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Key role of continental margin sediments in the oceanic mass balance of Zn and Zn isotopes

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ABSTRACT

Zinc is an essential micronutrient and its concentration and isotopic composition in marine sediments represent promising tracers of the ocean carbon cycle. However, gaps remain in our understanding of the modern marine cycle of Zn, including an explanation of the heavy Zn isotopic composition of seawater relative to the known inputs, and the identity of a required 'missing sink' for light Zn isotopes. Here we present Zn isotope data for organic- and trace metal-rich continental margin sediments from the east Pacific margins, which together provide the first observational evidence for the previously hypothesized burial of light Zn in such settings. In turn, this light Zn output flux provides a means to enrich the seawater dissolved pool in heavy isotopes. The size and isotopic composition of the margin sink is controlled by the uptake of Zn into organic matter in the photic zone and the fixation of this pool, probably in the form of Zn-

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sulfides, in sediments. An estimate of its significance to the overall Zn oceanic mass balance, both in terms of flux and isotopic composition, indicates that such settings can fulfill the requirements of the missing Zn sink. Taken together, these observations have important implications for the interpretation of Zn isotope data for marine sediments in the geologic record.

INTRODUCTION

Zinc is utilized in almost 100 Zn-specific enzymes across all five kingdoms of life (U.S. NRC, 2000). Its significance in the oceanic realm stems primarily from its role as a cofactor in two key enzymes: carbonic anhydrase, involved in carbon fixation, and alkaline phosphatase, active in phosphorus uptake and cycling (Sinoir et al., 2012). Under certain conditions, Zn may limit primary production (Morel et al., 1994). Its importance as a micronutrient, combined with procedural and analytical advances and the sampling capacity of the GEOTRACES program (SCOR Working Group, 2007), has motivated a new generation of studies of the modern oceanic cycling of Zn and its isotopes (e.g., Little et al., 2014; Zhao et al. 2014; Conway and John, 2014; John and Conway, 2014; Roshan and Wu, 2015; Janssen and Cullen, 2015).

Zinc isotopes offer insight both into the processes controlling water column Zn distributions, and constraints on its global oceanic mass balance. Furthermore, the likely strong biological control on dissolved Zn availability has motivated the use of δ^{66}Zn as a tracer of past ocean productivity (Kunzmann et al., 2012). However, there remains a considerable gap in our understanding of the modern Zn oceanic mass balance (Little et al., 2014), which limits our interpretation of paleo-Zn isotope data. An isotopically light sink is required both to balance the marine Zn budget, and to explain the isotopically

heavy composition of dissolved Zn in the modern ocean with respect to the primary Zn inputs (seawater ~0.5‰; cf. rivers, dust, hydrothermal fluids and sediments, all ≤0.3‰; see Fig. 1). In this study we present new Zn isotope data for organic-rich sediments from several oxygen-deficient sites along the east Pacific margin. These data provide the first observational evidence of a hypothesized light sink for Zn buried in organic-rich sediments (Little et al., 2014; Zhao et al., 2014).

SITES AND SAMPLING

We studied samples from well-characterized sites from the north- and south-eastern Pacific margin (Table 1, Fig. DR1). They include four California borderland basins (Santa Barbara, Santa Monica, San Nicolas and Tanner Basins), three sites from along the Mexican margin (Magdalena, Soledad Basin and Pescadero slope), and one site at the center of the intense oxygen minimum zone (OMZ) along the Peru margin. All three margins are slope-dominated, characterized by upwelling-driven productivity. Taken together, they encompass a range of reducing (low oxygen) conditions and diagenetic environments found along an open ocean margin (Table 1).

Sediment cores were collected using a multi-corer as described previously (McManus et al., 2006). Cores from the Mexico and Peru margins have low bottom water oxygen concentrations and cover a range of diagenetic regimes from ferruginous to sulfidic (Table 1, McManus et al., 2006; Chong et al., 2012). The borderland basins have a broader range in bottom water oxygen contents and include settings that are typically manganeous to ferruginous (Table 1).

