Amino acid $\delta^{13}C$ and $\delta^{15}N$ patterns from sediment trap time series and deep-sea corals: implications for biogeochemical and ecological reconstructions in paleoarchives

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Abstract:

Recent work using compound-specific stable isotopes of amino acids (CSI-AA) in proteinaceous deep-sea corals opens a new realm of high-fidelity reconstructions of biogeochemical and ecological changes in the ocean. However, underlying these CSI-AA paleoceanographic applications are a series of fundamental assumptions, which hold first that baseline-proxy AA isotope values fixed at the base of food webs represent integrated $\delta^{13}C$ and $\delta^{15}N$ values of primary production, and second they stay unaltered during subsequent export and incorporation from particles into corals. We explored long-term $\delta^{13}C$ and $\delta^{15}N$ CSI-AA data on a sediment trap time series together with contemporaneous deep-sea bamboo corals (*Isidella* sp.) in the California margin, to for the first time directly test these assumptions. Isotope values of essential ($\delta^{13}C_{EAA}$) and source AAs ($\delta^{15}N_{Phe}$) in sinking particles quantitatively tracked bulk $\delta^{13}C$ and $\delta^{15}N$ values of export production. These CSI-AA baseline proxies varied independently of carbon flux, trophic position ($TP_{CSI\text{-}AA}$) and microbial alteration, suggesting that they were well preserved in sinking particles. Paired comparisons between sinking particles and deep-sea corals revealed minor elevations of $\delta^{13}C_{EAA}$ (by ~2‰) and $\delta^{15}N_{Phe}$ (by ~1‰) in the coral skeletons. We hypothesize the difference in $\delta^{13}C_{EAA}$ is due to the geographic offset in $\delta^{13}C$ values of primary production expected between the (more offshore) sediment trap site and (more onshore) coral specimens, whereas the $\delta^{15}N_{Phe}$ offset is likely related to expected minor trophic fractionation. Using empirical models derived from the sediment trap time series, we demonstrate that CSI-AA in proteinaceous deep-sea corals reconstructs bulk $\delta^{15}N$ values of export production, source nitrogen $\delta^{15}N$ values, and exported $TP_{CSI\text{-}AA}$ values with very good fidelity. Together, these findings represent a major advance in our understanding of AA isotope behaviors in modern and paleoarchives, and will underpin the rapidly evolving use of CSI-AA-based tools in paleoceanographic studies.

1. INTRODUCTION

Stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) are invaluable tools for investigating element sources, biogeochemical processes, and ecological function in modern and ancient ecosystems (Peterson and Fry, 1987; Fry and Sherr, 1989; Post, 2002). The $\delta^{13}C$ and $\delta^{15}N$ of living organisms and nonliving suspended and sinking particulate organic matter (POM) are commonly used to infer modern ocean conditions (Goericke and Fry, 1994; Rau et al., 1998). The isotopic compositions of sinking POM collected in sediment traps enable longer and more continuous monitoring of surface ocean processes on timescales of months to years (Altabet et al., 1999; Dore et al., 2002; Woodworth et al., 2004; Montes et al., 2013), and isotopic analysis of cored marine sediments and other paleo-archives facilitates biogeochemical and ecological reconstructions far beyond the instrumental period, from centuries to millennia (Hayes et al., 1999; Thunell and Kepple, 2004; Galbraith et al., 2013; Batista et al., 2014).

Traditional 'bulk' stable isotope techniques have been used to investigate marine biogeochemical cycles on a spectrum of timescales, but understanding these changes is often not straightforward. One major problem is the difficulty of resolving the environmental or biological variables that create the bulk isotope values. A second is the typically large gap in temporal coverage between modern instrumental records (high resolution but short duration) and sedimentary archives (longer records but typically lower resolution). Recently, two separate lines of scientific progress, the development of compound-specific isotope analysis of amino acids (CSI-AA) and the development of deep-sea corals as bioarchives, have begun to address these issues in both open ocean and coastal margin.

CSI-AA offers a powerful set of new tracers allowing the direct resolution of many of the intertwined processes underlying the bulk isotopic signals (e.g., (Larsen et al., 2009; Ohkouchi et

al., 2017). This approach employs two independent analyses ($\delta^{13}C_{AA}$ and $\delta^{15}N_{AA}$) which exploit differences in isotopic fractionation among individual amino acids (AAs) during metabolic processing. $\delta^{13}C_{AA}$ applications are tied to a familiar dichotomy of "essential" versus "non-essential" AAs; the former AA group cannot be synthesized by metazoans, and so have unaltered $\delta^{13}C$ values up food chains (Howland et al., 2003; Jim et al., 2006; McMahon et al., 2010). As a result, the $\delta^{13}C$ value of essential AAs ($\delta^{13}C_{EAA}$) represents a direct proxy for the $\delta^{13}C$ value of primary production at the base of the food web. The application of $\delta^{15}N_{AA}$ is based on a different grouping, the "source" and "trophic" AAs, which fractionate differently during trophic transfer (Popp et al., 2007). The source AAs (e.g., phenylalanine) undergo little to no ^{15}N enrichment relative to diet during trophic transfer, because metabolic processes do not form or cleave bonds involving nitrogen. Therefore, source $\delta^{15}N$ values formed by primary producers are only minimally altered in higher trophic level organisms. By contrast, the "trophic" AAs (e.g., glutamic acid) exchange α-amino nitrogen atoms during metabolism and become significantly ^{15}N-enriched during trophic transfer, with predictable enrichment factors (McClelland and Montoya, 2002; Chikaraishi et al., 2009; McMahon and McCarthy, 2016). As such, paired analysis of $\delta^{15}N$ values for source ($\delta^{15}N_{SrcAA}$) and trophic AAs ($\delta^{15}N_{TrAA}$) can resolve the variations of bulk $\delta^{15}N$ values into two specific contributions: source nitrogen $\delta^{15}N$ shifts and trophic position changes. Complementary but fully independent $\delta^{13}C_{AA}$ and $\delta^{15}N_{AA}$ analyses are now producing novel insights into biogeochemical and ecological changes in coastal and open oceans (Ruiz-Cooley et al., 2014; Vokhshoori et al., 2014; McMahon and McCarthy, 2016; Ohkouchi et al., 2017; Sabadel et al., 2019).

Long-lived proteinaceous deep-sea corals represent relatively new bioarchives for past ocean conditions (e.g., (Thresher et al., 2004; Roark et al., 2009; Prouty et al., 2011; Guilderson

et al., 2013). These colonial animals are ubiquitous in the deep-sea wherever hard substrates occur. They derive their skeletal C and N from sinking particles, thereby recording a history of surface ocean processes (Sherwood et al., 2005; Sherwood et al., 2011; Hill et al., 2014; Glynn et al., 2019). The proteinaceous skeletons are slowly deposited in radial growth layers (50-150 μm/yr) for up to hundreds to thousands of years (e.g., (Thresher et al., 2004; Roark et al., 2005; Sherwood et al., 2006; Sherwood and Edinger, 2009; Sherwood et al., 2009), and are resistant to degradation over at least millennial time scales (Sherwood et al., 2006; Ehrlich, 2010; Strzepek et al., 2014; McMahon et al., 2015). As such, isotopic analysis of coral proteinaceous skeletons can provide long-term records of surface ocean processes with near annual resolution.

Only in the last decade have CSI-AA tools been applied to proteinaceous deep-sea coral records. Sherwood et al. (2011) measured the first $\delta^{15}N_{AA}$ values in annually-banded, proteinaceous deep-sea corals of the Northwest Atlantic margin. The resulting 75 year-long time series was able to decouple physical ocean from ecological changes, resolving a controversy regarding the recent change in source nitrate and showing its linkage to changes in water mass circulation. Subsequent studies of $\delta^{13}C_{AA}$ and $\delta^{15}N_{AA}$ in deep-sea corals of the subtropical North Pacific Ocean indicated centennial-scale changes in the source of new nitrogen (nitrate versus N_2 fixation) (Sherwood et al., 2014) and in plankton community composition (Sherwood et al., 2014; McMahon et al., 2015). A growing number of paleoceanographic studies have now expanded the application of CSI-AA to other oceanic regions (Prouty et al., 2014; Schiff et al., 2014; Williams et al., 2017). These results are providing detailed views of past ocean changes in primary production, nitrogen sources, planktonic food web structures, and long-term human impacts on marine ecosystems.

However, despite major progress in CSI-AA-based paleoceanographic applications, there remain a number of important uncertainties related to this approach. Chief among these is a detailed understanding of the linkage between exported surface production CSI-AA values and those recorded in paleoarchival coral skeletons. The working assumption is that isotope values incorporated into proteinaceous coral skeletons (i.e., coral's diet) represent those in the exported plankton production. One existing comparison between general CSI-AA distributions between corals and laboratory algal cultures seems to support this idea (Schiff et al., 2014). However, this assumption has not been rigorously investigated nor directly tested in the field. Surface food webs linked to variations in nutrient supply and planktonic community can shift dramatically and affect the exported CSI-AA patterns. In addition, possible microbial activity on sinking particles could also impact the preservation of CSI-AA values. Finally, the degree of correspondence between "real world" export production and preserved coral skeleton CSI-AA data, based on direct comparisons of coupled sinking POM-coral samples, has never been examined.

