



# Carbon isotope ( $\delta^{13}\text{C}$ ) differences between Late Cretaceous ammonites and benthic mollusks from Antarctica



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## ABSTRACT

Ammonites are one of the most common fossils of the Mesozoic, but there is little consensus on their mode of life. Isotopic studies have been used to reconstruct their preferred water temperature from  $\delta^{18}\text{O}$  measurements, but  $\delta^{13}\text{C}$  values have more ambiguous interpretations. Previous studies have recorded population differences in  $\delta^{13}\text{C}$  values between ammonite and benthic organisms without explaining the cause in detail. Here we examine a molluscan community from Seymour Island, Antarctica and find a 4‰ carbon isotope offset between ammonites and other benthic mollusks. The most likely cause of this anomaly is an increased metabolic carbon contribution to ammonite shell material when compared with other mollusks, but we cannot rule out the possibility of a methane seep contribution. Increased respired  $\text{CO}_2$  production could be generated by a more active lifestyle and increased energy demands, which may have increased the susceptibility of ammonites to the end Cretaceous mass extinction.

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## 1. Introduction

Ammonites, biostratigraphically and ecologically important shelled cephalopods, were one of the most notable casualties of the Cretaceous–Paleogene (K–Pg) mass extinction (66 Ma). Their complete and rapid extinction was one of the most important demonstrations of the rapidity of the K–Pg mass extinction event (Marshall and Ward, 1996; Marshall, 1995). While most other major molluscan groups survived the extinction, albeit with some losses, all ammonites went extinct rapidly at the end of the Cretaceous. While evidence for an asteroid impact at the K–Pg boundary remains overwhelming more than three decades after it was first proposed (Alvarez et al., 1980), the specific aspects of this catastrophe responsible for directly killing organisms (Archibald et al., 2010; Schulte et al., 2010), and the potential contributions of other events like Deccan Traps flood volcanism (Mitchell et al., 2012; Tobin et al., 2012, 2014), are still being debated. Any kill mechanism must explain the preferential extinction of ammonites compared to other molluscan groups, and this still unresolved question provides a compelling driver for continued research into their paleoecology.

It is not clear that there are any good modern analogs for ammonites, as the only nektonic or demersal carbonate secreting mollusks today are

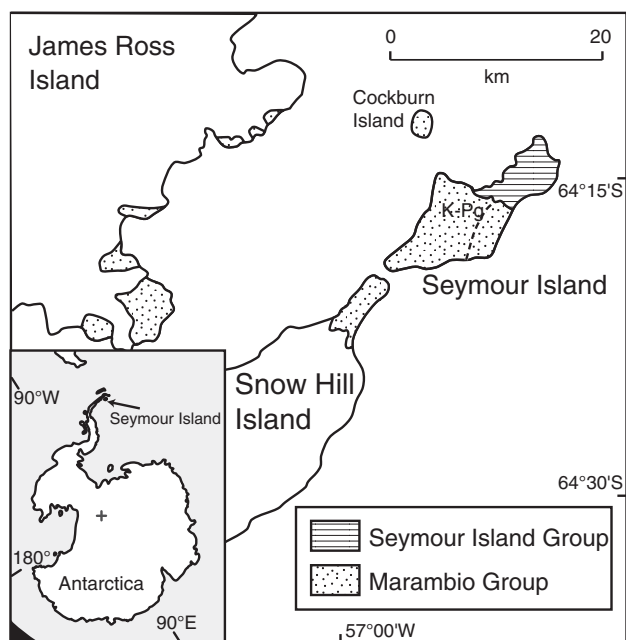
*Sepia*, *Spirula*, and *Nautilus*. Stable isotope and morphological evidence has been used to argue that ammonites lived in relatively shallow waters in a demersal, or nektobenthic, lifestyle (e.g. Moriya et al., 2003; Westermann, 1996) though recent work has argued for more complexity, both taxonomically between ammonite species and ontogenetically (Ritterbush and Bottjer, 2012; Ritterbush et al., 2014). *Nautilus* (Taylor and Ward, 1983) and *Spirula* (Warnke et al., 2010) both prefer deeper water and a more pelagic lifestyle, though they may come to the shallow waters at night to feed. Other morphological evidence also raises questions about *Nautilus* as an ammonite analog (Jacobs and Landman, 1993) as does the internal nature of the *Spirula* and *Sepia* shells.