ANALYTICAL METHODS

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For bulk concentration and isotope measurements, 100–500 mg of powdered sediment was treated with dilute nitric acid to dissolve carbonate, digested in a 3:1 mix of concentrated HF and HNO_3, and treated three times with concentrated HNO_3 to re-dissolve fluoride salts before final dissolution in 7M HCl. An aliquot of the total digest solutions was taken for elemental analysis on a Thermo Element 2 at the University of Bristol or ETH Zürich (for accuracy and precision data, see Little et al. (2014, 2015)). For isotope analysis, further aliquots were spiked with a ^{64}Zn-^{67}Zn double spike to achieve sample-spike ratios of close to unity (Bermin et al., 2006). These Zn fractions were purified via anion exchange (Bermin et al., 2006) and analyzed on a Neptune (Bristol) or Neptune Plus (ETH) MC-ICP-MS using previously published protocols (Archer and Vance, 2004; Little et al., 2014). Two-sigma external reproducibility on $\delta^{66}Zn$ analyses was estimated via double spike analysis of a secondary isotope standard, IRMM 3702, which gave $\delta^{66}Zn = 0.30 \pm 0.06‰$ relative to Lyons-JMC (n = 163 over 24 months). Other uncertainties are given as 2SD unless stated.

Organic carbon data are calculated as the difference between total carbon and inorganic carbon. Total carbon and sulfur were analyzed on a PerkinElmer Series 11 CNHSO Analyzer, and inorganic carbon was measured on a UCI Inc. Coulometrics CMS130 Coulometer.

RESULTS

No analytically discernable depth dependent variation in bulk sediment $\delta^{66}Zn$ values was observed for the sites we sampled (Fig. 2). $\delta^{66}Zn_{bulk}$ in the California and Mexican margin sites were consistently lighter than the lithogenic average (0.27 ± 0.07‰ (1SD); Fig. 1, Table DR1), at –0.05–0.15‰. No resolvable isotopic variation was

observed among the California Borderland basins (0.11 ± 0.08‰), which together encompass a broad range in bottom water oxygen conditions (Table 1). Of the Mexican margin sites, the Magdalena margin site is distinct, exhibiting greater Zn enrichment reflected in higher Zn/Al values (by mass, expressed as ppm/wt%) and a slightly heavier $\delta^{66}Zn_{bulk}$ than the Pescadero slope and Soledad basin (Madgalena: 0.12 ± 0.02‰, cf. Soledad/Pescadero: 0.01 ± 0.06‰). The Magdalena site represents an open ocean, unrestricted margin (Table 1). In this regard, it most closely resembles the Peru margin site, where mean $\delta^{66}Zn_{bulk}$ is significantly different and isotopically heavier, at 0.32 ± 0.06‰.

DISCUSSION

Lithogenic versus 'Bioauthigenic' Zn

Evaluation of the Zn flux from seawater into margin sediments requires a correction for the lithogenic (terrigenous) component of the sediment. Zinc is present at ~70 ppm in upper continental crust (Rudnick and Gao, 2003) and often at higher concentrations in shale (Wedepohl, 1991). The correction is made by assuming a homogenous Zn/Al ratio and isotopic composition of the lithogenic component, $(Zn/Al)_{lith}$ and $\delta^{66}Zn_{lith}$, and using the measured Al concentration of the sample (Al_{sample}) as a tracer of the terrigenous component, to calculate its lithogenic Zn fraction (X_{lith}) as follows:

$$X_{lith} = ((Zn/Al)_{lith} \times Al_{sample}) / Zn_{sample} \quad (1)$$

where Zn_{sample} is the total Zn concentration of the sample. The non-lithogenic, or 'bioauthigenic' component of the sediment, X_{auth}, which includes both authigenic