The central objectives of this study were to address these basic unknowns and provide a vital basis for the CSI-AA-based paleoceanographic applications. We analyzed individual $\delta^{13}C_{AA}$ and $\delta^{15}N_{AA}$ values in a deep-sea sediment trap time series (1999-2004), alongside contemporaneous proteinaceous deep-sea bamboo corals (*Isidella* sp.) in Monterey Bay, California. Our study addresses five central questions. First, can CSI-AA resolve factors behind the varying bulk $\delta^{13}C$ and $\delta^{15}N$ values of export production? Second, can CSI-AA in sinking particles quantitatively track bulk $\delta^{13}C$ and $\delta^{15}N$ values of export production? Considering the wealth of literature documenting and applying bulk isotope values of export production to study past ocean biogeochemical and ecological dynamics, there is utility in the ability to predict bulk values with the growing number of CSI-AA data. Third, do seasonal or other environmental factors drive

variation of CSI-AA baseline values (i.e., $\delta^{13}C_{EAA}$, $\delta^{15}N_{Phe}$) in sinking particles, and are these baseline values influenced by zooplankton or microbial alteration? Fourth, are individual AA isotope values in sinking particles faithfully incorporated into deep-sea coral skeletons? And lastly, can we use deep-sea coral CSI-AA values to accurately reconstruct bulk isotope values of export production, source nitrogen, and surface plankton community structures? The answers to these questions are fundamental to further applications of CSI-AA in paleoceanographic studies.

2. METHODS

2.1 Study region and sampling procedures

Sampling was conducted in Monterey Bay, a large open embayment on the central coast of California (Fig. 1). This region experiences strong seasonal upwelling and relaxation in response to local wind forcing and interaction with a California Current meander (Rosenfeld et al., 1994). The upwelled water, formed north of Monterey Bay at Pt. Año Nuevo (Rosenfeld et al., 1994), introduces nutrient-rich water into the central Bay during March-July promoting high primary production in spring and summer (1.5-2.5 g C m^{-2} d^{-1}) (Chavez, 1996; Pennington and Chavez, 2000). Spatial and temporal variations in nutrients and currents influence phytoplankton and zooplankton communities (Kudela and Dugdale, 2000; Fawcett and Ward, 2011; Messié and Chavez, 2017) and collectively affect the amount and composition of exported POM (Pilskaln et al., 1996; Castro et al., 2018), which is the main food source for deep-sea corals in Monterey Bay (Hill et al., 2014). High and variable rates of plankton productivity, complex plankton food web structures, and tight pelagic-benthic coupling make Monterey Bay an ideal region for testing the utility and reliability of CSI-AA-based proxies under varying conditions.

157 Sinking particles were collected at station M2 (36.697˚N, 122.378˚W; Fig. 1) using an
158 acid-cleaned cone-shaped Honjo Mark VI sediment trap (Honjo and Doherty, 1988). The trap was
159 deployed at 1200 m depth (~500 m above the seafloor) from January 1999 through December 2004.
160 The trap was outfitted with 13 collection cups that contained preservatives (3.0 mM of mercury
161 chloride and > 5 g/L of sodium chloride) and rotated every 14 days. There were gaps in the
162 sampling due to technical issues with sediment trap program or trap retrieval. The collection and
163 handling of samples followed the procedures described in Castro et al. (2018). The oven-dried
164 samples were ground in an agate mortar and stored in polyethylene vials or polycarbonate tubes at
165 room temperature in the dark until elemental and isotopic analyses.
166 Deep-sea corals were collected in Monterey Canyon (36.747˚N, 122.022˚W) inshore of the
167 M1 mooring station (Fig. 1). Two bamboo coral specimens (*Isidella* sp.), T1104-A2 and T1104-
168 A11, were live-collected in 2007 at depths of 915 m and 835 m using the Monterey Bay Aquarium
169 Research Institute (MBARI) vessel R/V *Western Flyer* and the ROV *Tiburon*. Coral collection
170 methods were previously reported in Schiff et al., (2014). Briefly, polyp and tissue material was
171 separated from skeletons upon collection, and the samples were washed in seawater and rinsed in
172 freshwater prior to air drying. An organic node (6-8 mm thick) was removed from near the basal
173 attachment of each coral skeleton and decarbonated in 10% HCl. Using scalpel and forceps,
174 organic peels (0.4 -0.5 mm thick) were dissected and then rinsed in Milli-Q water and dried. Based
175 on bomb-^{14}C dating, the growth rate of *Isidella* in Monterey Bay was estimated to be 0.14 mm/yr
176 (Schiff et al., 2014); thus each peel represents a 3-4-year time window. Below we present data
177 from only the second and third peels from each coral because they represent the best temporal
178 match to the sediment traps data (1999-2004).
179 **2.2 Bulk δ^{13}C and δ^{15}N analyses**

Sediment trap samples were separated into aliquots for bulk $\delta^{13}C$ and $\delta^{15}N$ analysis. Aliquots for $\delta^{13}C$ analysis were weighed (~10 mg) into silver boats and acidified by immersion in 6-8% sulfurous acid (H_2SO_3) followed by repeated rinses with Milli-Q water and drying at 60˚C overnight. The other aliquots for $\delta^{15}N$ analysis (~10 mg) were not pre-treated. Coral peels were acidified during the previous preparation (section 2.1) and did not undergo any further pre-treatment. Approximately 0.15 mg of coral peels was used for bulk $\delta^{13}C$ and $\delta^{15}N$. Bulk isotope analysis was performed at the UC Santa Cruz Light Stable Isotope Laboratory using a Carlo Erba 1108 elemental analyzer coupled to Thermo Finnigan Delta Plux XP isotope ratio mass spectrometer following standard procedures (https://websites.pmc.ucsc.edu/~silab/index.php). Isotopic values were corrected for sample size and instrumental drift and were reported in units of per mil (‰) relative to Vienna PeeDee Belemnite (VPDB) and air for $\delta^{13}C$ and $\delta^{15}N$, respectively. Analytical precision as monitored with acetanilide was <0.2‰ for $\delta^{13}C$ and $\delta^{15}N$.

2.3 Amino acid $\delta^{13}C$ and $\delta^{15}N$ analyses

Approximately 10-15 mg of dried sediment trap and coral material was used for amino acid $\delta^{13}C$ and $\delta^{15}N$ analyses. Hydrolysis, purification, and derivatization followed previously established protocols in batches of 5-7 samples (Silfer et al., 1991; McCarthy et al., 2013; McMahon et al., 2018). An AA mixture of known $\delta^{13}C$ and $\delta^{15}N$ values and an in-house biological reference standard (homogenized cyanobacteria) was analyzed along with each sample batch. The AA mixture was used to calibrate the $\delta^{13}C$ and $\delta^{15}N$ results. The cyanobacteria reference, processed in the same way as samples, was used to monitor the consistency of wet chemistry and instrumental analysis (Table EA1). $\delta^{13}C_{AA}$ and $\delta^{15}N_{AA}$ values were determined using a Thermo Trace Ultra gas chromatography (GC) coupled with a Finnigan MAT DeltaPlus XL IRMS at UCSC SIL following chromatographic conditions described in McCarthy et al. (2013) and McMahon et al. (2018).

Samples were injected in triplicate, bracketed by triplicate injections of the calibration standard. Final $\delta^{13}C_{AA}$ values were corrected for the added derivatizing reagents following the procedures of Silfer et al. (1991), and final $\delta^{15}N_{AA}$ values were corrected based on the offset between known and measured $\delta^{15}N_{AA}$ values of the calibration standard. The standard deviation of replicate injections for individual AAs in the samples ranged from 0.2‰ to 0.5‰ for $\delta^{13}C$ and from 0.1‰ to 0.6‰ for $\delta^{15}N$. The relative abundance (mol%) of amino acids was determined from peak areas measured during $\delta^{15}N$ analysis. Peak area response factors for individual AAs were calculated from the known-concentration external standards and then applied to sample peak areas to derive molar abundances.

A total of twelve amino acids (AAs) were analyzed for $\delta^{13}C$ and $\delta^{15}N$, including alanine (Ala), glycine (Gly), threonine (Thr), serine (Ser), valine (Val), leucine (Leu), isoleucine (Ile), proline (Pro), asparagine + aspartic acid (combined as Asx), glutamine + glutamic acid (combined as Glx), phenylalanine (Phe), and lysine (Lys). These AAs were further assigned to several groups based on established classifications (discussed in section 4.4). For $\delta^{13}C$ there are six essential AAs (EAA: Thr, Ile, Val, Phe, Leu, Lys) and six non-essential AAs (NEAA: Gly, Ser, Asx, Glx, Pro, Ala). For $\delta^{15}N$ there are two source AAs (SrcAA: Phe, Lys), seven trophic AAs (TrAA: Glx, Asx, Ala, Leu, Ile, Pro, Val), and three others (Gly, Ser, Thr). Mean $\delta^{13}C$ and $\delta^{15}N$ values of each group ($\delta^{13}C_{EAA}$, $\delta^{13}C_{NEAA}$, $\delta^{15}N_{SrcAA}$, $\delta^{15}N_{TrAA}$) were calculated as the simple average isotope values of AAs from corresponding groups. To facilitate cross-study comparison, mol%-weighted average was not used here, because mol% values were not routinely estimated by GC-IRMS.

2.4 Parameter calculations

CSI-AA-based trophic position values ($TP_{CSI\text{-}AA}$) of sinking particles were calculated based on the $\delta^{15}N$ values of Glx and Phe following the formulation of Chikaraishi et al. (2009):

$$TP_{CSI\text{-}AA} = 1 + (\delta^{15}N_{Glx} - \delta^{15}N_{Phe} - 3.4‰) / 7.6‰ \quad (1)$$

where 3.4‰ is the empirical offset between $\delta^{15}N_{Glx}$ and $\delta^{15}N_{Phe}$ determined in aquatic primary producers (cyanobacteria and algae) (McClelland and Montoya, 2002; Chikaraishi et al., 2009) and 7.6‰ is a trophic discrimination factor (TDF) of $\delta^{15}N_{Glx\text{-}Phe}$ (Chikaraishi et al., 2009). For detrital material such as sediment trap samples or sediment, this $TP_{CSI\text{-}AA}$ value represents the average trophic position of all proteinaceous material sources contained within the sample (McCarthy et al., 2007; Batista et al., 2014). $TP_{CSI\text{-}AA}$ values of coral skeletons ($TP_{skeleton}$) represents the trophic position of the coral animal at a given sampling interval, and were calculated based on the skeleton $\delta^{15}N_{Glx}$ and $\delta^{15}N_{Phe}$ values using the following equation:

$$TP_{skeleton} = 1 + [(\delta^{15}N_{Glx} + \partial) - \delta^{15}N_{Phe} - 3.4‰] / 7.6‰ \quad (2)$$

where ∂ is a correction factor (3.4‰) proposed by McMahon et al. (2018) to account for a negative $\delta^{15}N_{Glx}$ offset observed in *Isidella* between skeleton and polyp tissue.

