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$\delta^{18}O$ AND $\delta^{13}C$ VARIABILITY IN BRACHIOPODS FROM MODERN SHELF SEDIMENTS AND ITS UTILITY FOR UNDERSTANDING COMPLEX OCEANOGRAPHY, SOUTHERN AUSTRALIAN SHELF

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ABSTRACT: **The $\delta^{18}O$ and $\delta^{13}C$ values of brachiopod shell calcite are commonly used as proxies for ancient environmental marine conditions and secular changes in ancient ocean chemistry. The variability of $\delta^{18}O$ and $\delta^{13}C$ across modern shelf settings is, however, not well documented. This study presents $\delta^{18}O$ and $\delta^{13}C$ data from 407 Holocene (< 5000 yr BP) and living brachiopods collected from 220 sites across ~ 3000 km along Australia's southern shelf, the largest cool-water carbonate shelf in the modern world. Significant isotopic variability is present in separate specimens, at individual sites, and across the entire region. Individual specimens analyzed at multiple shell positions have an isotopic range of values up to 1.3‰ and 1.9‰ for $\delta^{18}O$ and $\delta^{13}C$ respectively. Multiple brachiopods at a single site have values that vary as much as 2.1‰ for $\delta^{18}O$ and 1.8‰ for $\delta^{13}C$. Regional variability ranges on the order of 3.6‰ and 3.4‰, for $\delta^{18}O$ and $\delta^{13}C$ respectively. The distribution of intrasite variability can be divided into areas of high and low variability. Areas characterized by low variability occur in zones of relatively consistent shelf water conditions. High-variability zones usually correspond to areas of seasonal upwelling onto the shelf, and this aspect is interpreted to be the main cause of isotopic variability. Upwelling waters are cold, leading to higher $\delta^{18}O$ values, and are commonly rich in respired dissolved inorganic carbon (DIC) and nutrients, promoting active phytoplankton growth and leading to variable $\delta^{13}C$ values. The extensive spatial coverage across this vast latitude-parallel region provides a valuable baseline illustrating the isotopic range that could occur in a single layer in the rock record. Furthermore, changes in isotopic signatures measured across stratigraphy might not necessarily reflect secular changes in ocean chemistry but, instead, could be recording local changes in shelf circulation and upwelling intensity.**

INTRODUCTION

It has long been known that brachiopods precipitate a large part of their shells in close stable isotopic equilibrium with the seawater in which they live (Lowenstam 1961; Veizer et al. 1986; Popp et al. 1986; Carpenter and Lohmann 1995; James et al. 1997; Brand et al. 2003). Recent research has shown that portions of brachiopod shell calcite are, however, not at chemical equilibrium with ambient seawater. Carpenter and Lohmann (1995) revealed that brachiopod primary layer calcite (PLC) is depleted in both ^{13}C and ^{18}O due to kinetic fractionation. Auclair et al. (2003) showed that disequilibrium fractionation effects continue into the outer secondary layer calcite (SLC) in a *Terebratalia transversa* specimen, and disequilibrium outer SLC has been observed in a variety of other brachiopod species (Yamamoto et al. 2011, 2013; Cusack and Pérez Huerta 2012). Detailed evaluation of shell chemistry from south Australian brachiopods confirms that PLC is influenced by kinetic effects but the $\delta^{18}O$ and $\delta^{13}C$ of SLC is not obviously influenced by disequilibrium fractionation (Dhillon et al., in preparation). PLC constitutes less than 6% by volume in south Australian brachiopod species (James et al. 1997) so nearly all of the shell calcite is at isotopic equilibrium with ambient seawater. Isotopic equilibrium precipitation has been confirmed in a variety of other modern marine environments (see Brand et al. 2003, their fig. 1) and has been used extensively to unravel the composition of ancient seawater chemistry (e.g., Veizer et al. 1999). Most of these seminal studies have been undertaken in specific environments utilizing a relatively small database. What is less well constrained is how variable the isotopic compositions are between organisms at single localities, at a variety of localities, between different species, and across a wide spectrum of environments in a single depositional realm. These relationships are critical if these shells are to be used in any high-resolution study in the rock record.

The southern margin of Australia, a latitude-parallel, cool-water carbonate depositional environment, offers the opportunity to address many of these unresolved issues. This region is the largest cool-water carbonate depositional system in the modern world. The seafloor is covered with biogenic carbonate sediments composed mainly of mollusks and bryozoans (James and Bone 2011). Among these organisms, brachiopods occur in low abundance but have a continuous distribution across the entire shelf. Their shells are composed of low-magnesium calcite (< 4 mol % $MgCO_3$), which is commonly well preserved and relatively resistant to diagenetic alteration. Furthermore, much of the physical oceanography is now known and thus can be related to the stable-isotope chemistry of brachiopods.

A possible advantage to studying the chemistry of temperate (heterozoan) carbonates is that slow growth rates minimize isotopic fractionation from kinetic effects (Bates and Brand 1991), since kinetic fractionation is attributed to rapid growth rates (McConnaughey 1989a, 1989b). A study by James et al. (1997) showed that the $\delta^{18}O$ of modern brachiopods from the Lacepede Shelf, a small segment of the southern margin, could be used to accurately reconstruct modern shelf water temperatures. The research presented here is a continuation of that

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preliminary study and has been expanded to include $\delta^{18}O$ and $\delta^{13}C$ of brachiopods across the entire southern shelf, west of Portland (Fig. 1). Holocene (< 5000 yr BP) and living brachiopods were sampled continuously across the study area from 220 sites over a latitudinal distance of ~ 3000 km. The large suite of brachiopod data presented here provides a substantial contribution to the global database.

The purpose of this paper is to 1) evaluate the intraspecimen and intrasite isotopic variability of all brachiopod species in the study area, 2) identify the areas of greatest $\delta^{18}O$ and $\delta^{13}C$ variability, and 3) determine the source of isotopic variability and identify the controls on brachiopod isotopic composition within this system.

SETTING AND OCEANOGRAPHY

Australia's southern margin is a latitude-parallel shelf spanning ~ 3000 km, a setting that is unique in the modern world. Most continental boundaries are meridional and extend across a variety of different atmospheric circulation cells, ocean current systems, and climates. This study area provides a view into the dynamics of a continental-scale shallow marine carbonate depositional system in a single climate and oceanographic zone. The climate in this region is arid to semiarid and, as a result, very little fresh water or terrestrial siliciclastic sediment is delivered to the shelf. Thus, the primary mode of sediment deposition is from the calcium carbonate shells and skeletons of marine organisms. Accumulation of carbonate sediment through the Cenozoic gave rise to the modern open shelf depositional environment (James et al. 2001; James and Bone 2011) which has a neritic zone that extends 20 to 230 km out from shore.

The biota is characteristic of a cool-water, heterozoan assemblage (James 1997) including bryozoans, mollusks, coralline algae, foraminifers, brachiopods, echinoderms, sponges, serpulid worm tubes, azooxanthellate corals, and a few local zooxanthellate corals. This study is concerned only with the brachiopods, which occur in low abundance but continuous distribution across the shelf. All the brachiopods of southern Australia are terebratulids, including five Terebratallidae, *Magellania flavescens*, *Anakinetica (Magadina) cumingi*, *Jaffaia jaffensis*, *Magadinella huleuri*, and *Magadinella mineuri*; and two Cancellothyridae, *Cancellothyris hedleyi* and *Terebratulina* cf. *cavata*. All are pedically attached forms except *A. cumingi*, which is free living and has the unique ability to move vertically in sandy substrates to adjust for changing sediment levels (Richardson and Watson 1975; Richardson 1981, 1987). All species precipitate punctate shells composed of low-magnesium calcite with primary and secondary layers.

The study area includes the southern shelf west of Portland to Cape Leeuwin. This area can be subdivided into three sectors (Fig. 1), which are, from west to east, the Albany Shelf, the Great Australian Bight (GAB) Shelf, and the South Australian Sea (SAS) Shelf. The Albany Sector is narrow (~ 30 to 80 km in width) and extends 900 km east–west from Cape Leeuwin of the western margin to Cape Pasley. The GAB Sector is a broad shelf (~ 125 to 250 km wide) that spans 1400 km from Cape Pasley eastward to the tip of the Eyre Peninsula. The SAS Sector extends 700 km from the Eyre Peninsula eastward to just south of the town of Portland and includes the broad Lincoln and Lacepede shelves (~ 100 to 180 km wide) to the west and the narrow Bonney Shelf (~ 25 to 50 km wide) to the east. For the sake of simplicity, this region is referred to as the SAS Sector.

The southern Australian shelf is a storm-dominated environment with wave energies high enough to potentially affect the sorting of shelf sand to depths of ~ 100 meters (James et al. 2001). Ocean currents in this area are complex (Fig. 1) and variable throughout the year due to the changing wind directions (James and Bone 2011). The Leeuwin Current (LC) is a surface current that is < 200 meters deep, < 100 km wide, relatively warm (from 21°C on the Albany Shelf to 18°C on the GAB Shelf), normal salinity (35.7–35.8‰), low nutrient, and high velocity (0.1–1.4 m s^{-1}) water body that flows south from the tropical western margin shelf and wraps around Cape Leeuwin to flow eastward along the southern shelf (Godfrey and Ridgeway 1985; Rochford 1986; Cresswell 1991; Pearce 1991; Ridgeway and Condie 2004; James and Bone 2011). Shallow shelf waters in the GAB are heated and evaporated to form a large plume of warm (up to 23°C) and saline (often > 36.0‰) water that combines with the LC to flow eastward as the South Australian Current (SAC) (Herzfeld 1997; James et al. 2001; Richardson et al. 2009; James and Bone 2011).