(chemically precipitated) and biogenic (cellular and/or skeletal) Zn, can then be simply calculated:

$$X_{auth} = 1 - X_{lith}, \quad (2)$$

The isotope ratio of this bioauthigenic Zn fraction can then be calculated as follows:

$$\delta^{66}Zn_{auth} = (\delta^{66}Zn_{bulk} - \delta^{66}Zn_{lith} \times X_{lith}) / X_{auth} \quad (3)$$

where $\delta^{66}Zn_{bulk}$ is the measured isotope value of the sample. Finally, the bioauthigenic or 'excess' Zn concentration, Zn_{XS}, can be calculated:

$$Zn_{XS} = Zn_{sample} - Al_{sample} \times (Zn/Al)_{lith}. \quad (4)$$

In the absence of measurements of local lithogenic materials from the east Pacific margin we use global average lithogenic values. The isotopic composition of lithogenic Zn ($\delta^{66}Zn_{lith}$) is 0.27 ± 0.07‰ (1SD, n = 50, Figure 1, Table DR1). We assume a Zn/Al ratio of 8.4×10^{-4} (the most recent upper continental crust estimate; Rudnick and Gao, 2003), and assign it a 1SD uncertainty of $\pm 1 \times 10^{-4}$. We then use a Monte-Carlo approach to evaluate the uncertainties on calculated $\delta^{66}Zn_{auth}$ values. The uncertain variables ($(Zn/Al)_{lith}$, $\delta^{66}Zn_{lith}$, and $\delta^{66}Zn_{bulk}$) were forced within their assigned uncertainties (1SDs of 1, 0.07‰, and 0.03‰ respectively) using normally-distributed pseudo-random numbers, and the $\delta^{66}Zn_{auth}$ calculation performed 100,000 times. $\delta^{66}Zn_{auth}$ values for each sample and site were then calculated as the mean and 2SD of these 100,000 iterations (Table DR2). The lithogenic correction is most significant and has a larger associated uncertainty for those samples with a high X_{lith} fraction and/or a large difference between $\delta^{66}Zn_{lith}$ and $\delta^{66}Zn_{bulk}$ (Figs. DR1, DR2). Nevertheless, strikingly light $\delta^{66}Zn_{auth}$ values are calculated for several of the sites, with values as low as –0.40 ±

0.37‰ (Pescadero slope, Table DR2). The validity of these calculated values remains to be tested, for example, through targeted sequential leaching of the non-lithogenic Zn pool.

Margin Sediments: An Important Sink for Light Zn Isotopes

The principal finding of this study is the presence of an isotopically light Zn fraction in oxygen-poor, organic-rich margin sediments (Fig. 3). The presence of this light Zn is likely the result of one or a combination of two processes: (1) biological uptake or (2) authigenic mineral precipitation.

Biological uptake may be accompanied by the preferential incorporation of light Zn isotopes by phytoplankton (John et al., 2007) and this signature may be preserved in the resultant organic-rich sediment. An apparent correlation of $\delta^{66}Zn_{auth}$ with C_{org} content (Fig. 3a) may hint at such a surface ocean (uptake) control. However, a similar pattern emerges for $\delta^{66}Zn_{auth}$ plotted versus total S (Fig. 3b), and there is no simple relationship between $\delta^{66}Zn_{auth}$ and Zn/Al (Fig. 2), suggesting that the processes contributing to $\delta^{66}Zn_{auth}$ are complex. Despite evidence for biological Zn isotope fractionation in cultures (John et al., 2007), a biological, kinetic isotope effect is rarely evident in recent upper ocean water column data, particularly in micronutrient-limited regimes like the Southern Ocean (Zhao et al., 2014). Scavenging of Zn by particulate matter has instead been proposed to explain upper water column Zn isotope distributions (John and Conway, 2014). Scavenging favors the heavy Zn isotope (John and Conway, 2014), however, and cannot be invoked to explain the light signature in margin sediments.

Alternatively, isotopic fractionation of Zn may occur during authigenic mineral precipitation, associated with the breakdown of, or desorption from, the carrier phase.