Analysis of  $\delta^{13}\text{C}$  values from modern *Nautilus* has encountered mixed results; some studies (Crocker et al., 1985; Taylor and Ward, 1983) found no significant changes in  $\delta^{13}\text{C}$  over the lifespan of the organism, while others have recorded a decreasing pattern (Auclair et al., 2004). In both cases  $\delta^{13}\text{C}$  values were at, or very near, equilibrium values expected from seawater. In contrast,  $\delta^{13}\text{C}$  values from modern *Spirula* record  $\delta^{13}\text{C}$  values out of equilibrium with seawater, a phenomenon attributed to the internal nature of their shell, and which may increase the incorporation of respired  $\text{CO}_2$  into their shell (Price et al., 2009). Ontogenetic series for *Spirula* are also inconsistent, showing both increasing and decreasing patterns, sometimes in the same shell (Price et al., 2009; Warnke et al., 2010). *Sepia* also show a ‘vital effect’ on their  $\delta^{13}\text{C}$  values, similar to that in *Spirula*, and probably from the same cause – the internal nature of the shell (Rexfort and Mutterlose, 2006).

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Much of the evidence for lifestyle patterns of ammonites has come from stable isotopic analysis of shell carbonate. In most of these analyses, both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are generated, but most studies focus primarily on the  $\delta^{18}\text{O}$  values as these can generally be used to reconstruct paleotemperature (Kim et al., 2007) with reasonable accuracy. Less well studied are the  $\delta^{13}\text{C}$  values, which have more ambiguous interpretations, and few attempts have been made to explicitly compare and explain the  $\delta^{13}\text{C}$  values of ammonites relative to their contemporary mollusks. Studies that have investigated fossil molluscan populations found that ammonites have lower  $\delta^{13}\text{C}$  values than benthic mollusks, including in the Jurassic of England and Poland (Malchus and Steuber, 2002), the Cretaceous of the United States (Da Silva, 2006; He et al., 2005) and Canadian Western Interior (Forester et al., 1977), the Cretaceous of Australia (Henderson and Price, 2012). Belemnites, another extinct fossil cephalopod group, have also shown a  $\delta^{13}\text{C}$  offset in the same direction (Alberti et al., 2012; Wierzbowski and Joachimski, 2007; Wierzbowski, 2002). Wierzbowski and Joachimski (2007) analyzed a wider variety of taxonomic groups and find that ammonites and belemnites have more negative  $\delta^{13}\text{C}$  values than oysters, but similar  $\delta^{13}\text{C}$  values to trigonid bivalves. In these studies, if the  $\delta^{13}\text{C}$  offset is commented on, it is generally briefly attributed to a vital effect or diagenesis, as most studies are focused on interpretation of the  $\delta^{18}\text{O}$  values for temperature.

Landman et al. (2012) examined a molluscan population from a Campanian aged deposit they convincingly argued is a methane seep environment based on overall morphology and very light  $\delta^{13}\text{C}$  values ( $-40$  to  $-45\text{‰}$ ) of matrix carbonate. Mollusk  $\delta^{13}\text{C}$  values were depleted relative to mollusks not at the seep, a discrepancy they attribute to the incorporation of relatively light methane carbon influencing the dissolved inorganic carbon (DIC) pool around the seep environment. Within the seep samples the  $\delta^{13}\text{C}$  values of ammonites are lower than those of the benthic mollusks (see 6. Conclusion for more). Here we examine another Late Cretaceous (Maastrichtian) molluscan community from Seymour Island, off the Antarctic Peninsula. We examine multiple stratigraphic horizons from two fossil collections and find consistently depleted  $\delta^{13}\text{C}$  values for ammonites when compared with benthic mollusks. We explore several hypotheses, but the most likely explanation is that this phenomenon is a vital effect caused by the incorporation of a significant percentage of respired, or metabolic, carbon into the shell.



**Fig. 1.** Field area map, samples for this study were collected from the uppermost Marambio Group on Seymour Island, which contains the K–Pg boundary. Inset shows location of Seymour Island in relation to Antarctica and the southernmost South America.