The Flinders Current (FC) is a cool, nutrient-rich northern boundary current that flows westward along the continental slope and extends from the surface (outboard of the on-shelf currents) to ~ 800 meters deep and flows underneath the LC and SAC that extend beyond the shelf margin (Bye 1971, 1972; Middleton and Cirano 2002; James and Bone 2011). The LC and SAC act as a barrier against the FC, blocking it from flowing up onto the shelf for most of the year. However, seasonal changes to coastal wind direction affect the flow of ocean currents on the south Australian shelf (cf. James and Bone 2011). In the winter, strong westerlies and the anticlockwise gyre send the LC eastward around Leeuwin Cape at its greatest velocity of the year; LC and SAC meet and mix in the GAB and downwelling persists across the southern shelf. In the summer, coastal atmospheric circulation switches to dominantly easterly winds; eastward-flowing coastal currents weaken, and upwelling of the FC is observed at several localities along the southern shelf, i.e., south of Albany,

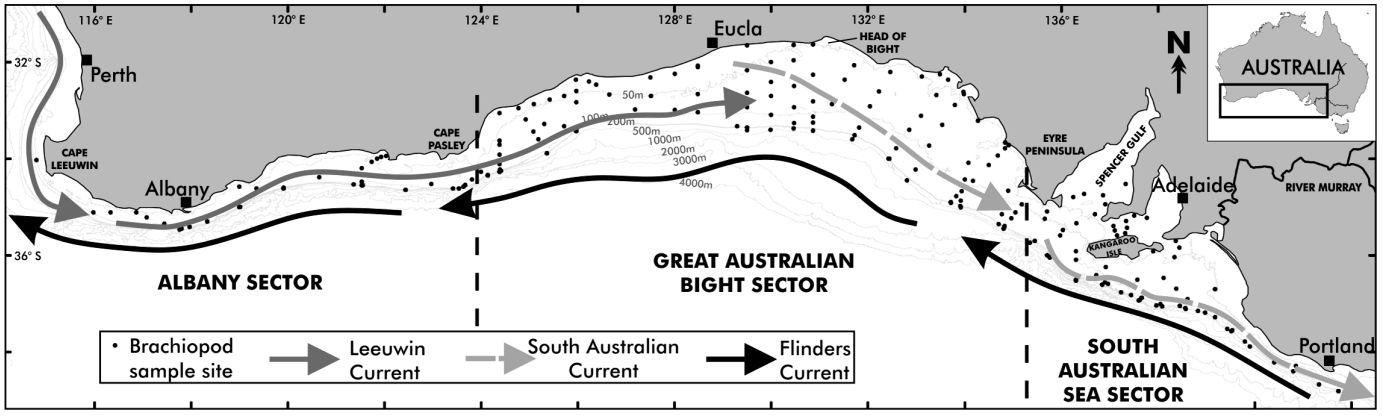


FIG. 1.—Map of the study area along the south Australian coast, which can be subdivided into three sectors, Albany Sector, Great Australian Bight (GAB) Sector, and South Australian Sea (SAS) Sector. The 200 m contour line is the approximate shelf margin. Gray arrows represent the eastward-moving shelf currents (Leeuwin and South Australian currents), and the black arrows represent the westward flow of the off-shelf Flinders Current. Small black circles show the location of sampled brachiopods.

west-central GAB sector, east GAB sector, south of Spencer Gulf, and east SAS sector (Griffin et al. 1997; Pearce and Pattiaratchi 1999; Middleton and Platov 2003; Kämpf et al. 2004; Sandery and Kämpf 2005; McClatchie et al. 2006; Ward et al. 2006; Middleton and Bye 2007; James and Bone 2011).

METHODS

Modern benthic shelf sediments were collected using a grab sampler on RV *Franklin*, during expeditions over the years of 1987 to 1998. The RV *Franklin* was Australia's first Marine National Facility oceanographic research vessel and was operated by the Commonwealth Scientific and Industrial Research Organization (CSIRO) from 1985 to 2002. Brachiopods were separated from the sediment onboard, cleaned, classified, and categorized. Only specimens that were living when collected or pristine shells with no evidence of abrasion or discoloration were selected for isotopic evaluation. Shells vary in length from about 0.5 to 2 cm but are most commonly $\leq$ 1 cm. Each sample was first soaked in 10% bleach dilute solution for 24 hours, to remove any organic material, and then thoroughly rinsed in deionized water. Inner SLC and bulk shell samples were collected from the ventral valve of each cleaned brachiopod specimen prior to isotopic analysis. Inner SLC samples were collected from the underside of the valve using a fine-tipped hand drill, and whole shells were crushed to powder for bulk samples. Parkinson et al. (2005) show that both the ventral and dorsal valves are acceptable for isotopic analysis, but this study utilizes only the ventral valve for a consistent sampling methodology. Carpenter and Lohmann (1995) conclude that $\delta^{18}O$ and $\delta^{13}C$ values are depleted in the primary skeletal layers and specialized shell structures of brachiopods. They therefore suggest sampling and geochemical analysis of the SLC only. However, James et al. (1997) determined that south Australian brachiopods have less than 6% by volume of PLC, and thus bulk shell samples are acceptable for geochemical analysis. To further test these hypotheses, four specimens were sampled for PLC, SLC, and bulk shell samples, and the results are discussed in the following sections.

Isotopic analyses were conducted at the Queen's Facility for Isotope Research. Powdered carbonate samples ($\sim$ 1 mg each) were digested in 100% phosphoric acid at 72°C for a minimum of 2 hours. The resulting CO_2 gas was measured for its $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios using a GasBench II coupled Delta-Plus XP stable-isotope mass spectrometer. All $\delta^{18}O$ and $\delta^{13}C$ data in this paper are reported in per mil (‰) relative to the Vienna Peedee belemnite (VPDB) reference material. Replicate analyses indicate a reproducibility of $\pm$ 0.05‰ (1σ) for both $\delta^{18}O$ and $\delta^{13}C$. The majority of brachiopod shells collected from shelf sediments were not living when collected, and the age of these specimens was uncertain, so a representative suite of 13 well-preserved specimens were selected for ^{14}C age dating. The CO_2 was extracted using the techniques described above and radiocarbon dated by accelerator mass spectrometry (AMS) at IsoTrace Laboratory (University of Toronto).

RESULTS

Intraspecimen Isotopic Variability

A total of 407 brachiopods were sampled from 220 sites across the southern shelf (Fig. 1), and of those brachiopod specimens, 67 were sampled at two or more positions across their shells (Fig. 2). The difference between the highest and lowest oxygen and carbon isotopic values ($\Delta^{18}O$ and $\Delta^{13}C$) in an individual shell was determined for all specimens (Fig. 2, Table 1). This study is concerned with the total range in isotopic values that is found in an individual brachiopod or at a single site and how it relates to on-shelf environments. The intraspecimen and intrasite data are not presented in terms of standard deviation because 1) there is no relationship between the isotopic range and number of samples analyzed, 2) the data frequently produces a non-normal distribution, and 3) there are an inconsistent number of data values between different specimens and sites, which would produce a bias in statistical data.

Comparison of *A. cumingi* specimens results in a $\Delta^{18}O$ maximum of 1.1‰ and average of 0.3‰; *A. cumingi* $\Delta^{13}C$ maximum of 1.5‰ and average of 0.4‰, whereas comparison of all species results in $\Delta^{18}O$ maximum of 1.3‰ and average of 0.4‰ and a $\Delta^{13}C$ maximum of 1.9‰ and average of 0.5‰ (Table 1). To better understand the primary isotopic variability in a single specimen, four *A. cumingi* specimens collected from three widely separated sites were each sampled for PLC, SLC, and bulk calcite and analyzed for $\delta^{18}O$ and $\delta^{13}C$. The resulting data and relative shell sample positions are shown in Figure 3. Relative to SLC values, PLC is consistently depleted in $\delta^{18}O$ and $\delta^{13}C$ (Fig. 3). Despite the inclusion of depleted PLC, bulk values all fall within the cloud of SLC values for a given specimen (Fig. 3). The details and implications of these results are discussed below.

Intrasite Isotopic Variability

A total of 101 sites yielded two or more brachiopod specimens, regardless of species, which were analyzed for their $\delta^{18}O$ and $\delta^{13}C$ to determine the non-species-specific intrasite isotopic variability (Fig. 4). Figure 4 shows the range in $\delta^{18}O$ and $\delta^{13}C$ of all sites with multiple specimens and includes all brachiopod species from the southern Australian shelf. *A. cumingi* is, by far, the most widely distributed brachiopod species in the study area and has been collected from water depths of 25 to 360 meters. This abundance and continuous geographic distribution makes *A. cumingi* a prime candidate for showing intrasite variability of one species from a variety of environmental situations. *A. cumingi* is, therefore, used in this study to show the intrasite $\Delta^{18}O$ and $\Delta^{13}C$ of a single species, i.e., the isotopic difference between two or more specimens of the same species at the same site. A total of 161 *A. cumingi* specimens from 58 sites were analyzed. Table 1 compares the intrasite $\Delta^{18}O$ and $\Delta^{13}C$ of all species and *A. cumingi* only, revealing that both have a very similar range of isotopic variability. The maximum $\Delta^{18}O$ observed at a single site is 2.1‰ when comparing either *A. cumingi* specimens alone or all species (Fig. 4, Table 1). The mean of all intrasite $\Delta^{18}O$ values is 0.5‰ for *A. cumingi* and 0.6‰ for all species. The difference in $\delta^{13}C$ of brachiopods at a single site shows a range similar to the $\Delta^{18}O$. Maximum intrasite $\Delta^{13}C$ is 1.5‰ for *A. cumingi* (mean = 0.6‰) and 1.8‰ for all species (mean = 0.6‰; Fig. 4, Table 1).

Total Isotopic Variability

Regional-scale isotopic variability of Holocene and living brachiopods from the south Australian shelf is large (Fig. 5). The total range in $\delta^{18}O$ and $\delta^{13}C$ for all species across the entire study area is –0.7 to 2.9‰ and 0.1 to 3.4‰, respectively (Table 2). Comparison of $\delta^{18}O$ and $\delta^{13}C$ values from all species indicates an isotopic range very similar to that of *A. cumingi* for each region in the study area (Fig. 5, Table 2). This similarity in isotopic range for both *A. cumingi* and all species implies that the source of variability is not caused by species specific fractionation effects.

INTERPRETATION AND DISCUSSION

Evaluating for Metabolic and Kinetic Fractionation

The significant differences in isotopic compositions of specimens at the same site might call into question whether brachiopod shell calcite is really in isotopic equilibrium with ambient seawater. Kinetic fractionation is characterized by simultaneous depletion in ^{18}O and ^{13}C and occurs in carbonate skeletons that precipitate rapidly (Turner 1982; McConnaughey 1989a, 1989b; McConnaughey et al. 1997; Auclair et al.