One such plausible mechanism is the precipitation of isotopically light authigenic ZnS phases (e.g., Fujii et al., 2011). Authigenic ZnS precipitation has been proposed to occur under certain conditions in the water column, associated with reducing microenvironments around biogenic particles (Conway and John, 2015; Janssen and Cullen, 2015). In other locations, contingent upon the location of redox fronts, ZnS precipitation may occur in sediments. Irrespective of the locus of sulfide precipitation, a corresponding heavy pool of dissolved Zn would be generated in the deep water or surface sediments, consistent with the observed isotopically heavy global seawater composition (~0.5‰). Apparently contrary to this view, however, light dissolved δ^{66}Zn values and elevated Zn concentrations have been observed in the water column along both continental margins in the North Atlantic as well as in the oxygen-poor San Pedro Basin off California (Conway and John, 2014; 2015). Neither Atlantic margin is strongly reducing, thus this data is not likely to be relevant to the sulfidization hypothesis. Conway and John (2015) explain light Zn in the San Pedro basin either through release of biogenic Zn, or redissolution of (water column) colloidal sulfide particles on periodic flushing of the deep basin with oxygenated water. While the latter may be consistent with the predictions in this study, further clarity awaits renewed efforts to obtain reliable Zn porewater data from similar settings.

We hypothesize that the markedly heavier Zn isotopic composition at the Peru margin site reflects near-complete (quantitative) Zn uptake from surface waters with a local isotopic composition distinctly lighter than the global average, as is observed in the North Atlantic (Conway and John, 2014), and quantitative trapping of this Zn in the strongly reducing sediment pile. The Peru upwelling region is micronutrient-limited (Fig.

DR1; e.g., Bruland et al., 2005). Such limitation is likely reflected in very low Zn concentrations in surface waters (indicating quantitative uptake). Furthermore, similar micronutrient-limited regions elsewhere in the ocean appear not to fractionate Zn isotopes (Zhao et al., 2014).

We calculate an average Pacific margin $\delta^{66}Zn_{auth}$ composition weighted by Zn_{XS} concentrations (Table DR2) and margin area (Table 1) of 0.12‰. If the Peru margin site is considered exceptional, and is excluded, this value decreases to –0.09‰. The global significance of this margin sink to oceanic mass balance depends on the magnitude of the Zn flux into margin sediments. Comparing the continental margin organic C deposition rate with the Zn/C ratio in plankton yields a preliminary flux estimate. Reported Zn/C ratios in phytoplankton vary widely (0.008 – 0.11 mmol Zn/ mol C: Twining and Baines, 2013). The mean of compiled values is 0.036 mmol Zn/ mol C (Little et al., 2015). Jahnke (2010) estimates organic C deposition along the east pacific margins to be 2.28×10^{12} mol/yr, and globally to be 15.6×10^{12} mol/yr. Taking these estimates at face value, we calculate a Pacific margin Zn deposition rate of 0.8×10^{8} mol/yr, and a global rate of 5.6×10^{8} mol/yr. Such a flux would make margin sediments of equal or greater significance to the global oceanic mass balance compared to the oxic sink via sorption to Fe-Mn oxides, and is of the same order of magnitude as the projected missing Zn sink ($\sim 3 \times 10^{8}$ mol/yr; Little et al., 2014). This approximation assumes that the Zn is solely supplied to sediment via cellular uptake, and that it is retained (e.g., in a sulfide phase) in the sediments following degradation of the organic matter. If some other means of Zn supply (e.g., direct diffusion from bottom waters, scavenging, or water column sulfide precipitation) is significant, then the sink may be larger. On the other hand, diffusion of

Zn back to the water column would reduce the flux magnitude. Nevertheless, to first order, the data presented in this study strongly support the hypothesis that modern continental margin sediments represent a significant isotopically light sink for Zn.