Two independent AA-based parameters (DI and ΣV) were calculated to assess the bacterial degradation and resynthesis of organic matter, respectively. The degradation index (DI) was derived from multivariate analysis of mol% of protein AAs following Dauwe et al. (1999):

$$DI = \Sigma (var_i - AVG_i / STD_i) \times Fact.coef_i \quad (3)$$

where var_i is the mole % of individual AA_i in our samples and the AVG_i, STD_i and $Fact.coef_i$ are the mean mol%, standard deviation, and factor coefficient of corresponding AA_i from the reference dataset (i.e., Table 1 in Dauwe et al., 1999). More positive DI values are indicative of less biodegradation of organic matter. ΣV, an indicator of microbial resynthesis, is a measure of $\delta^{15}N$ deviation during trophic AA resynthesis and was calculated according to McCarthy et al. (2007):

$$\Sigma V = 1/n \, \Sigma(|\chi_i - \chi_{mean}|) \quad (4)$$

where n is the number of trophic AAs included in this calculation (Ala, Leu, Ile, Pro, Asx, Glx) and χ_i and χ_{mean} are the $\delta^{15}N$ values of each and the mean of all trophic AAs, respectively. Higher ΣV values are indicative of a greater extent of resynthesis of organic matter.

A number of abbreviations and terminology were used in this study (see Table EA2 for full descriptions). Specifically, 'CSI-AA-based proxies' used below refer to $\delta^{13}C_{Phe}$, $\delta^{13}C_{EAA}$, $\delta^{15}N_{Phe}$, $\delta^{15}N_{SrcAA}$, or/and TP_{CSI-AA}, the first four of which are further referred to as 'CSI-AA baseline proxies'. The 'baseline' isotope values refer to the source nitrogen $\delta^{15}N$ value or/and primary production $\delta^{13}C$ value at the base of the food web.

2.5 Statistical analysis

The coral record has a lower resolution than the sediment trap cord. Therefore, the average and standard deviation of bulk and amino acid $\delta^{13}C$ and $\delta^{15}N$ values in the sediment trap time series were flux-weighted so that they are comparable to the coral record. Data used for statistical analysis were checked for normality and homogeneity of variances using Kolmogorov–Smirnov test (two-tailed, $\alpha = 0.05$) and Levene's test (two-tailed, $\alpha = 0.05$), respectively. Significance of group comparison was tested using Mann-Whitney U-test (two-tailed, $\alpha = 0.05$). Relationship between variables and the associated best fit lines were determined using a type II least-squares linear regression. The statistical analyses were performed in SPSS 23.0 (IBM Statistical Package for the Social Sciences Inc.).

3. RESULTS

3.1. Temporal patterns of sinking particles

269 *3.1.1. Organic carbon flux*

270 Organic carbon flux varied over 25-fold from 5 to 142 mg C m^{-2} d^{-1} over the 6-yr sampling
271 period (Jan 1999- Dec 2004), with maximum flux during the spring and summer upwelling months
272 (Fig. 2, Table 1). The observed temporal pattern and amplitude of carbon flux were comparable to
273 previous sediment trap records in Monterey Bay during non-El Niño years (e.g., Pilskaln et al.
274 (1996).

275 *3.1.2. Bulk and amino acid $\delta^{13}C$ values*

276 Bulk $\delta^{13}C$ values of sinking particles ($\delta^{13}C_{bulk}$) varied ~5‰ from -19.2‰ to -24.0‰ in
277 1999-2004 (Fig. 2a, Table 1). The flux-weighted average value of $\delta^{13}C_{bulk}$ (-21.5±1.3‰) is
278 consistent with the expected marine origin of sinking particles. Temporal variation of $\delta^{13}C_{bulk}$
279 roughly followed the trend of carbon flux ($R^2 = 0.345$, $p < 0.01$), i.e., values became more positive
280 from winter into the more productive spring period.

281 Compound-specific $\delta^{13}C$ values of amino acids differed between the groups of EAA
282 ($\delta^{13}C_{EAA}$) and NEAA ($\delta^{13}C_{NEAA}$). Similar to $\delta^{13}C_{bulk}$, $\delta^{13}C_{EAA}$ varied ~5.0‰ from -18.4‰ to -23.4‰
283 (flux-weighted avg.: -20.9±1.2‰; Table 1). The $\delta^{13}C_{EAA}$ values closely followed $\delta^{13}C_{bulk}$
284 throughout the sampling period with minimal offsets (by 0.4±0.7‰) ($R^2 = 0.614$, $p < 0.001$; Figs.
285 2a, 3b). $\delta^{13}C$ values of Phe ($\delta^{13}C_{Phe}$) also paralleled the changes of $\delta^{13}C_{bulk}$ values, but with a
286 weaker relationship ($R^2 = 0.537$, $p < 0.001$) and a larger offset (by 4.2±0.7‰) (Figs. 2a, 3a).
287 Compared to $\delta^{13}C_{EAA}$, $\delta^{13}C_{NEAA}$ values were more enriched (by 6-11‰) and more variable (-9.5‰
288 to -16.6‰; flux-weighted avg.: -13.7±1.4‰; Fig. 2a, Table 1). No significant relationship was
289 found between $\delta^{13}C_{NEAA}$ and $\delta^{13}C_{bulk}$ ($R^2 = 0.1$, $p > 0.2$) or carbon flux ($R^2 = 0.05$, $p > 0.2$).

290 *3.1.3. Bulk and amino acid $\delta^{15}N$ values*

291 Bulk $\delta^{15}N$ values of sinking particles ($\delta^{15}N_{bulk}$) ranged from 6.8‰ to 10.0‰ with a
292 flux-weighted average value of 7.8±0.9‰ (Table 2). Slightly higher $\delta^{15}N_{bulk}$ values (e.g., > 9‰)
293 were observed mostly during fall and winter periods (Fig. 2b, Table 2). Consistent with previous
294 observations (Altabet et al., 1999), the $\delta^{15}N_{bulk}$ values were not related to carbon flux ($R^2 = 0.0$, $p >$
295 0.5) or $\delta^{13}C_{bulk}$ values ($R^2 = 0.1$, $p > 0.1$).

296 The $\delta^{15}N$ values of Phe ($\delta^{15}N_{Phe}$), the most commonly used AA proxy for source nitrogen
297 $\delta^{15}N$ value, varied ~4‰ from 6.9‰ to 11.3‰ with a flux-weighted average value of 8.7±1.2‰
298 (Table 2). The mean source AAs $\delta^{15}N$ values ($\delta^{15}N_{SrcAA}$) varied ~3‰ from 7.5‰ to 11.0‰, with
299 a flux-weighted average of 9.1±0.9‰ (Table 2). The $\delta^{15}N_{Phe}$ values closely followed $\delta^{15}N_{bulk}$
300 values ($R^2 = 0.703$, $p < 0.001$; Fig. 3c) with small offsets (by 0.9±0.7‰). Values of $\delta^{15}N_{SrcAA}$, also
301 followed those of $\delta^{15}N_{bulk}$, but with a weaker relationship ($R^2 = 0.643$, $p < 0.001$; Fig. 3d) and a
302 larger offset (by 1.2±0.6‰). In comparison, $\delta^{15}N$ values of trophic AAs ($\delta^{15}N_{TrAA}$) were more
303 variable (10.6‰ to 19.3‰; flux-weighted avg.: 13.4±2.2‰) and on average ~5‰ more enriched
304 than the $\delta^{15}N_{SrcAA}$ or $\delta^{15}N_{Phe}$ values (Fig. 2b, Table 2).

305 *3.1.4. $TP_{CSI\text{-}AA}$, DI, and ΣV*

306 The $TP_{CSI\text{-}AA}$ values in sinking particles were consistently greater than 1.0, varying from
307 1.3 to 1.9 with a flux-weighted average value of 1.5±0.2 (Table 2). $TP_{CSI\text{-}AA}$ values were mostly
308 below 1.5 during spring and summer (March-August) and then fluctuated and peaked during fall
309 and winter (Fig. 2b; Table 2). No significant relationships were found between $TP_{CSI\text{-}AA}$ and
310 $\delta^{13}C_{bulk}$ ($R^2 = 0.0$, $p > 0.1$) or $\delta^{15}N_{bulk}$ values ($R^2 = 0.14$, $p > 0.1$). Values of DI and ΣV varied from
311 -0.5 to 0.9 (flux-weighted avg.: 0.3±0.4), and from 0.9 to 2.2 (flux-weighted avg.: 1.7±0.3),

312 respectively, and displayed no temporal patterns (Table 2). There were no strong relationships
313 among TP, DI, and ΣV parameters ($TP_{CSI\text{-}AA}$ vs. DI: $R^2 = 0.01$, $p > 0.1$; $TP_{CSI\text{-}AA}$ vs. ΣV: $R^2 = 0.31$,
314 $p < 0.05$; DI vs. ΣV: $R^2 = 0.17$, $p > 0.05$).