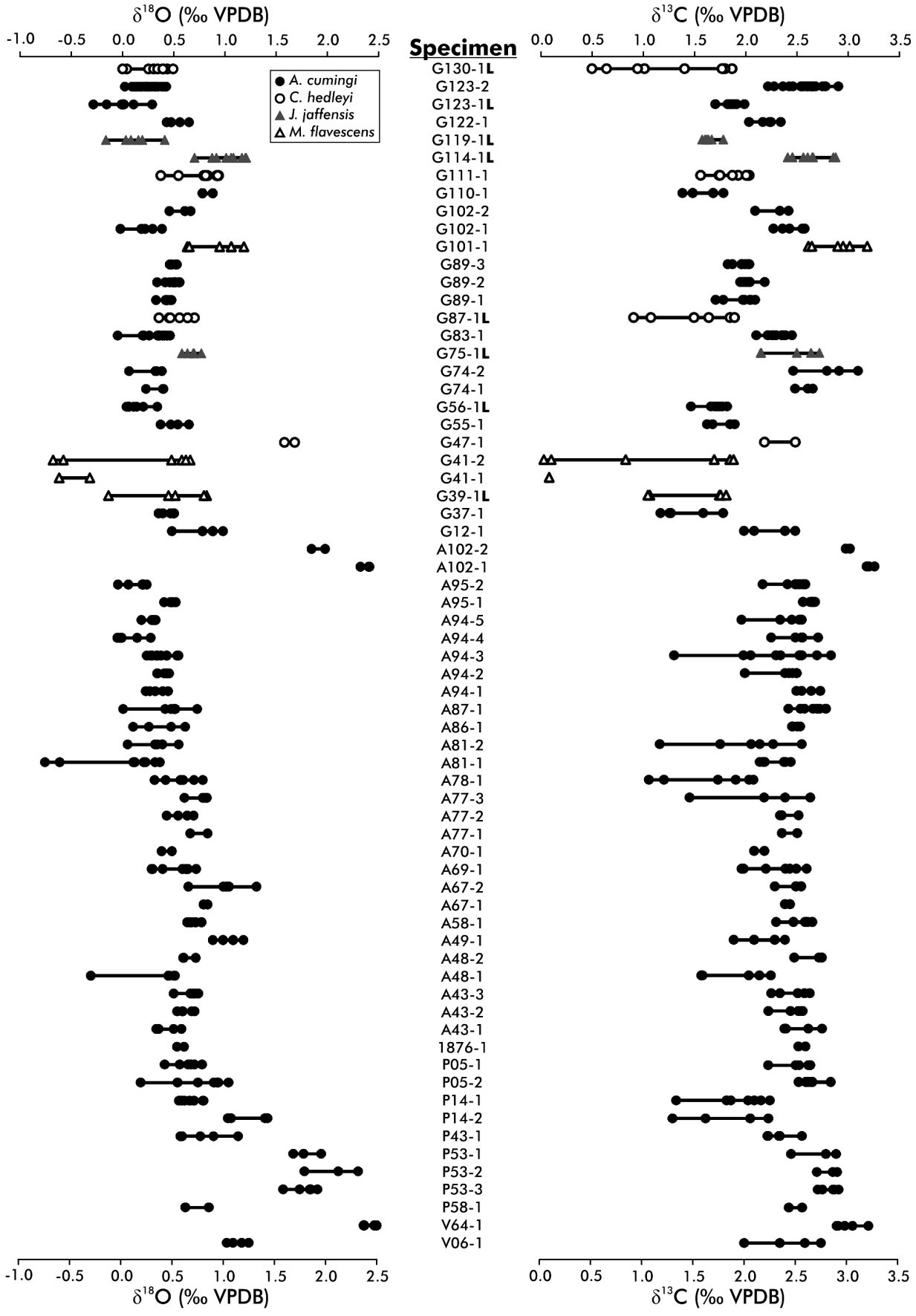

δ18O (‰ VPDB)
-1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5
A. cumingi
C. hedleyi
J. jaffensis
M. flavescens
Specimen
G130-1L
G123-2
G123-1L
G122-1
G119-1L
G114-1L
G111-1
G110-1
G102-2
G102-1
G101-1
G89-3
G89-2
G89-1
G87-1L
G83-1
G75-1L
G74-2
G74-1
G56-1L
G55-1
G47-1
G41-2
G41-1
G39-1L
G37-1
G12-1
A102-2
A102-1
A95-2
A95-1
A94-5
A94-4
A94-3
A94-2
A94-1
A87-1
A86-1
A81-2
A81-1
A78-1
A77-3
A77-2
A77-1
A70-1
A69-1
A67-2
A67-1
A58-1
A49-1
A48-2
A48-1
A43-3
A43-2
A43-1
1876-1
P05-1
P05-2
P14-1
P14-2
P43-1
P53-1
P53-2
P53-3
P58-1
V64-1
V06-1
δ13C (‰ VPDB)
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5

TABLE 1.—*A compilation of all data on isotopic variability from the entire study area showing the mean and total range in $\delta^{18}O$ and $\delta^{13}C$ for intrasite and intraspecimen data from across the shelf.*

	Intraspecimen $\delta^{18}O$	Intraspecimen $\delta^{13}C$	Intrasite $\delta^{18}O$	Intrasite $\delta^{13}C$
All Species				
Range:	0–1.3‰	0–1.9‰	0–2.1‰	0–1.8‰
Mean:	0.4‰	0.5‰	0.6‰	0.6‰
A. cumingi Only				
Range:	0.1–1.1‰	0–1.5‰	0–2.1‰	0–1.5‰
Mean:	0.3‰	0.4‰	0.5‰	0.6‰

2003). Metabolic fractionation is characterized by the enrichment or depletion of ^{13}C in a carbonate shell and is caused by respiration or photosynthesis of the organism (cf. Spero et al. 1997). Rahimpour-Bonab et al. (1997) report that $\delta^{13}C$ values of Lacepede Shelf brachiopod shells fall within or near the expected $\delta^{13}C$ equilibrium range (~ 1.5 to 2.5‰), but report a +1‰ enrichment in brachiopod $\delta^{18}O$, relative to estimated equilibrium values, which they attribute to vital effects. Additionally, Parkinson et al. (2005) suggest that bulk sampling techniques and inclusion of non-equilibrium PLC is the source for isotopic variability. However, James et al. (1997) show that these ^{18}O-enriched specimens occur in a zone of upwelling and conclude that Lacepede Shelf brachiopods are precipitated in isotopic equilibrium with ambient seawater.

Brachiopod shells on Australia's southern shelf are precipitated in relatively cool water, resulting in slow shell growth rates, thereby minimizing kinetic effects (McConnaughey 1989a, 1989b; Bates and Brand 1991). Four *A. cumingi* specimens from three different sites across the study area were sampled for PLC, SLC, and bulk shell samples to evaluate sampling methods and test for isotopic disequilibrium (Figs. 3, 6). The $\delta^{18}O$ and $\delta^{13}C$ values are reported on cross-plots in Figure 6, and the results are similar to those of Carpenter and Lohmann (1995). The SLC of each specimen is confined to a relatively narrow isotopic range, and $\delta^{18}O$ values fall within or very near the estimated range of calcite precipitated at equilibrium with ambient seawater; PLC values plot on a linear trend, which suggests that this shell layer is influenced by kinetic fractionation, and bulk calcite samples always fall within the same range as SLC, suggesting that bulk samples approximate equilibrium with ambient seawater (Fig. 6). No enrichment or depletion in ^{13}C is apparent in the SLC or bulk calcite, indicating that these samples are not affected by metabolic fractionation. Furthermore, these results support the assumption of James et al. (1997) that bulk calcite samples approximate ambient seawater because PLC makes up less than 6% of the total shell volume in specimens of the southern Australian shelf.

To further clarify this point, specimen 1 from site P14 (Fig. 6) is used as an example to show the possible error associated with including PLC in bulk samples. This specimen has an average SLC value of 0.70‰ for $\delta^{18}O$ and 1.95‰ for $\delta^{13}C$. For the sake of this argument, the PLC sample with greatest offset from SLC values is used to show the maximum possible influence from including PLC in bulk samples. This PLC sample has a $\delta^{18}O$ of –0.30‰ and $\delta^{13}C$ value of –1.10‰. Assuming the shell to be composed of 6% PLC and 94% SLC, the resulting bulk shell sample is estimated to have $\delta^{18}O$ and $\delta^{13}C$ values of 0.64‰ and 1.77‰, respectively. Therefore, the inclusion of PLC in bulk shell samples will theoretically cause a maximum error of 0.06‰ for $\delta^{18}O$ and 0.18‰ for $\delta^{13}C$. This error is insignificant compared to the isotopic variability observed in the SLC values, which is why bulk samples consistently fall within the range of equilibrium SLC values.

Distribution of Isotopic Variability

The greatest intraspecimen variability occurs in the same areas as the highest intrasite variability (e.g., sites A48, A81, and G41; Figs. 2, 4). Thus, intraspecimen and intrasite variability appear to be intrinsically linked and the source of isotopic variability is likely the same. Intrasite