## 2. Geologic setting

Seymour Island is located on the northeastern end of the Antarctic Peninsula (Fig. 1), and has continuous sedimentation of Maastrichtian to Danian age, including a Cretaceous–Paleogene (K–Pg) boundary section. The sediments comprise the uppermost Marambio group, and an unconformity separates them from overlying Eocene Seymour Island Group (see Olivero, 2012; Olivero et al., 2007 for more information). All the samples were collected from the López de Bertodano Formation (LBF), which contains the K–Pg interval and is interpreted as continental shelf deposition (Macellari, 1988) during the uplift of the Antarctic Peninsula. Since deposition, the area has seen little change in its paleogeographic location or paleolatitude ( $\sim 62^\circ\text{S}$ ) since deposition (Tobin et al., 2012; Torsvik et al., 2008). Additionally there has been little tectonic influence, with only minor homoclinal tilting ( $5^\circ$ – $10^\circ$ ) and minimal burial history.

The LBF is well exposed during austral summer when not covered in snow, and it is highly fossiliferous, particularly in the uppermost “molluscan units” as defined by Macellari (1988, 1986). Fossils are not only abundant, but are very well preserved, both physically in their three-dimensional structure, but also chemically, in the persistence of primary mineralogy, principally aragonite, with a small number of taxa precipitating calcite. Two similar but separate collections of fossils were analyzed to obtain  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. The first group (hereafter: ‘UW collection’) was collected by the authors and assisting field workers during field seasons between 2008 and 2011. The second group (hereafter: ‘PRI collection’) was collected by expeditions lead by Zinsmeister (e.g. Zinsmeister, 1998; Zinsmeister et al., 1989) over many field seasons during the 1980s and 1990s, and is currently housed at the Paleontological Research Institute (PRI). We sampled an analyzed sample from the PRI collection in 2012 and 2013.

The UW collection was collected for the purposes of generating an isotopic record across the K–Pg boundary (Tobin et al., 2012) and as such was collected with attention to stratigraphic coverage, but for logistical reasons, we did not often collect large numbers of specimens at any stratigraphic level. The  $\delta^{18}\text{O}$  values for this collection were explored in Tobin et al. (2012) to reconstruct paleotemperature, but the  $\delta^{13}\text{C}$  values were not, and required further investigation. The PRI collection has stratigraphic information, though with larger uncertainties than the UW collection (Zinsmeister, 2001), but is much larger in terms of numbers, and has many localities with a variety of taxa represented. These collections cannot be placed in a 1:1 stratigraphic correspondence with each other, as the K–Pg boundary horizon is the only suitable correlative bed. The collections must be treated separately, but that is not a major drawback of this study.

## 3. Methods

Sample processing for the collections differed due to restrictions necessary for the curated PRI museum collection. Fossil shells from the UW collection were cut, polished, and drilled using a computer controlled Merchantek micromill to generate powder for isotopic analysis. When drilling, a drill bit substantially finer than the shell thickness was employed, and sampling goals aimed to average over seasonal variation. This process allowed access to the interior of the fossil shell, which is less likely to experience diagenetic alteration. Samples analyzed for the UW collection were also checked for diagenesis using cold cathodoluminescence microscopy, trace element concentrations, and X-Ray diffraction to assess primary mineralogy (see further details of sampling and diagenetic testing in Tobin et al., 2012). Some of the first samples to be analyzed from the UW collection were prepared using tool tip made of carbide. While there was no variance in these isotopic values with relation to  $\delta^{18}\text{O}$ , these samples were often significant outliers in  $\delta^{13}\text{C}$  space, and all analyses made using this tool were removed from this analysis. Fossils from the PRI collection could not be subjected to the same destructive cutting process, so small ( $<1\text{ cm}^2$ )

pieces of shell were either pried off the shell for later powdering, or spot-drilled at PRI using a Dremel tool to powder the shell directly from the fossil. In both cases shells were not sampled near cracks or near any location where iridescent aragonite was not observed, and before drilling the outermost layer of shell was abraded and removed to avoid any potential surficial diagenetic effects.

Sample powders were then weighed and analyzed along with internal lab standards calibrated to NBS-18 and NBS-19 for  $\delta^{18}\text{O}$  and NBS-19 and LSVEC for  $\delta^{13}\text{C}$ . Samples were reacted at 70 °C with anhydrous phosphoric acid at 70 °C in a Kiel III Carbonate Device attached to Delta Plus isotope ratio mass spectrometer at the IsoLab at the University of Washington. Any sample powder generated with a drill was corrected for time sensitive isotopic reset in the Kiel Device (Tobin et al., 2011). In most cases multiple analyses were completed on each powder aliquot and averaged together for mean shell  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values.