CONCLUSIONS

This study provides a means to explain the isotopically heavy Zn isotopic composition of seawater; that is, removal of light Zn isotopes to organic-rich continental margin sediments. In addition, we move a step closer to a quantitative understanding of the modern oceanic mass balance of Zn. A general framework can be envisaged whereby Zn is delivered to the deep ocean or sediment in organic matter, which may (or may not) be isotopically fractionated from the input value (typically of ~0.3‰). Once in the reducing deep ocean or sediment, the Zn is sequestered in authigenic precipitates, either quantitatively, or partially. If sequestration is non-quantitative, there is potential for isotope fractionation, for example via precipitation of light Zn sulfides. Thus, it does not follow that the most sulfidic regime should necessarily exhibit the largest Zn isotope fractionation.

Isotopically heavy marine sediment Zn isotope ratios (Fig. 1) have previously been hypothesized to record biological processing in the surface ocean (e.g., Kunzmann et al., 2012). The implication of this study, supported by recent water column data and experimental studies (e.g., Bryan et al., 2014), is that this view may need to be revised. Instead, authigenic mineral formation in reducing environments may be the driver of the present-day heavy isotopic composition of seawater. Future studies should examine the transformation of biogenic Zn into more stable phases under different depositional redox conditions, both beneath highly productive margins and in locations with moderate to low

primary productivity, where anoxia is the result of restricted circulation (e.g., the Black Sea). Such studies will provide the basis for future application of Zn isotopes as a proxy for the past environment.

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332
333 FIGURES
334 Figure 1. Range of compiled data sets (Table DR1) illustrating the natural variability in
335 $\delta^{66}Zn$ in the marine realm, divided into the inputs to and outputs from the ocean. Where
336 sufficient data exists, mean and 1SD are given as a symbol and thick black line. Shaded
337 gray bars emphasize the respective isotopic compositions of the lithogenic and seawater

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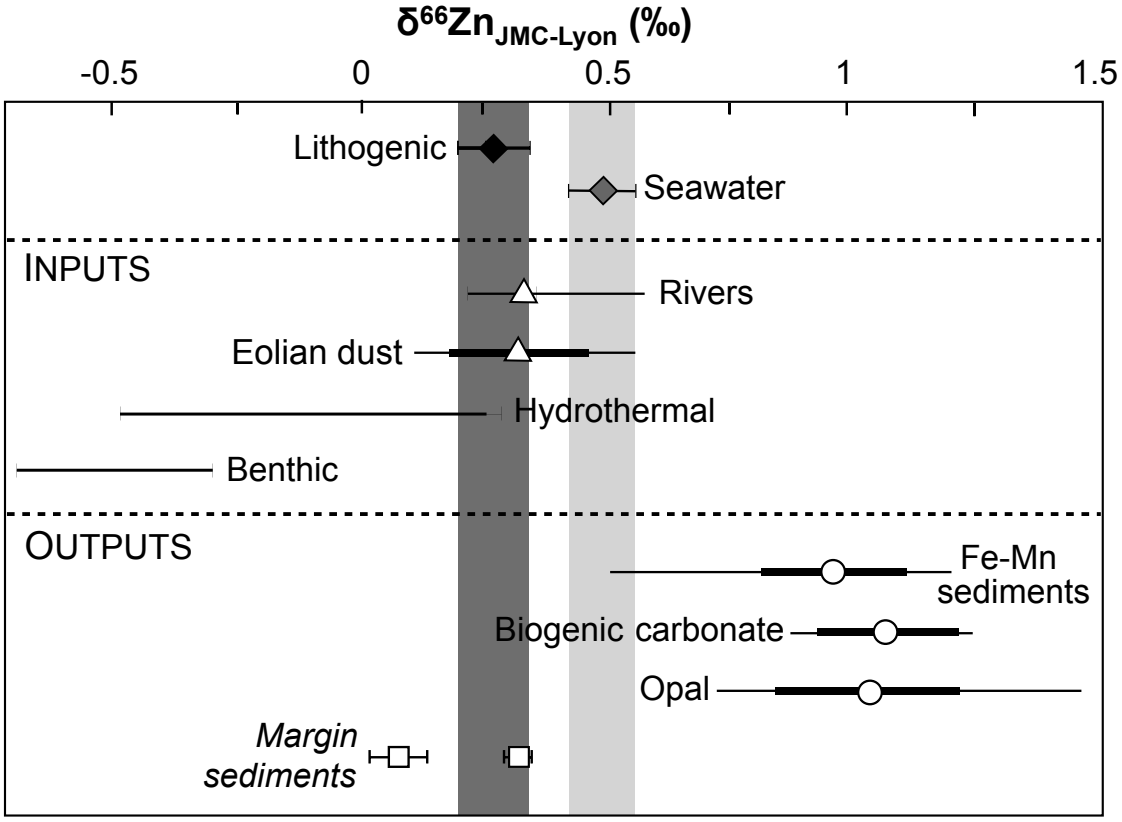
338 reservoirs. Mean and 1SD of measured bulk $\delta^{66}Zn$ for margin sediments from this study