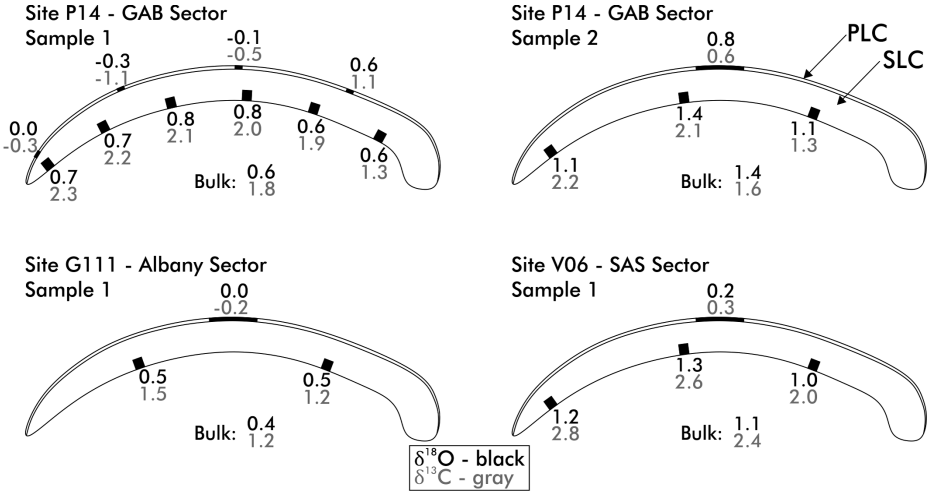
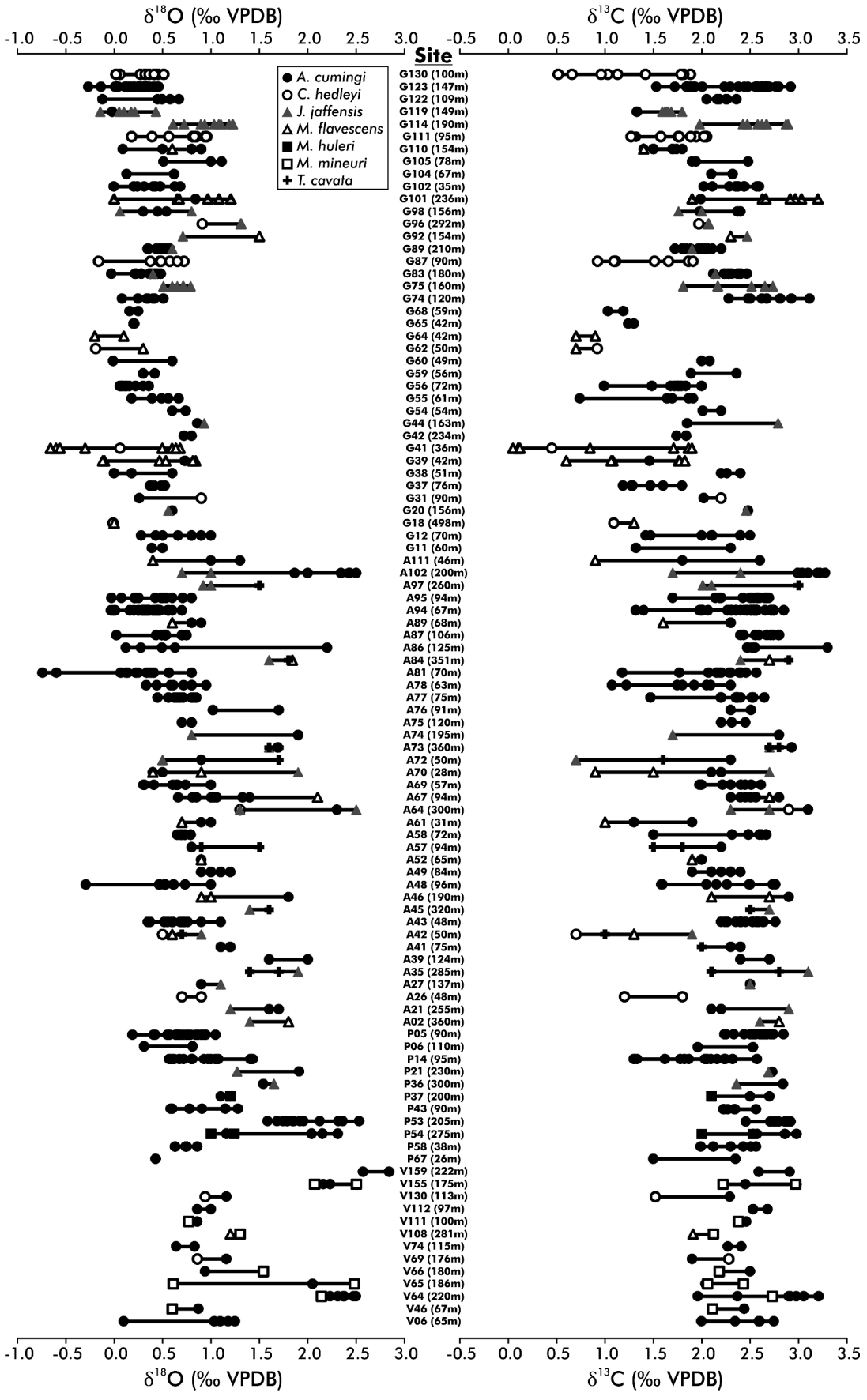


FIG. 3.—Isotopic compositions of various samples from four *A.cumingi* specimens that were analyzed for $\delta^{18}O$ (black) and $\delta^{13}C$ (gray) at multiple positions in single shells. Squares show the approximate sample locations. The thin outer shell layer is primary layer calcite (PLC), and the thick inner layer is secondary layer calcite (SLC). Bulk shell samples, including both PLC and SLC, were sampled and analyzed and the values are shown below each shell. Shells vary in length from about 0.5 to 2 cm but are mostly commonly ≤ 1 cm.

←

FIG. 2.—Intraspecimen range in $\delta^{18}O$ and $\delta^{13}C$ values measured from secondary layer calcite or whole shell samples of individual specimens. Each sample number represents an individual specimen, and the list is roughly organized to reflect the spatial succession from west (top) to east (bottom). Specimens that were living when collected are indicated with a bold "**L**" after the sample number.


δ18O (‰ VPDB)
δ13C (‰ VPDB)
Site
A. cumingi
C. hedleyi
J. jaffensis
M. flavescens
M. huleri
M. mineuri
T. cavata
G130 (100m)
G123 (147m)
G122 (109m)
G119 (149m)
G114 (190m)
G111 (95m)
G110 (154m)
G105 (78m)
G104 (67m)
G102 (35m)
G101 (236m)
G98 (156m)
G96 (292m)
G92 (154m)
G89 (210m)
G87 (90m)
G83 (180m)
G75 (160m)
G74 (120m)
G68 (59m)
G65 (42m)
G64 (42m)
G62 (50m)
G60 (49m)
G59 (56m)
G56 (72m)
G55 (61m)
G54 (54m)
G44 (163m)
G42 (234m)
G41 (36m)
G39 (42m)
G38 (51m)
G37 (76m)
G31 (90m)
G20 (156m)
G18 (498m)
G12 (70m)
G11 (60m)
A111 (46m)
A102 (200m)
A97 (260m)
A95 (94m)
A94 (67m)
A89 (68m)
A87 (106m)
A86 (125m)
A84 (351m)
A81 (70m)
A78 (63m)
A77 (75m)
A76 (91m)
A75 (120m)
A74 (195m)
A73 (360m)
A72 (50m)
A70 (28m)
A69 (57m)
A67 (94m)
A64 (300m)
A61 (31m)
A58 (72m)
A57 (94m)
A52 (65m)
A49 (84m)
A48 (96m)
A46 (190m)
A45 (320m)
A43 (48m)
A42 (50m)
A41 (75m)
A39 (124m)
A35 (285m)
A27 (137m)
A26 (48m)
A21 (255m)
A02 (360m)
P05 (90m)
P06 (110m)
P14 (95m)
P21 (230m)
P36 (300m)
P37 (200m)
P43 (90m)
P53 (205m)
P54 (275m)
P58 (38m)
P67 (26m)
V159 (222m)
V155 (175m)
V130 (113m)
V112 (97m)
V111 (100m)
V108 (281m)
V74 (115m)
V69 (176m)
V66 (180m)
V65 (186m)
V64 (220m)
V46 (67m)
V06 (65m)
-1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0
-0.5 0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5

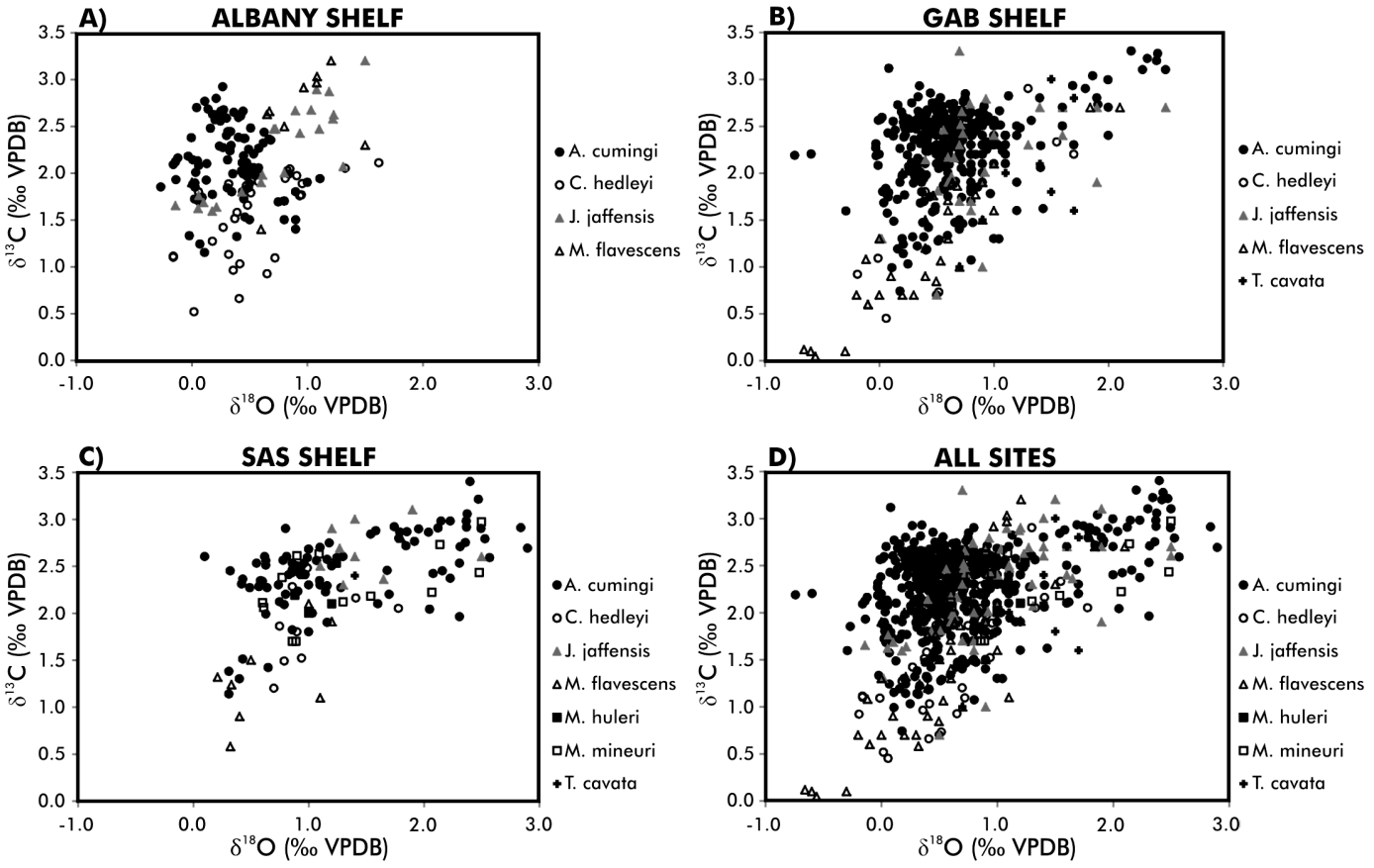


FIG. 5.—Relationship between $\delta^{18}O$ and $\delta^{13}C$ values for secondary-layer calcite and bulk calcite samples from brachiopods of all species. Plots A, B, and C show data from each region, and Plot D is a compilation of all data from the entire study area.