315 **3.2. Estimation of export production bulk isotope values using sinking particle CSI-AA values**

316 Explicitly, we assume that sinking particles collected in sediment traps are a direct
317 reflection of export production. As noted above, there were strong relationships between $\delta^{13}C_{bulk}$
318 and $\delta^{13}C_{EAA}$ values in the sediment trap time series (and between $\delta^{15}N_{bulk}$ and $\delta^{15}N_{Phe}$ values; Figs.
319 3b, 3c), indicating one can be used to estimate the other. Two empirical models were developed
320 based on the entire data set ($n = 22$):

321 $$\delta^{13}C_{export\ production}\ (‰) = 0.75 \times \delta^{13}C_{EAA} - 5.9‰ \quad (5)$$

322 $$\delta^{15}N_{export\ production}\ (‰) = 0.63 \times \delta^{15}N_{Phe} + 2.3‰ \quad (6)$$

323 The accuracy of these models was evaluated by comparing the measured $\delta^{13}C_{export\ production}$
324 and $\delta^{15}N_{export\ production}$ values with those estimated using these models (Fig. EA1, Table EA3). The
325 differences between the estimated and measured values represent the errors (or uncertainties) of
326 the empirical models. The errors in the estimates of $\delta^{13}C_{export\ production}$ and $\delta^{15}N_{export\ production}$ using
327 $\delta^{13}C_{EAA}$ and $\delta^{15}N_{Phe}$ were found to be mostly within ±1.0‰ and ±0.5‰, respectively, and they
328 were distributed consistently over the entire range of data (see Fig. EA1).

329 The two equations (5) and (6) were also able to reproduce the observed temporal patterns
330 of $\delta^{13}C_{export\ production}$ and $\delta^{15}N_{export\ production}$ values throughout the 6-yr study period (Fig. 4). The
331 average offsets between the estimated and measured records were relatively small (≤ 1.0‰) and
332 were not significantly different between high and low carbon flux periods (Mann-Whitney *U*-Test,
333 $p > 0.1$; Fig. EA2). These empirical relationships can potentially be applied to paleoarchives to

reconstruct past bulk isotope values of export production using the preserved CSI-AA values (further discussed in section 4.5).

3.3. Environmental and biological influences on CSI-AA baseline proxies

To evaluate the potential influence of changing productivity, plankton food webs, or particle diagenetic status on CSI-AA baseline proxy values, the time-series sediment trap records of $\delta^{13}C_{EAA}$ and $\delta^{15}N_{Phe}$ (as well as $\delta^{13}C_{Phe}$ and $\delta^{15}N_{SrcAA}$) were regressed against the values of carbon flux, $TP_{CSI\text{-}AA}$, DI and ΣV. The results of the regression analysis revealed no significant relationships in any case examined ($R^2 \leq 0.2$, $p > 0.1$; Fig. 5), indicating that the observed changes in $\delta^{13}C_{EAA}$, $\delta^{13}C_{Phe}$, $\delta^{15}N_{SrcAA}$, and $\delta^{15}N_{Phe}$ values were independent of the variations in carbon flux, trophic transfer, and microbial alteration.

3.4. CSI-AA comparisons of sinking particles and deep-sea corals

To evaluate the correspondence of export production and the preserved skeletal CSI-AA data, values of $\delta^{13}C_{AA}$ and $\delta^{15}N_{AA}$ were compared between sediment traps (i.e., sinking particles) and contemporaneous coral outer skeletons (second and third peels) (Fig. 6). In addition, the sediment trap flux-weighted average values of $\delta^{13}C_{AA}$ and $\delta^{15}N_{AA}$ were calculated (Fig. EA3) and subtracted from the mean values in coral skeletons, in order to estimate the mean offsets in $\delta^{13}C_{AA}$ and $\delta^{15}N_{AA}$ values between corals and sinking particles (Fig. 7).

The individual $\delta^{13}C_{AA}$ values in coral skeletons were within the upper range of sinking particle $\delta^{13}C_{AA}$ values (Fig. 6a). The average $\delta^{13}C_{EAA}$ value was slightly more positive in coral skeletons than in sinking particles (by 2.0±1.3‰; Mann-Whitney *U*-Test, $p < 0.05$; Fig. 7a). However, this offset was largely driven by a large and apparently unique degree of enrichment in the Val $\delta^{13}C$ value (by 5.5±2.8‰). Without Val, the average offset reduced to 1.3±1.2‰ (Fig. 7a). In comparison, the $\delta^{13}C_{NEAA}$ value in corals was slightly depleted (by -1.7±1.4‰; Mann-Whitney

U-Test, $p < 0.05$). Offsets in individual NEAA $\delta^{13}C$ values varied between +0.8‰ and -3.1‰, and were mostly comparable to the magnitudes of propagated errors (Fig. 7a).

The comparison of individual $\delta^{15}N_{AA}$ values between coral skeletons and the sinking particle data varied strongly by AA groupings (Figs. 6b, 7b). The two source AAs (Phe, Lys; McMahon and McCarthy, 2016) in skeletons showed only small $\delta^{15}N$ offsets relative to sinking particle values (Phe: by 0.6±1.3‰; Lys: by 1.2±0.9‰; Fig. 7b), close to analytical error (Mann-Whitney *U*-Test, $p > 0.1$). Gly and Ser were termed as "intermediate" AAs in this study (see section 4.4.2) and they had substantially higher offsets (Gly: by 3.5±1.1‰; Ser: by 5.8±1.6‰; Mann-Whitney *U*-Test, $p < 0.05$; Fig. 7b). Trophic AAs had by far the largest offsets (by 5-12‰; Mann-Whitney *U*-Test, $p < 0.05$; Fig. 7b). Finally, a large negative offset was observed for Thr (by -12.8±1.8%; Mann-Whitney *U*-Test, $p < 0.05$; Fig. 7b). The high trophic AA $\delta^{15}N$ values and low Thr ^{15}N values are as expected for animals feeding on POM.

3.5. Reconstructions of surface biogeochemistry and export using coral $\delta^{13}C_{AA}$ and $\delta^{15}N_{AA}$

Based on the empirical models established from our time series sediment traps (section 3.2), we reconstructed $\delta^{15}N_{bulk}$ values of export production ($\delta^{15}N_{export\ production}$), source nitrogen $\delta^{15}N$ values, and $TP_{CSI\text{-}AA}$ values of export production using the coral $\delta^{15}N_{AA}$ records (Fig. 8). As discussed below (section 4.4.4), a geographic offset in $\delta^{13}C$ primary production values was expected between sites of coral and sediment trap. To avoid this geographical sampling bias, the carbon records were not reconstructed. Such geographic offset was not apparent in source nitrogen $\delta^{15}N$ in Monterey Bay (discussed in section 4.4.1). In each case of reconstruction, we performed two calculations using the original and the offset-corrected version of $\delta^{15}N_{Phe}$. The corrected version of $\delta^{15}N_{Phe}$ value was calculated by subtracting 0.6‰ from the original $\delta^{15}N_{Phe}$ value to account for the hypothesized small trophic ^{15}N enrichment of Phe in coral skeletons (see section

380 4.4.1). The calculated results were then compared with the corresponding reference values to
381 determine the accuracy of the reconstruction. Reference values were obtained from this study and
382 previous multi-year measurements in Monterey Bay (see below).

383 Average $\delta^{15}N_{export\ production}$ values (8.5±0.3‰) derived from the original coral $\delta^{15}N_{Phe}$ (using
384 Eq. 6) were similar to the contemporaneous records (7.8±0.9‰, i.e., flux-weighted average
385 $\delta^{15}N_{bulk}$ values of our sediment traps). Correcting for the observed 0.6‰ offset resulted in lower
386 $\delta^{15}N_{export\ production}$ values (7.8±0.3‰), which were almost identical to the reference ranges (Mann-
387 Whitney *U*-Test, $p > 0.1$; Fig. 8). The source nitrogen $\delta^{15}N$ record was directly inferred from the
388 canonical source AA $\delta^{15}N_{Phe}$ value in corals. The original coral $\delta^{15}N_{Phe}$ values indicated higher
389 source nitrogen $\delta^{15}N$ values (9.3±0.4‰; Fig. 8) compared to the range suggested by prior work
390 (7.8±0.8‰; i.e., average of prior subsurface nitrate $\delta^{15}N$ values in 1997 and 2002-2004; Altabet et
391 al., 1999; Wankel et al., 2007). However, correcting for the $\delta^{15}N_{Phe}$ offset reproduced more
392 comparable source nitrogen $\delta^{15}N$ values (8.7±0.4‰; Mann-Whitney *U*-Test, $p > 0.1$; Fig. 8).
393 Finally, the $TP_{CSI\text{-}AA}$ of export production, a measure of the average trophic position of plankton
394 communities that contribute material to the sinking particles, was calculated by subtracting the
395 coral $TP_{skeleton}$ values by one. The coral $TP_{skeleton}$ was estimated based on $\delta^{15}N_{Phe}$ and $\delta^{15}N_{Glx}$ and
396 Eq. (2) (after McMahon et al., 2018). The estimated export production $TP_{CSI\text{-}AA}$ values (~1.6) using
397 either the original or offset-corrected $\delta^{15}N_{Phe}$ values were both within the range of direct $TP_{CSI\text{-}AA}$
398 measurements in our sediment traps (1.5±0.2) (Mann-Whitney *U*-Test, $p > 0.1$; Fig. 8).
399

400 # 4. DISCUSSION

401 **4.1. Mechanisms behind varying bulk $\delta^{13}C$ and $\delta^{15}N$ values of export production**

402 The large temporal changes in $\delta^{13}C_{bulk}$ (by ~ 5‰) and $\delta^{15}N_{bulk}$ values (by ~3‰) of sinking
403 particles could be driven by changes in environmental (e.g., source $\delta^{13}C_{DIC}$ and $\delta^{15}N_{nitrate}$ values)
404 and/or biological (e.g., trophic transfer) processes. The CSI-AA data allow us to explicitly
405 differentiate between these intertwined factors. For carbon, the sinking particle $\delta^{13}C_{bulk}$ values
406 were strongly related to $\delta^{13}C_{EAA}$ values ($R^2 = 0.614$; Fig. 3b), but not to $TP_{CSI\text{-}AA}$ ($R^2 < 0.1$; Fig.
407 2b). Given that $\delta^{13}C_{EAA}$ directly trace $\delta^{13}C$ values of primary production, this indicates $\delta^{13}C_{bulk}$
408 values of export production in Monterey Bay are derived from primary production $\delta^{13}C$ values at
409 the base of the food web and are relatively unaffected by overlying planktonic food web structure.
410 We also observed seasonal variation in sinking particle $\delta^{13}C_{bulk}$ values (i.e., more positive during
411 spring and summer), which generally followed the pattern of previous primary production $\delta^{13}C$
412 values in Monterey Bay (Fig. 1A in Rau et al., 2001). The seasonal variation in primary production
413 $\delta^{13}C$ values seems not to be driven by the relatively small changes in surface DIC $\delta^{13}C$ values (by
414 < 3‰), and instead is more likely related to the highly variable carbon isotopic fractionation during
415 photosynthesis (by 16‰) (Rau et al., 2001). Factors contributing to the variable photosynthetic
416 ^{13}C fractionation in Monterey Bay have not been well resolved and may be in part due to the
417 seasonal supply of trace metal (Rau et al., 2001).