339 are shown as two points, representing the Peru margin and all other sites.



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341

342 Figure 2. Down-core variability in (A) Zn/Al (by mass, $\times 10^{-4}$) and (B) $\delta^{66}Zn_{bulk}$ for the

343 three continental margin locations (California Borderland basins: triangles; Mexican

344 sites: squares; Peru margin: circles). 2-sigma uncertainty on isotope measurements

345 (0.06‰) is shown as a stand-alone error bar. Labeled gray-dashed vertical bars represent

346 estimated $(Zn/Al)_{lith}$ and $\delta^{66}Zn_{lith}$, with average deep seawater $\delta^{66}Zn$ for comparison.

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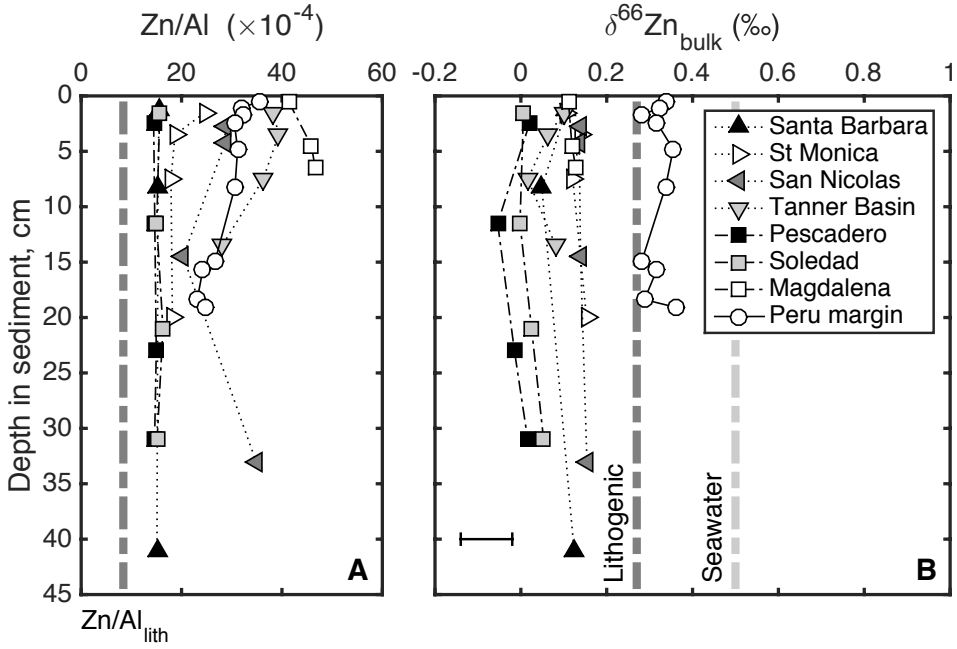