$\Delta^{18}O$ and $\Delta^{13}C$ values of all species and *A. cumingi* are mapped in Figure 7 to show the spatial distribution of isotopic variability. As mentioned above, isotopic variability from all species exhibits trends similar to the corresponding *A. cumingi* data (Fig. 7), suggesting that the cause of isotopic variability is not related to differences between species (e.g., vital effects) but instead is some process that influences all species similarly. Figure 8 shows the general spatial distribution of high and low intrasite isotopic variability. High-variability zones include sites with interspecies $\Delta^{18}O$ and $\Delta^{13}C$ values that exceed 0.6‰ and 0.7‰, respectively. The high-variability and low-variability zones for $\Delta^{18}O$ coincide with those of $\Delta^{13}C$ across the study area, as shown by the similarity of the two plots in Figure 8, and the cause of isotopic variability is likely the same for both $\Delta^{18}O$ and $\Delta^{13}C$. The areas of low $\Delta^{18}O$ and $\Delta^{13}C$ represent shelf areas with relatively consistent environmental conditions. The areas of high $\Delta^{18}O$ and $\Delta^{13}C$ correspond to areas of variable shelf conditions. The majority of environmental conditions are

TABLE 2.—*Regional-scale oxygen and carbon isotope values from all brachiopod species and* A. cumingi *only.*

	$\delta^{18}O$, ‰				$\delta^{13}C$, ‰			
	Range	Mean	SD (1σ)	N	Range	Mean	SD (1σ)	N
All Species								
Albany Shelf:	–0.3 to 1.6	0.5	0.4	166	0.5 to 3.2	2.1	0.5	166
GAB Shelf:	–0.7 to 2.5	0.7	0.5	422	0.1 to 3.3	2.2	0.6	422
SAS Shelf:	0.1 to 2.9	1.3	0.7	136	0.6 to 3.4	2.4	0.5	136
All Sites:	–0.7 to 2.9	0.7	0.6	724	0.1 to 3.4	2.2	0.5	724
A. cumingi Only								
Albany Shelf:	–0.3 to 1.1	0.4	0.3	104	1.2 to 2.9	2.1	0.4	104
GAB Shelf:	–0.7 to 2.5	0.6	0.4	330	0.7 to 3.3	2.3	0.4	330
SAS Shelf:	0.1 to 2.9	1.3	0.7	90	1.1 to 3.4	2.5	0.4	90
All Sites:	–0.7 to 2.9	0.7	0.6	524	0.7 to 3.4	2.3	0.4	524

←

FIG. 4.—Intrasite $\delta^{18}O$ and $\delta^{13}C$ values measured from secondary-layer calcite or whole shell samples of two or more specimens at a single site. Each sample number represents an individual site, and the list is roughly organized to reflect the spatial succession from west (top) to east (bottom).

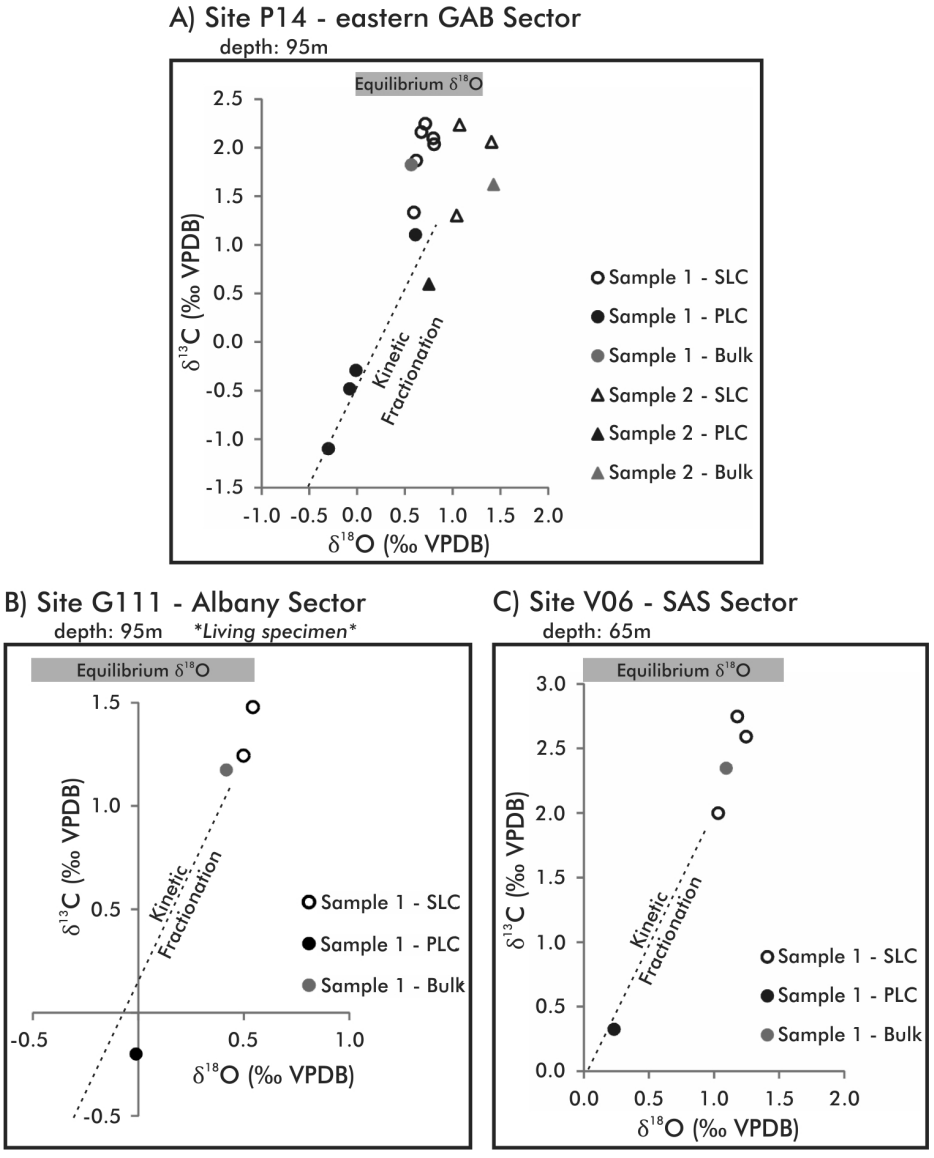


FIG. 6.—Relationship between $\delta^{18}O$ and $\delta^{13}C$ for four *A.cumingi* specimens from three different sites. Primary-layer calcite (PLC) is shown in black, secondary-layer calcite (SLC) is shown in white, and bulk calcite samples are shown in gray. Kinetic fractionation lines (slope of 2) represent the expected offset from equilibrium values for calcite precipitated at rapid growth rates (e.g., McConnaughey 1989a, 1989b; McConnaughey et al. 1997). Equilibrium $\delta^{18}O$ was calculated using the O'Neil et al. (1969) paleotemperature equation, as recalculated by Hays and Grossman (1991) [$TC = 15.7 - 4.36(\delta^{18}O_{CaCO3} - \delta^{18}O_{water}) + 0.12(\delta^{18}O_{CaCO3} - \delta^{18}O_{water})^2$]; the average southern Australian shelf seawater $\delta^{18}O$ of 0.4‰ (VSMOW) (L.E. Richardson, personal communication 2014); and data on shelf water temperature are from CSIRO Marine and Atmospheric Research data trawler.

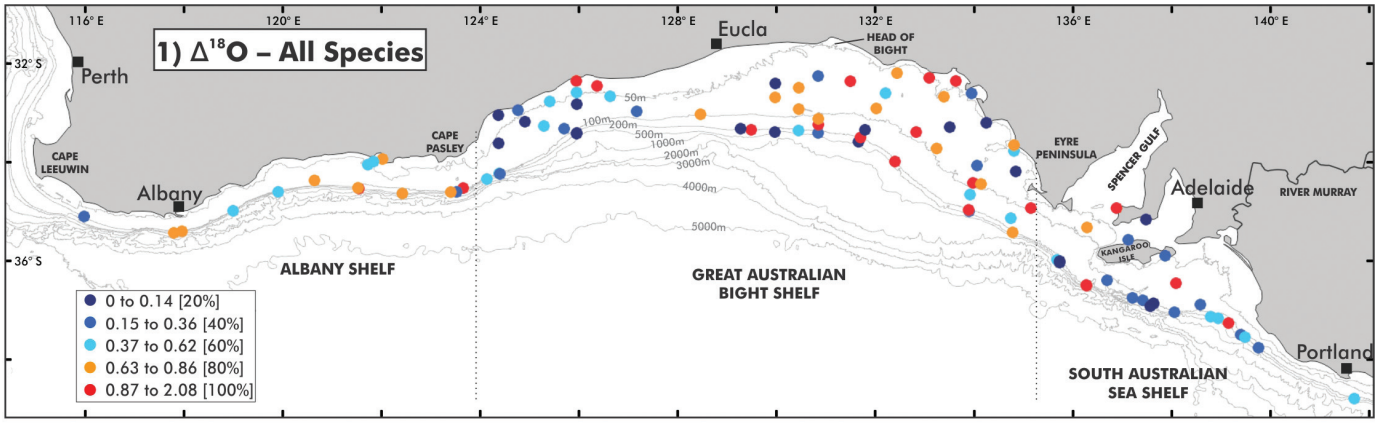
relatively constant across Australia's southern shelf—wave energy is consistently high, fluvial input is negligible due to the arid climate, shelf water temperature gradually cools from west to east, and salinity is variable only on the local scale in shallow areas affected by high evaporation rates. None of these variables can be the cause of the large zones of high variability seen in Figure 8. Seasonal upwelling, however, is found to overlap with high-variability zones (Fig. 8).