418 For nitrogen, $\delta^{15}N_{bulk}$ values of export production represent the combined signal of source
419 nitrogen $\delta^{15}N$ values, extent of nitrogen utilization (Rau et al., 1998; Altabet et al., 1999), and
420 potentially a larger impact of trophic alteration. However, as with carbon, the $\delta^{15}N_{bulk}$ values in
421 sinking particles were not related to $TP_{CSI\text{-}AA}$ values ($R^2 < 0.2$; Fig. 2b), but were strongly related
422 to $\delta^{15}N_{Phe}$ values ($R^2 = 0.703$; Fig. 3c). This indicates $\delta^{15}N_{bulk}$ values of export production in
423 Monterey Bay are not strongly influenced by trophic alteration, but instead are primarily set by

$\delta^{15}N$ values of source nitrogen ($\delta^{15}N_{source\ nitrogen}$) and utilization patterns by primary producers. An important nitrogen source for primary production in Monterey Bay is upwelled nitrate occurring during spring/summer (10-20 μM with a $\delta^{15}N_{nitrate}$ range of 6-9‰; Altabet et al., 1999; Wankel et al., 2007; Pennington et al., 2010). In general, $\delta^{15}N$ values of primary production are expected to vary temporally during and after upwelling: upwelling would first lead to production of POM with lower $\delta^{15}N$ values due to partial nitrate utilization and then to elevated POM $\delta^{15}N$ values when most nitrate has been consumed, with the average $\delta^{15}N$ values of POM ultimately reflecting those of upwelled nitrate if utilization is complete (Altabet et al., 1991; Nakatsuka et al., 1992; Altabet et al., 1999). Isotope fractionation associated with partial utilization of surface nitrate in Monterey Bay can be significant, as reflected in the wide-ranging bulk $\delta^{15}N$ values of suspended POM (1‰ to 8‰; Rau et al., 1998). Such fractionation is reflected to a lesser extent in the bulk $\delta^{15}N$ values of sinking POM (6‰ to 10‰; Altabet et al., 1999; this study).

The impact of these nitrogen isotope dynamics is clearly reflected in our long-term sinking particle $\delta^{15}N_{Phe}$ data. The observed $\delta^{15}N_{Phe}$ range (7-11‰) is a good reflection of contemporaneous subsurface nitrate $\delta^{15}N$ value ranges in this same region (6-9‰; Wankel et al., 2007). Temporally, $\delta^{15}N_{Phe}$ values of sinking particles were lower (e.g., 7-8‰) during spring and summer and higher (e.g., 9-11‰) during fall and winter (Fig. 2b; Table 2), matching the expected seasonal trends of nitrogen utilization and plankton $\delta^{15}N$ values described above. In addition, we also observed a marked $\delta^{15}N_{Phe}$ elevation (by ~3‰) during the 2002-2003 moderate El Niño period. This isotopic signal is consistent with the limited upwelling and more complete nitrate utilization typical of El Niño conditions, which lead to more positive $\delta^{15}N$ values in the surface nitrogen pool and thereby elevated $\delta^{15}N$ values in phytoplankton and zooplankton biomass (Chavez, 1996; Rau et al., 2003; Décima et al., 2013). Overall, these observations suggest that $\delta^{15}N_{Phe}$ values of sinking particles

447 in this region closely reflect baseline shifts in nitrate $\delta^{15}N$ values, as well as seasonal and
448 longer-term shifts in upwelling dynamics.

449 **4.2. Tracking bulk $\delta^{13}C$ and $\delta^{15}N$ values of export production with sinking particle CSI-AA**

450 The strong relationships between bulk and AA isotope values show that empirical models
451 can be used to reconstruct past export production isotope values from CSI-AA baseline proxies
452 (e.g., $\delta^{13}C_{EAA}$, $\delta^{15}N_{Phe}$) in paleoarchives. Compared to bulk isotope values, both essential and
453 source AAs undergo little to no isotope fractionation during trophic transfer (Chikaraishi et al.,
454 2009; McMahon et al., 2010; McMahon and McCarthy, 2016) and during incorporation into
455 paleoarchives (further discussed in section 4.4). However, these CSI-AA proxy values can be used
456 to reconstruct past ocean export production isotope values only if their initial relationships with
457 bulk isotope values are known.

458 To date, such relationships have not been quantitatively determined, due to very limited
459 paired observations of bulk and AA isotope values in exported POM. Our sediment trap data
460 demonstrate the $\delta^{13}C_{bulk}$ and $\delta^{15}N_{bulk}$ values of export production can be accurately reproduced
461 from measured $\delta^{13}C_{EAA}$ and $\delta^{15}N_{Phe}$ values, respectively (Figs. 3 and 4; Eqs. 5 and 6). The
462 uncertainties of the models (C: ±1.0‰; N: ±0.5‰; Fig. EA1) were much smaller than the actual
463 temporal variations in bulk isotope values (C: by ~5‰; N: by ~3‰), suggesting these models can
464 accurately resolve both seasonal and interannual bulk stable isotopic changes in this system. In
465 addition, the uncertainties were very similar during low and high flux extremes (Fig. EA1),
466 suggesting robust performance of the models under varying productivity conditions. These
467 empirical relationships, derived from a long-term record of export production in a highly dynamic
468 coastal system, are the first of their kind and will allow well-grounded quantitative reconstructions
469 of modern and paleo-ocean export production bulk isotope values in similar environments.

4.3. Preservation and fidelity of CSI-AA proxy values in sinking particles

The time series data also allow us to examine the temporal variability of CSI-AA-based proxies in sinking particles and evaluate how they are affected by varying extents of plankton productivity, trophic transfer, and microbial reworking. As noted above, prior studies have shown minimal trophic fractionation of source and essential AAs (McClelland and Montoya, 2002; McCarthy et al., 2007; Chikaraishi et al., 2009; Hannides et al., 2009; McMahon et al., 2010; McCarthy et al., 2013; Batista et al., 2014). However, all such studies were based on limited CSI-AA measurements in short-term culture experiments or discrete field samples.

Our multi-year sediment trap records showed no relationships between CSI-AA baseline proxies (i.e., essential and source AA isotope values) and carbon flux, $TP_{CSI\text{-}AA}$, or the degradation parameters (ΣV and DI) (Fig. 5). The lack of dependence of CSI-AA baseline proxies on carbon flux suggests they are applicable across a wide range of productivity. It also supports the fundamental CSI-AA assumption that essential and source AA isotope values minimally fractionate during trophic transfers. In contrast to previous work using samples of widely separated trophic levels (e.g., Chikaraishi et al., 2009), our sediment trap time-series resolved fluctuations in $TP_{CSI\text{-}AA}$ values at far higher resolution (~0.1 interval on monthly and seasonal time scales). This corroborates the independence of CSI-AA baseline proxies from $TP_{CSI\text{-}AA}$ in natural system, and at the same time it suggests TP can be applied in plankton systems at a much finer scale.

4.3.1. Influence of bacterial degradation

In contrast to metazoan trophic transfer, the influence of microbial reworking on AA isotopic fractionation patterns remains poorly understood. Bacteria attached to the sinking particles can produce ectoenzymes to respire and transform POM (Smith et al., 1992; Hansman et al., 2009), potentially altering AA isotopic composition. While different studies have observed multiple

493 CSI-AA patterns during microbial alteration, the baseline proxies ($\delta^{13}C_{EAA}$ and $\delta^{15}N_{Phe}$) have so
494 far been observed to retain their isotopic information (McCarthy et al., 2007; Hannides et al., 2013;
495 Steffan et al., 2015; Ohkouchi et al., 2017; Yamaguchi et al., 2017). However, to date the potential
496 linkage of microbial degradation to CSI-AA baseline proxy values has never been
497 comprehensively investigated over a large sample set of detrital organic matter.

498 The two independent AA-based parameters (DI and ΣV) used for our sediment trap time
499 series track separate aspects of microbial alteration. The DI indicates the extent of microbial
500 degradation based on mol% changes of protein AA composition. DI values have been found to
501 decrease from fresh phytoplankton (1-1.5) to refractory sediment organic matter (< -2) (Dauwe et
502 al., 1999). The moderate level of our DI values (flux-weighted average: 0.3±0.4) suggests the
503 sinking particles have been partially degraded during transit to the deep ocean. However, the lack
504 of relationship between $\delta^{13}C_{EAA}$ (or $\delta^{15}N_{Phe}$) values and DI values suggests negligible impact of
505 microbial degradation on these CSI-AA baseline proxies in sinking particles. This finding contrasts
506 strongly with results on marine suspended particles, which have shown increasing $\delta^{15}N_{AA}$ and
507 $\delta^{13}C_{AA}$ values with depth due to non-selective isotopic enrichment during extracellular enzymatic
508 hydrolysis (Hannides et al., 2013; Yamaguchi et al., 2017). The discrepancy is mirrored in relative
509 bulk isotope changes, and is most likely associated with the relatively rapid settling of sinking
510 particles (16-95 m/day in Monterey Bay) (Shanks and Trent, 1980; Pilskaln et al., 1998) that limits
511 extensive microbial isotopic fractionation.

