary with ambient seawater phosphate. Changes in host-symbiont P recycling in response to seawater phosphate availability [*Falkowski et al.*, 1993] could influence skeletal P incorporation. We speculate that an inorganic skeletal P/Ca response to surface water phosphate may be augmented by changes in the phosphorus content of skeletal organic matter (P/C) or perhaps the concentration of organic matter itself responding to ambient seawater phosphate availability.

[19] The results presented here constitute evidence for a quantitative P/Ca proxy for seawater phosphate in surface dwelling scleractinian corals. The data are thus far limited to a single *Pavona gigantea* specimen from one site, in the context of well known variations in seasonal phosphate, but as yet lack strict calibration with contemporaneous seawater data. The possible sensitivity of P/Ca to other, potentially co-varying, environmental variables such as temperature needs to be explored further, as well as the natural variability among coral colonies and species, before the P/Ca proxy can be adopted as broadly applicable. The approach is sufficiently encouraging however, that it should be tested further at sites with distinct nutrient dynamics and physical regimes. The intracrystalline nature of total skeletal phosphorus makes P/Ca records amenable to rapid analysis in situ by LA-ICP-MS without the need for rigorous sample cleaning. Since bulk intracrystalline organic matter is preserved over at least century timescales in surface corals, and the skeletal incorporation of macromolecules responds to environmental conditions, there is strong potential for the application of this proxy to older and fossil coral skeletons [*Gupta et al.*, 2007; *Ingalls et al.*, 2003]. The use of coral skeletal P/Ca as a direct seawater nutrient proxy will be useful for studying past nutrient distributions, temporal dynamics, coastal eutrophication, and coral reef decline in the context of global changes in climate and marine biogeochemical processes.

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