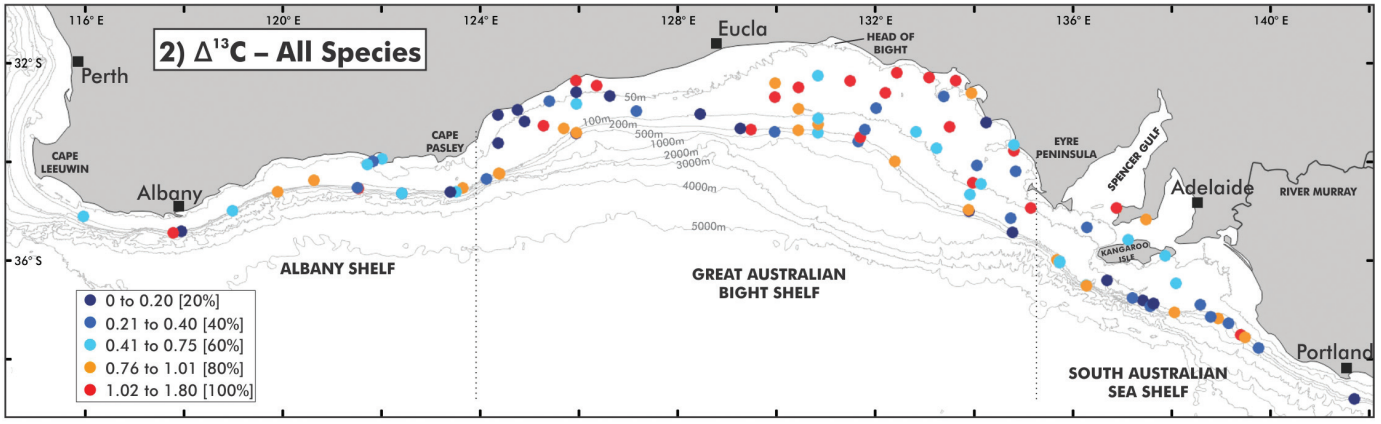
Upwelling and High Isotopic Variability

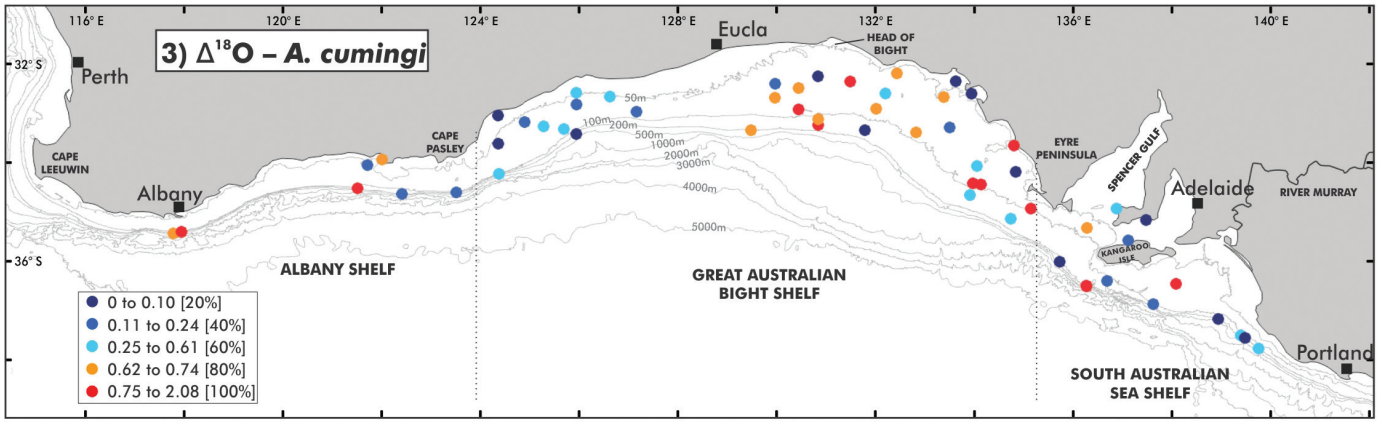
Seasonal upwelling on Australia's southern shelf has been an important topic of oceanographic research for many years (e.g., Lewis 1981; Ridgeway and Condie 2004; Middleton and Bye 2007), and the results from these studies provide a good understanding of the locations and extent of upwelling in the study area (cf. James and Bone 2011). The majority of high $\Delta^{18}O$ and $\Delta^{13}C$ coincides with areas of identified seasonal upwelling, i.e., south of Albany, west-central GAB sector, east GAB sector, south of Spencer Gulf, and east SAS sector (Fig. 8). Thus, seasonal upwelling is interpreted to be the reason for high variability in $\delta^{18}O$ and $\delta^{13}C$ observed in brachiopod shells at these locations. Cool, deep upwelled waters of the Flinders Current flow onto the shelf and temporarily lower the local shelf water temperature, which should result in more positive $\delta^{18}O$ values of brachiopod shells being precipitated at this time. Dissolved inorganic carbon (DIC) from deep, off-shelf waters are generally enriched in ^{12}C due to the oxidation of organics and remineralization of isotopically light organic carbon (e.g., Tagliabue and Bopp 2008). Therefore, upwelling zones may be expected to introduce isotopically light DIC which would mix with and reduce the $\delta^{13}C$ of shelf waters. These deep waters, however, are also rich in nutrients and will

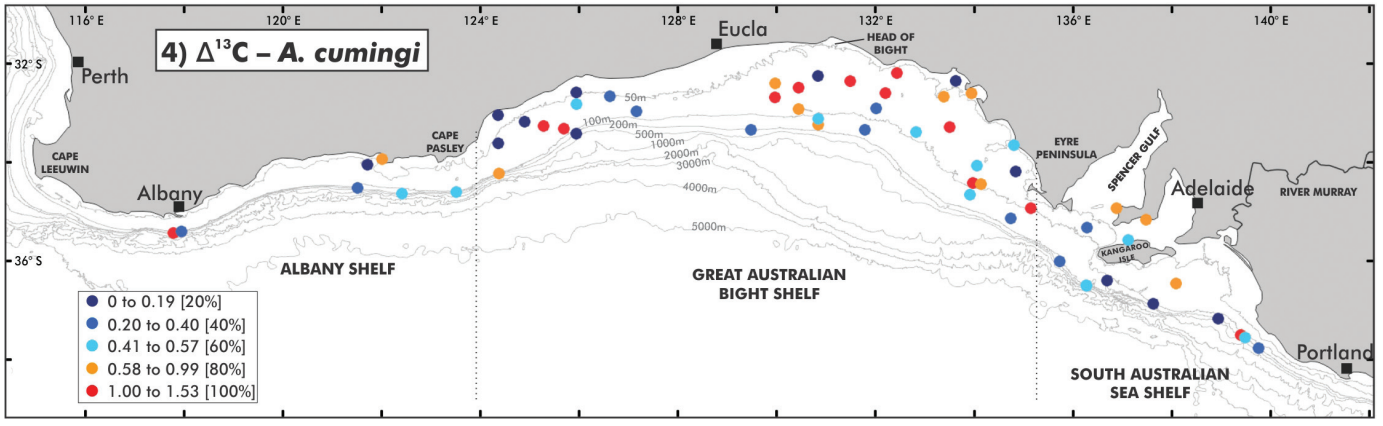
→

FIG. 7.—Maps showing the spatial oxygen and carbon isotope variability ($\Delta^{18}O$ and $\Delta^{13}C$) for all sites with multiple brachiopod specimens. Maps 1 and 2 show the intrasite variability when comparing all species and maps 3 and 4 show the intrasite variability when comparing just *A.cumingi*. The variability data are presented in five equal ranges; sites with the greatest variability (highest 20%) are bright red and sites with lowest variability (lowest 20%) are dark blue.


1) Δ18O – All Species
116° E
120° E
124° E
128° E
132° E
136° E
140° E
32° S
36° S
Perth
Eucla
HEAD OF BIGHT
CAPE LEEUWIN
CAPE PASLEY
Albany
EYRE PENINSULA
SPENCER GULF
Adelaide
RIVER MURRAY
KANGAROO ISLE
Portland
50m
100m
200m
500m
1000m
2000m
3000m
4000m
5000m
ALBANY SHELF
GREAT AUSTRALIAN BIGHT SHELF
SOUTH AUSTRALIAN SEA SHELF
0 to 0.14 [20%]
0.15 to 0.36 [40%]
0.37 to 0.62 [60%]
0.63 to 0.86 [80%]
0.87 to 2.08 [100%]


2) Δ13C – All Species
116° E
120° E
124° E
128° E
132° E
136° E
140° E
32° S
36° S
Perth
Eucla
HEAD OF BIGHT
CAPE LEEUWIN
CAPE PASLEY
Albany
EYRE PENINSULA
SPENCER GULF
Adelaide
RIVER MURRAY
KANGAROO ISLE
Portland
50m
100m
200m
500m
1000m
2000m
3000m
4000m
5000m
ALBANY SHELF
GREAT AUSTRALIAN BIGHT SHELF
SOUTH AUSTRALIAN SEA SHELF
0 to 0.20 [20%]
0.21 to 0.40 [40%]
0.41 to 0.75 [60%]
0.76 to 1.01 [80%]
1.02 to 1.80 [100%]


3) Δ18O – A. cumingi
116° E
120° E
124° E
128° E
132° E
136° E
140° E
32° S
36° S
Perth
Eucla
HEAD OF BIGHT
CAPE LEEUWIN
CAPE PASLEY
Albany
EYRE PENINSULA
SPENCER GULF
Adelaide
RIVER MURRAY
KANGAROO ISLE
Portland
50m
100m
200m
500m
1000m
2000m
3000m
4000m
5000m
ALBANY SHELF
GREAT AUSTRALIAN BIGHT SHELF
SOUTH AUSTRALIAN SEA SHELF
0 to 0.10 [20%]
0.11 to 0.24 [40%]
0.25 to 0.61 [60%]
0.62 to 0.74 [80%]
0.75 to 2.08 [100%]