512 The ΣV parameter, in contrast to DI, indicates the extent of isotope fractionation driven by
513 microbial resynthesis based on deviations of the common autotrophic $\delta^{15}N_{AA}$ pattern (McCarthy
514 et al., 2007). Elevated ΣV values in the organic matter pool indicate microbial addition of
515 resynthesized proteinaceous material (Fogel and Tuross, 1999; McCarthy et al., 2007; Calleja et

al., 2013). Some of our sediment trap ΣV values (0.9-2.2) were slightly higher than commonly observed ΣV values in fresh marine plankton (mostly 0.5-1.5) (McCarthy et al., 2007; Hannides et al., 2013; Batista et al., 2014). These values suggest some microbial biomass has been incorporated into sinking particles, consistent with our DI values and prior bacterial biomarkers (D-amino acids) and radiocarbon dating analysis in other oceanic regions (McCarthy et al., 2007; Hansman et al., 2009). However, the lack of correlation between ΣV and $\delta^{13}C_{EAA}$ (or $\delta^{15}N_{Phe}$) align with the DI data and suggest modest bacterial alteration has minor impact on CSI-AA baseline proxy values.

4.3.2. Sinking particle $TP_{CSI\text{-}AA}$: tracing planktonic food web structure

The $TP_{CSI\text{-}AA}$ data suggest a close correspondence between seasonal changes in surface planktonic food web structure and fine-scale changes in sinking particle $TP_{CSI\text{-}AA}$. The calculated range of $TP_{CSI\text{-}AA}$ (1.3-1.9) indicates a mixed planktonic source of sinking particles, consistent with previous microscopic observations of coexisting phytoplankton and zooplankton components in sediment traps (Pilskaln et al., 1996; Beaulieu and Smith, 1998). Seasonally, lower $TP_{CSI\text{-}AA}$ values observed in spring and summer (Fig. 2b) suggest shorter planktonic food webs during productive months, likely due to a phytoplankton community shift to larger cells with less grazing. This interpretation is supported by previous field measurements that showed increasing phytoplankton cell size with productivity (Chavez, 1996; Wilkerson et al., 2000). Further, most of the highest $TP_{CSI\text{-}AA}$ values were observed during the 2002-2003 moderate El Niño period (Fig. 2b), consistent with a previous zooplankton study that reported enhanced carnivory during El Niño (Décima et al., 2013). Together, these results strongly support the application of $TP_{CSI\text{-}AA}$ in paleoarchives as an indicator of planktonic food web structure, and also suggest that at least in ocean margins small fluctuations of $TP_{CSI\text{-}AA}$ (e.g., by ~ 0.2 to 0.5) may indicate meaningful change.

538 **4.4. Incorporation of sinking particle CSI-AA values into proteinaceous coral skeletons**

539 A core, yet so far untested, assumption for many CSI-AA paleoceanographic applications
540 is that baseline AA isotope values being recorded in corals match those in their food sources,
541 assumed to be essentially sinking particles (e.g., Sherwood et al., 2005; Hill et al., 2014). Our data
542 allows us to directly examine this assumption and investigate incorporations of other groups of
543 AAs, by taking into account the export dynamics in Monterey Bay. Carbon budget estimates
544 indicate a large fraction of fixed carbon is advected offshore by upwelling filaments prior to
545 vertical sinking as export flux (Pilskaln et al., 1996; Olivieri and Chavez, 2000; Pennington et al.,
546 2010). As a consequence, sinking particles and coral skeletons collected in deep water should
547 integrate isotopic signals from both overlying surface water and adjacent inshore water.

548 *4.4.1. Source AA $\delta^{15}N$ (Phe and Lys)*

549 We observed a close match between sinking particles and coral skeletons in the $\delta^{15}N$ values
550 of the best source AAs, Phe and Lys (Fig. 7b). We note that the traditional source AA grouping
551 includes Gly and Ser (and also Met, which was not measured in this study). However, in contrast
552 to Phe and Lys, these other AAs showed moderate to large ^{15}N enrichments in corals (Fig. 7b).
553 Accumulated literature on $\delta^{15}N_{AA}$ fractionation with trophic transfer has now shown that only Phe,
554 Lys, and Met reliably meet the basic assumption of minimal fractionation with trophic transfers
555 (recently reviewed by McMahon and McCarthy, 2016). Our results are consistent with this
556 expectation, and support a shift in categorization of Phe and Lys as 'true' source AAs.

557 The small offsets in Phe and Lys $\delta^{15}N$ values between corals and sediment traps are close
558 to the propagated uncertainties (Phe: by 0.6±1.3‰; Lys: by 1.2±0.9‰). However, they could
559 potentially be derived from the small kinetic fractionations expected for a minor metabolic
560 transamination of Phe and an irreversible transamination of Lys, respectively, during trophic

561 transfer (Chikaraishi et al., 2007; Chikaraishi et al., 2009; McMahon and McCarthy, 2016). In fact,
562 our observed offsets for Phe and Lys ^{15}N enrichments are remarkably similar to previous trophic
563 discrimination factor (TDF) values in the literature (Phe: 0.4±0.5‰, Lys: 0.8±1.5‰; Chikaraishi
564 et al., 2009; McMahon and McCarthy, 2016). The small offsets observed in source AA $\delta^{15}N$ values
565 are unlikely related to the geographic difference in sampling locations. In Monterey Bay, nitrate
566 concentrations onshore (near our coral site) are in general higher than those of the offshore
567 sediment trap site (Chavez et al., 2017), suggesting different nutrient and water-mass post-
568 upwelling trajectories. However, prior independent $\delta^{15}N$ measurements for subsurface nitrate in
569 Monterey Bay (Wankel et al., 2007) and for source AAs in California margin deep-sea bamboo
570 corals have both suggested very similar $\delta^{15}N$ values between nearshore and offshore regions.
571 Overall, the small isotopic offset of source AAs (particularly Phe) in coral skeletons reaffirms the
572 reliability of coral Phe (or Lys) as direct proxies for source nitrogen $\delta^{15}N$ values. At the same time,
573 the correspondence to expected trophic offsets also suggests baseline reconstructions might be
574 improved by small trophic corrections (discussed in section 4.5).

575 *4.4.2. "Intermediate" AA $\delta^{15}N$ (Gly and Ser)*

576 As noted above, Gly and Ser were originally designated as source AAs (Popp et al., 2007)
577 given the low trophic fractionations (<1‰) observed in initial feeding experiments (McClelland
578 and Montoya, 2002). However, accumulated studies in the last decade have consistently shown
579 extremely variable, and often large, trophic fractionations for Gly and Ser mainly in higher level
580 consumers (Germain et al., 2013; Hoen et al., 2014; Nielsen et al., 2015; McMahon and McCarthy,
581 2016). For these reasons, a recent review on this subject emphasized that Gly and Ser cannot be
582 reliably used as source AAs (McMahon and McCarthy, 2016). Our comparisons between deep-sea
583 corals and their sinking POM food source support this conclusion. We found that Gly and Ser

584 exhibited a trophic enrichment of 4-6‰ in the coral skeletons, a range falling between those of
585 source AAs (by ~1‰) and trophic AAs (by 5-12‰).

586 The moderate $\delta^{15}N$ fractionations of Gly and Ser are likely associated with their different
587 modes of amino nitrogen transfers compared to other AAs. Compared to the source Phe and Lys,
588 Gly and Ser potentially express higher degrees of isotopic fractionations because Gly and Ser can
589 interconvert with each other via the reversible transamination that involves cleavage of C-N bond
590 (in the presence of enzyme serine-glyoxylate transaminase) (Berg et al., 2002). However, unlike
591 the trophic AAs (e.g., Glx, Asx, Ala, Leu, Ile, etc.), Gly and Ser do not readily exchange amino
592 nitrogen with the heavily fractionated central nitrogen pool, and so would be expected to have
593 lower isotopic fractionations than the traditional "trophic" AA group (O'Connell, 2017). Given
594 the distinct metabolic pathways of Gly and Ser and their intermediate extent of trophic
595 fractionations, we propose a separate classification for Gly and Ser as "intermediate" AAs. This
596 term is in particular appropriate in any study involving higher level consumers.

597 *4.4.3. Trophic AA $\delta^{15}N$ (Glx, Asx, Ala, Leu, Ile, Pro, Val): first TDF values for deep-sea corals*

598 Trophic AAs were all substantially ^{15}N-enriched in coral skeletons compared to sinking
599 particles (by 5-12‰; Fig. 7b), as would be expected for a consumer. The enrichment of nitrogen
600 isotopes from diet to consumer, a key factor commonly known as the trophic discrimination factor
601 (TDF), has never been determined in deep-sea proteinaceous corals. Accurate estimation of TDF
602 values often relies on feeding experiments (McMahon and McCarthy, 2016). However, such
603 feeding experiment is not practical and has not been done for deep-sea corals, because maintaining
604 deep-sea coral species in aquaria is very difficult, let alone feeding them realistic food sources.
605 Therefore, field observations are likely the most realistic way to estimate TDF values for deep-sea
606 corals. Sinking particles consumed by deep-sea corals are first assimilated by coral polyp tissue

607 before being deposited into protein skeleton. We did not measure coral polyp in this study.
608 However, McMahon et al. (2018) recently showed that trophic AAs incorporated into protein coral
609 skeletons have a consistent negative 3-4‰ offset compared to the same AAs present in the living
610 coral polyp animal. We therefore applied McMahon et al.'s correction factors (i.e., skeleton minus
611 polyp tissue) to our coral skeleton data to evaluate the true TDF values of trophic AAs during the
612 one trophic-level transfer from sinking particles to live coral tissues (Fig. EA4b). Assuming the
613 trophic level of coral polyp is one greater than that of flux-weighted average sediment trap material,
614 the TDF value of each trophic AA was calculated as below:

615 $$TDF_{polpy\ -\ sinking\ particle} = \Delta^{15}N_{skeleton\ -\ sinking\ particle} - \Delta^{15}N_{skeleton\ -\ polyp} \quad (7)$$

616 where $\Delta^{15}N_{skeleton\ -\ sinking\ particle}$ is the ^{15}N enrichment of individual AA from sinking particle to coral
617 skeleton (as in Fig. 7b) and $\Delta^{15}N_{skeleton\ -\ polyp}$ is the previously observed correction factor for
618 individual AA (i.e., skeleton minus polyp; Table 1 in McMahon et al., 2018).