347

348 Figure 3. a) Mean organic carbon (wt%) and b) Mean total S (wt%) versus mean

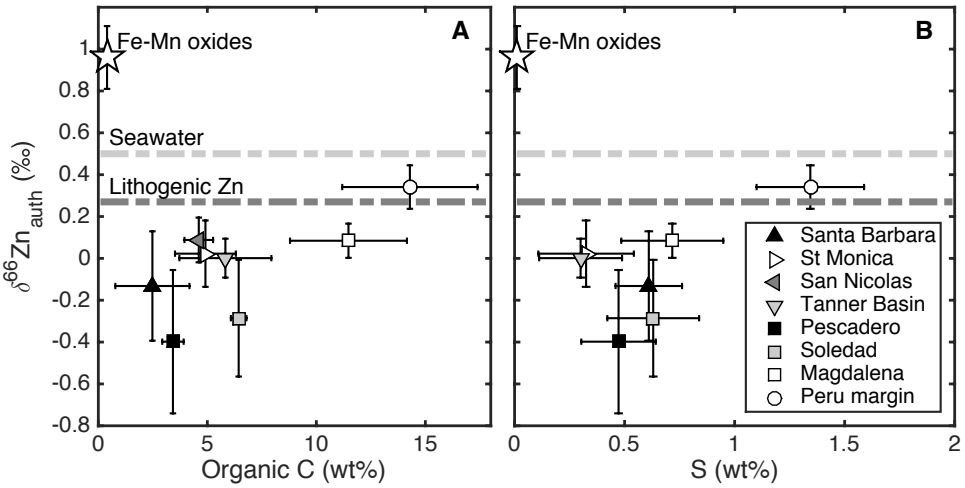
349 calculated $\delta^{66}Zn_{auth}$ values for each site. Error bars on C_{org} and S values reflect the 2SD

350 for the whole sediment core, as thus reflect depth-dependent variation. Uncertainties on

351 $\delta^{66}Zn_{auth}$ are calculated via a Monte Carlo simulation carried out as described in the text.

352 For comparison, the mean and 1SD (Table DR1) of Fe-Mn oxide sediments are

353 represented by a star.



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362 TABLE 1. SITE DESCRIPTIONS

Site	Latitude °N	Longitude °W	Margin area 10^6 km^2	Sediment core m	OMZ m	Sill depth m	Basin depth m	Bottom-water O_2 µM	Diagenetic class*	Sediment accumulation rate mg cm^{-2} yr^{-1}	Organic C burial flux mg cm^{-2} yr^{-1}	*Refs*
Peru Margin	-13.7	76.7	0.2	264	100–700	na	na	0–10	Ferr-Sulf	25	3.6 ± 0.4	*1*
Mexican Margin			0.1		500–1000							
Soledad Basin	25.2	112.7		544		250	545	0	Sulf	50–90	3.7 ± 0.1	*1, 2, 3*
Pescadero slope	24.3	108.2		616		na	na	0.4	Ferr	77	-	*3*
Magdalena	23.5	111.6		692		na	na	0.9	Ferr-Sulf	4–12	-	*4*
California Borderland Basins			0.1		200–1000							
Santa Barbara	34.3	120.0		493		475	600	0–10	Ferr-Sulf	92	-	*5*
Santa Monica	33.7	118.8		905		740	910	2–10	Ferr	16	0.7 ± 0.2	*1*
Tanner Basin	33.0	119.7		1514		1160	1550	~30	Mn-Ferr	12	0.8 ± 0.1	*1*
San Nicolas	32.8	118.8		1750		1100	1832	15–35	Mn	14	-	*1*

*Diagenic classifications are as follows: Sulf – sulfidic, Ferr – ferruginous, Mn – Mn-rich, sub-oxic.
1 McManus et al., 2006; *2* Chong et al., 2012; *3* Deutsch et al., 2014; *4* Hartnett et al., 1998; *5* Zheng et al., 2000

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