4) Δ13C – A. cumingi
116° E
120° E
124° E
128° E
132° E
136° E
140° E
32° S
36° S
Perth
Eucla
HEAD OF BIGHT
CAPE LEEUWIN
CAPE PASLEY
Albany
EYRE PENINSULA
SPENCER GULF
Adelaide
RIVER MURRAY
KANGAROO ISLE
Portland
50m
100m
200m
500m
1000m
2000m
3000m
4000m
5000m
ALBANY SHELF
GREAT AUSTRALIAN BIGHT SHELF
SOUTH AUSTRALIAN SEA SHELF
0 to 0.19 [20%]
0.20 to 0.40 [40%]
0.41 to 0.57 [60%]
0.58 to 0.99 [80%]
1.00 to 1.53 [100%]

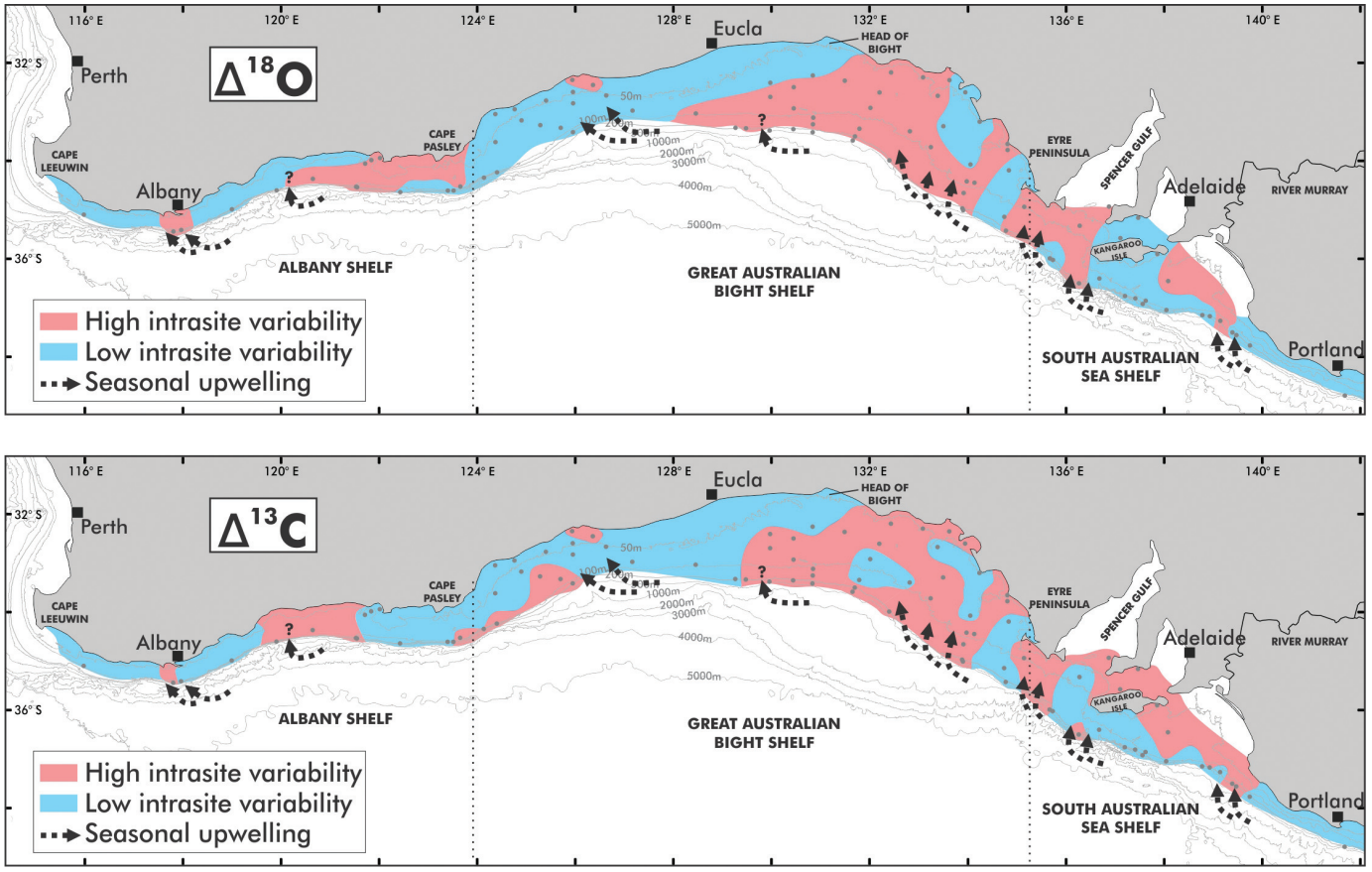


FIG. 8.—Generalized maps of intrasite isotopic variability showing trends in high (red) and low (blue) $\Delta^{18}O$ and $\Delta^{13}C$. Gray circles show the locations of sites from Figure 7. All identified areas of seasonal upwelling (cf.James and Bone 2011) are represented by black arrows with dashed lines. Arrows with question marks indicate unconfirmed areas of upwelling (Pattiaratchi 2007; Richardson et al. 2009).

facilitate phytoplankton blooms when upwelled onto the shelf and into the photic zone. ^{12}C is preferentially fixed in the organic material during phytoplankton growth, and DIC in the surrounding water becomes enriched in ^{13}C, which has a greater effect on shelf water chemistry than the introduction of isotopically light DIC from deep water and results in increased $\delta^{13}C$ values downstream of upwelling zones (Kroon and Ganssen 1989; Gruber et al. 1999; Tagliabue and Bopp 2008). Therefore, high intraspecimen and intrasite isotopic variability is evidence of these regional impacts from seasonal upwelling because brachiopod shells growing in these areas would record a combination of normal shelf conditions and the upwelling conditions described above, resulting in a wide range of isotopic values.

Two other regions show high $\Delta^{18}O$ and $\Delta^{13}C$, the east-central GAB sector, and the central to eastern Albany sector (Fig. 8), and are in zones of suspected upwelling but have not been confirmed with detailed oceanographic studies. The east-central GAB sector appears to be a continuation of the eastern GAB upwelling zone, and it is possible that upwelling continues farther to the west to include this area. Richardson et al. (2009) mapped the distribution of water masses in this area and was the first to suggest upwelling in the east-central GAB. Intense summer heating also forms a hot, saline plume in the central GAB which flows eastward. Summer upwelling in the east and central GAB moves water from the Flinders current up onto the shelf, where it interacts with the GAB plume to form patches of each water body and complex mixtures of the two (Richardson et al. 2009). The large region of high isotopic variability in this area is interpreted to be a product of the seasonal upwelling and complex mixing described above.

The central to east Albany shelf is also an area of high isotopic variability (Fig. 8), but very little oceanographic research has been conducted in this area and no published articles have identified it as an upwelling zone. A recent report prepared for the Australian Department of Environment, Water, Heritage and the Arts suggests that upwelling zones do occur along the Albany Shelf, where deep water migrates up continental slope canyons onto the shelf during periods of weak shelf currents (Pattiaratchi 2007). His report presents water temperature data and identifies an upwelling zone at the Bremer Canyon head (see Pattiaratchi 2007, fig. 3.3), which is in the central Albany sector and lies on the western margin of the zone of high isotopic variability (Fig. 8). Upwelling at this location and other surrounding submarine canyons would continue to flow down-current to the east and could produce the distribution of high isotopic variability seen here. Just to the east, in the western GAB, is a zone of high carbon isotope variability (Fig. 8). It is unclear why $\Delta^{13}C$ is high and $\Delta^{18}O$ is low in this area; however, one possible explanation is that upwelling-induced phytoplankton blooms on the Albany Shelf lead to fall-out of decomposing organics in the western GAB and alters local bottom-water $\delta^{13}C$.

Defining Intraspecimen and Intrasite Variability

The range in intraspecimen and intrasite $\delta^{18}O$ and $\delta^{13}C$ values is interpreted to be a result of fluctuating environmental conditions (temperature, nutrients, seawater chemistry, etc.), specifically seasonal upwelling-induced changes in this study area. Intraspecimen variability is an archive of short-term changes that occurred over the lifetime of the

TABLE 3.—*Carbon-14 age estimates of thirteen well preserved brachiopod shells collected from sites across Australia's southern shelf.*

Sample	Species	^{14}C Age Date (years before present)
G12-A	*A. cumingi*	5360 ± 52
G39-A	*A. cumingi*	0
G42-A	*A. cumingi*	621 ± 36
G65-A	*A. cumingi*	0
G83-A	*J. jaffensis*	806 ± 36
G85-A	*A. cumingi*	2707 ± 47
G103-A	*A. cumingi*	0
G122-A	*A. cumingi*	1962 ± 46
A77-A	*A. cumingi*	0
P05-A	*A. cumingi*	779 ± 36
P43-A	*A. cumingi*	4362 ± 48
P58-A	*A. cumingi*	600 ± 46
WI-A	*M. flavescens*	0

single specimen. Brachiopods can live to an age of 30 years (Bitner and Cohen 2013) so isotopic variability within a single shell is a result of seasonal to decadal changes in local oceanography. Brachiopods growing in a seasonal upwelling zone should, therefore, record a combination of normal shelf conditions and upwelling conditions over a year and possibly fluctuations in upwelling intensity, or other ecological parameters, that occur over multiple years.

Intrasite variability can be caused by changing environmental conditions over a much longer period, depending on the age of specimens being compared. Sediment production on this cool-water shelf is slow and surficial sediments range from modern to early Holocene in age (James and Bone 2011). Our study, however, uses only shells that show little to no evidence of weathering. A representative suite of these well preserved brachiopods were analyzed for ^{14}C (Table 3) to determine their relative ages. Values from the 13 samples analyzed range from 0 to 5360 years before present (BP), five samples with 0 values are post-bomb; four samples range from 600 to 806 years BP; and four samples range from 1962 to 5360 years BP. Thus, intrasite variability is a record of changing environmental conditions (e.g., upwelling intensity, mixing shelf currents, etc.) that occurred sometime in the latter half of the Holocene, but most commonly within the last 1000 years. For example, Figure 6A shows two specimens at a single site wherein the range in intraspecimen variability is about the same for both shells and is interpreted to be a product of local environmental changes that occurred seasonally or over a few years. Sample 2 is, however, consistently higher in $\delta^{18}O$, resulting in relatively high intrasite variability and suggesting that this site has experienced significant environmental variability sometime within the last few thousand years. This environmental variability does not necessarily suggest a gradually changing climate but might instead represent the subtle differences in environment and circulation from year to year.