619 Making these corrections allows us to for the first time directly evaluate TDF values in
620 deep-sea proteinaceous corals. Compared to the uncorrected data (Fig. 7b), the corrected data
621 showed greater ^{15}N enrichments from sinking particles into coral polyps for all trophic AAs,
622 ranging from 8.7±1.9‰ in Glx to 15.7±2.9‰ in Ile (mean trophic AAs: 11.4±2.0‰). The TDF
623 value of Glx (by 8.7±1.9‰) is within range observed for almost all organisms (McClelland and
624 Montoya, 2002; Chikaraishi et al., 2009; Yamaguchi et al., 2017). Further, we calculated an
625 additional TDF value based on the most commonly used isotope difference between trophic AA
626 Glx and source AA Phe, i.e., $TDF_{Glx\text{-}Phe}$. The calculated $TDF_{Glx\text{-}Phe}$ value for coral polyp was 7.9‰,
627 essentially identical to the commonly applied 7.6‰ value (McClelland and Montoya, 2002;
628 Chikaraishi et al., 2009), which is now understood to be characteristic of ammonia-excreting
629 primary and secondary consumers (McMahon and McCarthy, 2016). Our results show that trophic

630 $\delta^{15}N$ fractionation for the canonical trophic AA Glx is very similar to many other taxa, confirming
631 the robustness of the correction factors for coral skeleton $TP_{CSI\text{-}AA}$ calculation proposed by
632 McMahon et al. (2018).

633 One unexpected observation, however, was that several trophic AAs (Leu, Ile, Val) had
634 substantially greater $\delta^{15}N$ fractionations (up to 12‰) than Glx (Fig. 7b). After correcting for the
635 negative skeleton-to-polyp offsets, these AAs therefore had far greater TDF values (12-16‰; Fig.
636 EA4b) than would be expected based on work across multiple other taxa (McMahon and McCarthy,
637 2016). These unusual trophic AA fractionations were not due to sampling artifacts, because the
638 same pattern was observed in all skeletal layers, and in both corals. We also re-analyzed the
639 previously published trophic AA $\delta^{15}N$ values in *Isidella* polyps and skeletons in Sur Ridge off the
640 California coast (McMahon et al., 2018), and we found that this earlier data contained exactly the
641 same patterns (i.e., greater $\delta^{15}N$ fractionations in Leu, Ile and Val than in Glx). Specific
642 mechanisms behind the extremely large Leu, Ile, and Val TDF values are not clear but they appear
643 to be a consistent feature in deep-sea bamboo corals. Microbial degradation is not a likely
644 explanation, given that the corals were live-collected and had ΣV values (~1.0) lower than those
645 in sinking particles. A provocative speculation is that there may be additional catabolic pathways
646 for several highly fractionated trophic AAs (e.g., Leu, Ile, and Val) in protein corals, through which
647 the lighter ^{14}N is preferentially removed from the metabolic pool. Future labelling studies tracing
648 biochemical transformations of individual AAs in coral tissues will help untangle this riddle.

649 *4.4.4. Essential AA $\delta^{13}C$ (Thr, Ile, Val, Phe, Leu, Lys)*

650 The slightly elevated $\delta^{13}C_{EAA}$ values observed in coral skeletons than in sinking particles
651 (by 2.0±1.3‰; Fig. 7a) is likely due to a geographic offset of the sampling locations. Unlike
652 trophic AA $\delta^{15}N$ values, there are almost no $\delta^{13}C_{EAA}$ offsets between coral skeleton and polyps

for this (or other) deep-sea proteinaceous coral species (McMahon et al., 2018). The observed $\delta^{13}C_{EAA}$ offsets between corals and sediment traps are consistent with the expected $\delta^{13}C$ production gradients in California margin. Our coral collection site was located inshore near the bay mouth with generally higher productivity and more positive $\delta^{13}C$ values of surface POM, in comparison to the less productive offshore sediment trap site (Chavez et al., 1991; Miller et al., 2008). Prior data from deep-sea bamboo corals collected along the central California margin have shown exactly this same trend, with bulk $\delta^{13}C$ values increasing from offshore sites to nearshore sites (Hill et al., 2014). The general spatial trend in phytoplankton production is expected to lead to a positive $\delta^{13}C$ offset between corals and sediment traps, as we observed. Nevertheless, given the complex export patterns and spatially heterogeneous productivity of Monterey Bay, the degree of agreement in $\delta^{13}C_{EAA}$ values between the two sample sets is relatively high.

4.5. Can proteinaceous deep-sea coral CSI-AA reconstruct surface ocean conditions?

The ultimate goal of this study was to evaluate the robustness of CSI-AA applications in paleoarchival coral skeletons. As discussed above (section 4.4.4), a geographic offset in $\delta^{13}C_{EAA}$ values was observed between the corals and sediment trap samples. Therefore, we reconstructed and evaluated only the nitrogen records.

The $\delta^{15}N_{\text{export production}}$, $\delta^{15}N_{\text{source nitrogen}}$, and exported $TP_{CSI\text{-}AA}$ values reconstructed using the coral $\delta^{15}N_{AA}$ data compared well with the reference records, particularly after correcting for the minor trophic transfer fractionation (by 0.6‰) in Phe values (Fig. 8). It thus appears that the observed $\delta^{15}N_{Phe}$ offsets between coral skeletons and sediment traps, although small, are real and likely linked to the expected small trophic fractionation in Phe values. This inference may also extend to other coral genera, but constraining the potential range of this metabolic/trophic transfer

676 effect requires direct examination in other coral species. Overall, these results support our main
677 conclusion of faithful preservation of CSI-AA-based proxies in coral skeletons and also highlight
678 the robust performance of empirical models for reconstructing bulk isotope values of export
679 production in Monterey Bay.

680 Applicability of these empirical models to other oceanic regions remains to be tested. The
681 specific values of our models might potentially be applicable in similar highly productive ocean
682 margin systems. However, given the general regional disparities in environmental conditions,
683 source of nutrient (e.g., N_2 vs. nitrate), and composition and physiological status of plankton
684 communities, region-specific model parameterization using suitable samples sets is likely needed.
685 Supporting this idea are the results from several previous CSI-AA studies, which used empirical
686 models derived from laboratory phytoplankton cultures to estimate bulk $\delta^{13}C$ values of primary
687 production from $\delta^{13}C_{EAA}$ values (e.g., Schiff et al., 2014; Vokhshoori et al. 2014). A direct
688 application of these culture-derived models to our sediment trap $\delta^{13}C_{EAA}$ time series produced
689 $\delta^{13}C_{export\ production}$ values that had the same temporal trends, but were 1-3‰ more positive than our
690 field measurements (Fig. EA5). This suggests the laboratory culture organisms used previously
691 did not well reflect the mix of actual organisms contributing to export production in Monterey Bay.
692 We therefore suggest using sediment trap samples from the region of interest with paired bulk and
693 amino acid isotope values for model retraining.

694 Our data also suggest that prior to the implementation of models in coral archives, it will
695 be useful to determine the spatial patterns of primary and export production in the study region.
696 This can greatly improve the accuracy of biogeochemical and ecological reconstructions. For
697 example, we observed a +2‰ offset in $\delta^{13}C_{EAA}$ between the inshore coral and offshore sediment
698 trap, which we have hypothesized is due to the combined effect of onshore/offshore gradient in

699 primary production $\delta^{13}C$ and the horizontal export of primary production (Chavez et al., 1991;
700 Olivieri and Chavez, 2000; Pennington et al., 2010). As a consequence, applying $\delta^{13}C_{EAA}$ to the
701 inshore coral without first correcting this offset could overestimate the $\delta^{13}C$ values of primary and
702 export production for offshore region. Nevertheless, even for a system without such contextual
703 data, the CSI-AA records should still be able to reveal the temporal fluctuations of isotope values
704 of primary and export production and the associated overlying ocean conditions.