The $\delta^{13}C$ of atmospheric and oceanic CO_2 has decreased substantially over the last 200 years (^{13}C Suess effect) due to combustion of isotopically light fossil fuels (Druffel and Benavides 1986; Francey et al. 1999). Therefore, intrasite comparison of living and very recent (< 200 years old) brachiopods with older Holocene brachiopods could reflect this change in $\delta^{13}C$ of atmospheric CO_2. The high variability within individual specimens, however, cannot be attributed to the ^{13}C Suess effect. Furthermore, significant intrasite variance in both oxygen and carbon, rather than $\delta^{13}C$ alone, suggest that local environmental changes are the main source of isotopic variability recorded in southern Australian brachiopods.

Evaluating Other Possible Causes

If such a large intraspecimen, intrasite, and lateral variability were observed in an ancient system of the rock record, the data and estimates of environmental parameters might be deemed unreliable. The observed range in intrasite $\delta^{18}O$ can lead to seawater temperature estimates that vary more than 8°C at a single site—when using the O'Neil et al. (1969) paleotemperature equation, as recalculated by Hays and Grossman (1991) [$T°C = 15.7 - 4.36(\delta^{18}O_{CaCO3} - \delta^{18}O_{water}) + 0.12(\delta^{18}O_{CaCO3} - \delta^{18}O_{water})^2$] and the average southern Australian shelf seawater $\delta^{18}O$ of 0.4‰ (VSMOW) (L.E. Richardson, personal communication 2014). An evaluation of other possible sources of isotopic variability is important for two reasons: to verify that data from this study truly reflect modern environmental conditions, and to determine if such a range in $\Delta^{18}O$ and $\Delta^{13}C$ observed in the rock record could be caused by normal environmental variability. Potential alternative explanations include 1) seafloor diagenetic alteration of brachiopod shells, 2) shells are allochthonous, i.e., they have been transported from their original growth area, and 3) non-equilibrium isotopic ratios via metabolic or kinetic fractionation. Fractionation effects are discussed above and are deemed unlikely to be responsible for the isotopic variability observed in these specimens. Diagenetic alteration is unlikely because all samples are living to mid-Holocene specimens with low-magnesium calcite shells in excellent condition. Transportation of shells might be possible in this high-energy environment but is not likely because all brachiopod species present are either pedically attached to the substrate or semi-infaunal (Richardson and Watson 1975; Richardson 1981, 1987). Transport would result in abrasion and disarticulation of the shells, whereas only living or pristine samples were analyzed in this study. Additionally, pebble-size skeletal grains are not likely to migrate great distances (tens of kilometers) across the nearly flat, shallowly dipping shelf. If shells were to be transported, they would dominantly move downslope. Furthermore, if transport were a factor the high isotopic variability would occur only on deep portions of the shelf, when in fact some of the highest isotopic variability occurs within the upper 50 meters water depth (Fig. 4).

IMPLICATIONS FOR THE ROCK RECORD

The significant range in brachiopod carbon and oxygen isotope values appears to be a result of environmental variability on the southern Australian shelf. Thus, high intraspecimen, intrasite, and lateral variability reflect normal shelf conditions, and this aspect should be considered when evaluating ancient shelf systems. Data with high $\Delta^{18}O$ and $\Delta^{13}C$ values (up to ~ 2‰) should not be discarded because it could reflect normal environmental conditions, nor should a small suite of samples be used to estimate shelf conditions for an entire region. Surficial sediments from the southern Australian shelf range in age from Holocene to modern (James and Bone 2011) and if this "layer" were to be preserved in the rock record, it would represent more than 5 kyr of geologic history. Well preserved brachiopods collected from the same location in this "layer" show isotopic variability of up to ~ 2‰, which can be explained by environmental fluctuations through time, from seasonal variability to changes that occurred over thousands of years.

Zones of upwelling coincide with each area of high isotopic variability, which is why the hypothesized source of intrasite and/or intraspecimen variability is change in ocean temperature and chemistry induced by seasonal upwelling. Other processes may contribute as well, including intense summer heating and evaporation of shallow shelf water and subsequent migration and mixing with other shelf water bodies. This occurs with the GAB plume in the central to east GAB sector (Richardson et al. 2009) and also in the gulfs and shallow areas surrounding Kangaroo Island in the SAS sector (James and Bone 2011). Future work in modern or ancient settings that wish to apply this method should consider all these options as possible sources for variability as well as any others that may apply, such as areas affected by fluvial input, salinity fluctuations, or diagenesis.

Previous work on ancient carbonate shelves and epeiric seas has revealed similar ranges in isotopic variability from brachiopods collected globally (e.g., Popp et al. 1986; Veizer et al. 1986; Grossman et al. 1991, 1993; Wenzel and Joachimski 1996; Mii et al. 1999, 2001). For example, well preserved Carboniferous brachiopods from the midcontinent region of North America record an intraspecimen isotopic variability of 0–1.5‰ and 0–1.6‰ for $\Delta^{13}C$ and $\Delta^{18}O$, respectively (Mii et al. 1999). Multiple brachiopods collected from the same stratigraphic interval reveal an isotopic variability up to about 2‰ for $\Delta^{13}C$ and $\Delta^{18}O$ (Mii et al. 1999). The intraspecimen and intrasite variability of south Australian brachiopods is remarkably similar (Table 1).

Carbonates from the Late Ordovician Mohawkian Sea of eastern Laurentia record a spatial $\delta^{13}C$ variability of 4.5‰, which is attributed to local-scale carbon cycling and seawater ageing in shallow areas with restricted circulation (Holmden et al. 1998; Panchuck et al. 2005, 2006). Panchuck et al. (2006) further suggest that changes in circulation patterns drive secular carbon excursions by changing the rate of exchange of dissolved inorganic carbon between deep basinal waters and shallow marginal waters. Immenhauser et al. (2003) present carbonate $\delta^{18}O$ and $\delta^{13}C$ data from four stratigraphic sections through a late Carboniferous platform and conclude that shelf waters are depleted in $\delta^{18}O$ and $\delta^{13}C$ relative to deep basinal currents principally due to restricted circulation and warmer shelf water temperatures. Rise in sea level results in enhanced circulation with basinal water and an isotopic shift to more positive $\delta^{18}O$ and $\delta^{13}C$ in shelf carbonates (Immenhauser et al. 2003). Seawater ageing in shallow environments with restricted circulation is also found to occur in the modern Florida Bay and Bahama Banks, where $\delta^{13}C$ of dissolved inorganic carbon is depleted up to 4‰ relative to open marine waters (Lloyd 1964; Patterson and Walter 1994).

The $\delta^{13}C$ of dissolved inorganic carbon from the southern Australian shelf water has not yet been analyzed. Results from this study, however, suggest that south Australian shelf currents have limited exchange with open-ocean currents and reflect local environmental controls and possibly shelf water ageing, similar to the modern and ancient shelves described above. Exchange between shelf currents and basinal currents occurs in areas of upwelling on Australia's southern shelf and is recorded as high isotopic variability in brachiopods at individual sites and in individual brachiopod specimens in these areas. Therefore, brachiopod shell chemistry can be used to reconstruct ambient seawater conditions, but on-shelf environments do not necessarily reflect global marine conditions. Moreover, isotopic excursions measured across stratigraphy do not necessarily reflect secular changes in ocean chemistry, but instead may be sourced from local environmental variability and changes in shelf water circulation. Pufahl et al. (2006) evaluated the isotopic composition of brachiopods from the Miocene epeiric sea of the Murray Basin, South Australia, and revealed that $\delta^{18}O$ and $\delta^{13}C$ values largely reflect local to regional conditions but the open-ocean secular record is still discernible. Similarly, Katz et al. (2007) analyzed sediments of the early Mississippian Madison carbonate ramp from the western North American epeiric sea and report $\delta^{13}C$ values with long-term fluctuations that correlate with other global successions; however, the $\delta^{13}C$ of Madison ramp samples have significantly higher maximum values—up to 2‰ greater than in other localities. These greater $\delta^{13}C$ values are interpreted to have been caused by local processes superimposed on the secular seawater $\delta^{13}C$ variations, such as restricted water masses, increased nutrient cycling, and enhanced biological pumping (Katz et al. 2007). Therefore, an understanding of on-shelf conditions is crucial in order to remove "noise" produced by local effects and estimate global ocean chemistry.

CONCLUSIONS

A suite of 407 brachiopods in modern shelf sediments from 220 sites across Australia's southern shelf were analyzed for $\delta^{18}O$ and $\delta^{13}C$. The resulting values reveal that a significant range can occur within an individual specimen ($\Delta^{18}O$ up to 1.3‰ and $\Delta^{13}C$ up to 1.9‰) and at a single site ($\Delta^{18}O$ up to 2.1‰ and $\Delta^{13}C$ up to 1.8‰), which results in substantial lateral variability across the shelf. Areas of intraspecimen variability and areas of intrasite variability are spatially related and are intrinsically linked. Zones of high $\Delta^{18}O$ and $\Delta^{13}C$ coincide with areas of identified seasonal upwelling, which is the hypothesized source of isotopic variability. Intraspecimen variability is an archive of normal shelf conditions and seasonal upwelling that occurred over the life of that specimen (up to 30 years). Intrasite variability can be caused by changing environmental conditions over a much longer period, depending on the age of specimens being compared (up to ~ 5000 years BP). Other possible sources for isotopic variability were evaluated, including diagenesis, shell transport, and fractionation effects during shell growth, but no evidence was found to support these alternatives. Isotopic variability within an individual shell, at a single site, or across a large region is, therefore, a phenomenon caused by natural variability in shelf water conditions. Similar ranges in isotopic variability have been observed in brachiopods from ancient carbonate shelves, which suggest that seasonal and longer-term variability in local environmental conditions are normal occurrences on carbonate shelves. An understanding of these local, on-shelf effects is crucial to estimating global ocean chemistry.

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