705 Further, the results from our contemporaneous corals suggest great promise for extending
706 the CSI-AA-based proxies to older coral skeletons for paleoceanographic study. Amino acids
707 preserved in the deep-sea proteinaceous coral skeletons are highly resistant to decomposition
708 (Strzepek et al., 2014; McMahon et al., 2015) and could therefore retain their isotopic
709 compositions that allow reconstructions of export production isotope values, source nitrogen
710 isotope values, and plankton food web trophic structure from both living and fossil specimens. On
711 the California margin specifically, we suggest that CSI-AA and our new empirical models can now
712 be applied to older bamboo corals in this region to reconstruct high-resolution ecosystem changes
713 over at least centennial time scales. There are also other deep-sea coral genera that have far greater
714 longevity (e.g., corals *Gerardia* sp. and *Leiopathes* sp.; Roak et al., 2009), which bears the
715 potential to unveil millennial or longer records when the calibrated models are in place.
716

717 5. SUMMARY & CONCLUSIONS

718 This study has presented the first coupled bulk and amino acid $\delta^{13}C$ and $\delta^{15}N$ values for a
719 multi-year sediment trap time series, and then exploited these data by comparison to
720 contemporaneous deep-sea proteinaceous corals, to address a series of fundamental questions
721 concerning the CSI-AA paleo-application. We found that the compound-specific baseline proxies

722 $\delta^{13}C_{EAA}$ and $\delta^{15}N_{Phe}$ in sinking particles can accurately reproduce bulk $\delta^{13}C$ and $\delta^{15}N$ values of
723 export production over multi-year time scales. The variations in essential and source AA isotope
724 values in sinking particles were found to be independent of carbon flux, trophic transfer,
725 biodegradation and microbial resynthesis, together indicating excellent preservation of these
726 CSI-AA baseline proxies during export from the surface to deep ocean. Temporal patterns
727 observed in several CSI-AA-based proxies (e.g., $\delta^{15}N_{Phe}$, TP_{CSI-AA}) reflect major biogeochemical
728 and ecological changes in surface ocean, such as seasonal shifts in plankton structures and
729 occurrence of unusual dynamical conditions (e.g., El Niño).

730 From sinking particles into deep-sea corals we observed small (1-2‰) isotopic enrichments
731 in essential AA $\delta^{13}C$ and source AA $\delta^{15}N$ values. For $\delta^{13}C_{EAA}$ the offsets match expected
732 geographic gradients in $\delta^{13}C$ values of primary production within Monterey Bay region, and so are
733 consistent with the expectation of no trophic change for $\delta^{13}C_{EAA}$ values. For source AA $\delta^{15}N$, while
734 the offsets we observed (~1‰) are near analytical variation, they are likely a real result from the
735 expected trophic fractionation for Phe and Lys. We therefore propose that applying a small
736 correction for trophic fractionation of source AA $\delta^{15}N$ in coral paleoarchives can improve the
737 accuracy of reconstructions. By contrast, the substantial ^{15}N enrichments observed for Gly and Ser
738 strongly suggests that these AA do not act as "source" AA in deep sea corals. Coupled with recent
739 literature documenting similar behaviors in other taxa, we propose that Gly and Ser should be
740 considered within a new "intermediate" AA classification, at least in corals or higher-level
741 consumers. In addition, based on the previously observed 3-4‰ $\delta^{15}N_{TrAA}$ offsets between coral
742 skeletons and polyp tissues (McMahon et al., 2018) we calculated the first $TDF_{Glx-Phe}$ value for
743 deep-sea coral animal (i.e. living Polyp), with a value (7.9‰) almost identical to the commonly
744 used 7.6‰ value seen across many taxa. These findings further validate the use of TP_{CSI-AA}

calculation (Eq. 2) proposed for paleoarchival deep-sea coral skeletons by McMahon et al., (2018). However, these results also indicate extremely high, but repeatable, $\delta^{15}N$ TDF values for Val, Ile, and Leu incorporated in coral skeletal protein. While this result bears further investigation, it suggests caution in using multi-AA approaches for estimating trophic position of coral archives.

Finally, building on the empirical models (e.g., Eq. 6) and observed offsets in CSI-AA baseline values (e.g., $\delta^{15}N_{Phe}$), we demonstrate that CSI-AA in deep-sea coral skeletons are able to reconstruct contemporaneous $\delta^{15}N_{bulk}$ values of export production, source nitrogen $\delta^{15}N$ values, and exported $TP_{CSI\text{-}AA}$ values with good accuracy. These new results demonstrate that the powerful diagnostic ability of CSI-AA-based proxies is maintained in deep-exported POM, transmitting a record of surface ocean processes into deep sea, and finally into coral or sedimentary archives. Taken together, these data have wide-ranging implications for CSI-AA biogeochemical and ecological applications, providing novel insight into the systematics of AA isotope values in export production and representing the first strong field-based validation for emerging CSI-AA paleoceanographic studies (e.g., Sherwood et al., 2011; Sherwood et al., 2014; McMahon et al., 2015; Williams et al., 2017). We suggest that future work calibrating our empirical models for different ocean regions will allow extension of these approaches to deep-sea protein coral archives worldwide.

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769

770 ## Research Data

771 Research Data associated with this article can be accessed at http://dx.doi.org/10.17632/6hy8tsrkf9.1
772 and will be submitted to BCO-DMO.

773

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Figure captions

Figure 1. Study area and sampling locations in Monterey Bay, California. Sediment trap and coral samples were collected at ~1200 m and ~900 m at M2 and M1 mooring stations, respectively.

Figure 2. Temporal patterns of bulk and amino acid $\delta^{13}C$ and $\delta^{15}N$ values in sediment trap samples from January 1999 through December 2004. The vertical brown bar denotes the flux of particulate organic carbon (POC) during the sampling period, and the gaps represent missing sampling due to technical issues. Avg EAA and avg NEAA refer to the simple average (not mol%-weighted) $\delta^{13}C$ values of the six essential AAs (Thr, Ile, Val, Phe, Leu, Lys) and six non-essential AAs (Gly, Ser, Asx, Glx, Pro, Ala), respectively. Avg SrcAA and avg TrAA are the simple average (not mol%-weighted) $\delta^{15}N$ values of the two most reliable source AAs (Phe and Lys; see section 4.4.1) and seven trophic AAs (TrAA: Glx, Asx, Ala, Leu, Ile, Pro, Val), respectively.

Figure 3. Relationships between bulk and amino acid $\delta^{13}C$ and $\delta^{15}N$ values in sinking particles. (a) $\delta^{13}C_{bulk}$ vs. $\delta^{13}C_{Phe}$, (b) $\delta^{13}C_{bulk}$ vs. $\delta^{13}C_{EAA}$, (c) $\delta^{15}N_{bulk}$ vs. $\delta^{15}N_{Phe}$, and (d) $^{15}N_{bulk}$ vs. $\delta^{15}N_{SrcAA}$. The blue lines represent the best fit lines (least square method). $\delta^{13}C_{EAA}$: mean $\delta^{13}C$ values of the six essential amino acids; $\delta^{15}N_{SrcAA}$: mean $\delta^{15}N$ value of the two source amino acids (Phe and Lys).

Figure 4. Temporal variation of measured and estimated $\delta^{13}C_{export\ production}$ and $\delta^{15}N_{export\ production}$ values between January 1999 and December 2004. The measured $\delta^{13}C_{export\ production}$ and $\delta^{15}N_{export\ production}$ refer to the bulk $\delta^{13}C$ and $\delta^{15}N$ values determined in sediment traps. The estimated

1048 $\delta^{13}C_{export\ production}$ and $\delta^{15}N_{export\ production}$ values were back calculated from sediment trap $\delta^{13}C_{EAA}$

1049 and $\delta^{15}N_{Phe}$ values using Eqs. (5) and (6), respectively.

1050

1051 **Figure 5**. Isotope values of essential and source AAs plotted against values of carbon flux,

1052 trophic position ($TP_{CSI\text{-}AA}$), degradation index (DI), and ΣV. There are two variables on each

1053 y-axis (panel a: $\delta^{13}C_{Phe}$ and $\delta^{13}C_{EAA}$; panel b: $\delta^{15}N_{Phe}$ and $\delta^{15}N_{SrcAA}$) and four variables on the

1054 x-axis. The coefficient of determination for each regression is labeled as R^2. The *p* values are not

1055 shown and are all greater than 0.1.

1056

1057 **Figure 6**. Comparisons of individual amino acid $\delta^{13}C$ and $\delta^{15}N$ values between sinking particles

1058 and coral skeletons. The dashed box indicates the range of isotope values determined in sinking

1059 particle samples (1999-2004). The circle and triangle symbols refer to individual skeletal peels of

1060 the two corals. There were three outer skeletal peels sampled from each coral. However, only the

1061 second and third peels were included in this comparison, because they best matched the sampling

1062 time of sinking particles (see Methods 2.1). EAA^1: average $\delta^{13}C$ value of all six essential AAs;

1063 EAA^2: average $\delta^{13}C$ value of essential AAs without Val. $\delta^{13}C$ values for Gly were not

1064 determined in the coral samples.

1065

1066 **Figure 7**. Mean offsets in individual amino acid $\delta^{13}C$ and $\delta^{15}N$ values between coral skeletons

1067 (average of the second and third peels) and sinking particles (flux-weighted average). Error bars

1068 represent propagated standard deviations. EAA^1: average $\delta^{13}C$ value of all six essential AAs;

1069 EAA^2: average $\delta^{13}C$ value of essential AAs without Val.

1070

Figure 8. Reconstructions of (a) bulk $\delta^{15}N$ values of export production, (b) source nitrogen $\delta^{15}N$ values and trophic position ($TP_{CSI\text{-}AA}$) of export production using $\delta^{15}N_{Phe}$ values of coral skeletons (second and third peels, as in Fig. 6). Each calculation was repeated with an offset-corrected $\delta^{15}N_{Phe}$ (minus 0.6‰) to account for the observed small trophic offset between sinking particles and coral skeletons (Fig. 7b). The dashed line and grey shaded area are the average and range (i.e., average ± standard deviation) of reference values. The reference values used for $\delta^{15}N_{export\ production}$ and exported $TP_{CSI\text{-}AA}$ were the flux-weighted average and standard deviation of $\delta^{15}N_{bulk}$ and $TP_{CSI\text{-}AA}$ values measured in our sediment traps (7.8±0.9‰ and 1.5±0.2, respectively). Reference values of source nitrogen $\delta^{15}N$ were the mean and standard deviation (7.8±0.8‰) of prior subsurface nitrate $\delta^{15}N$ values in Monterey Bay [8.0±0.2‰ in 1997 (Altabet et al., 1999) and 7.6±0.8‰ in 2002-2004 (Wankel et al., 2007)]. Error bars represent propagated standard deviations.