## 4. Results

### 4.1. Diagenesis

The PRI collection was unable to be tested extensively for diagenesis, though every effort was made to avoid any fossils with signs of potential diagenesis (see 3. Methods). However, previous work on the UW collection demonstrated that these measures were sufficient to generate a reliable data set (Tobin et al., 2012). Diagenesis is more likely to affect the  $\delta^{18}\text{O}$  composition of carbonate material (Banner and Hanson, 1990), and here we demonstrate the PRI collection data set records essentially the same stratigraphic  $\delta^{18}\text{O}$  pattern as the UW collection (Fig. 2) though the two records can only be reliably correlated using the K–Pg boundary horizon. We conclude that given the correspondence of the  $\delta^{18}\text{O}$  records, it is unlikely that the  $\delta^{13}\text{C}$  values of the PRI collection fossils has been altered. Similarly, there is no strong correlation between individual shell  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in either the entire PRI or UW data set, or when broken down into ammonite or benthic data sets ( $R^2$  values

between 0.03 and 0.22), which adds circumstantial evidence to support a lack of diagenesis, where diagenesis would be implied by covariance between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. Tobin et al. (2012) found that many samples exceeded one or more trace element threshold values, but that the exclusion of these samples did not affect overall  $\delta^{18}\text{O}$  patterns. The same is true in  $\delta^{13}\text{C}$  values, as all observations described later are true for a data subset where all trace element exclusions are applied. Additionally, no co-variance is found between any measured trace element and  $\delta^{13}\text{C}$  value.

### 4.2. Overall $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ comparisons

In both collections there is an overall  $\delta^{13}\text{C}$  offset between the ammonites and other benthic mollusks, while there is no offset in  $\delta^{18}\text{O}$  values (Fig. 2). The PRI collection has a lower average ammonite  $\delta^{13}\text{C}$  ( $-3.6\text{‰}$ ,  $n = 23$ ,  $s.d. = 4.1\text{‰}$ ) than average benthic mollusk  $\delta^{13}\text{C}$  values ( $1.4\text{‰}$ ,  $n = 126$ ,  $s.d. = 1.9\text{‰}$ ) for the whole data set; the UW collection records a smaller offset in mean values (average ammonite  $\delta^{13}\text{C}$  value =  $-1.1\text{‰}$ ,  $n = 27$ ,  $s.d. = 2.5\text{‰}$ , average benthic  $\delta^{13}\text{C}$  value =  $1.8\text{‰}$ ,  $n = 72$ ,  $s.d. = 1.8\text{‰}$ ). In both cases, the mean value of ammonite and benthic groups are statistically separate using Student's *t*-test (two tailed, unequal variance) with *p*-values of  $6.0 \times 10^{-6}$  and  $2.9 \times 10^{-6}$  for the PRI and UW collections respectively. Average  $\delta^{18}\text{O}$  values are not significantly different than each other; for the PRI collection average  $\delta^{18}\text{O}$  values were  $0.7\text{‰}$  ( $s.d. = 0.7\text{‰}$ ) and  $0.9\text{‰}$  ( $s.d. = 0.6\text{‰}$ ) for ammonites and benthic mollusks respectively, and  $0.8\text{‰}$  ( $s.d. = 0.6\text{‰}$ ) and  $1.0\text{‰}$  ( $s.d. = 0.5\text{‰}$ ) for the UW collection.

### 4.3. Stratigraphic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ comparisons

The differences in  $\delta^{13}\text{C}$  values are most apparent when plotted in their stratigraphic context, though differences are apparent in  $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$  crossplots (Fig. 3). Because ocean water  $\delta^{13}\text{C}$  values (and local environmental factors) can change through time, averaging  $\delta^{13}\text{C}$  values across a long stratigraphic range may incorporate these changes as “noise” in an attempt to discern  $\delta^{13}\text{C}$  differences between ammonites and their contemporary benthic mollusks. In an effort to make the stratigraphic patterns clear,  $\delta^{13}\text{C}$  values were plotted in their stratigraphic context (Fig. 4—top), and horizons from which both ammonite and benthic fauna were recovered are separated out and plotted (Fig. 4—bottom). A horizon was defined in the PRI collection as a single collecting locality. In the UW collection, samples were collected along a stratigraphic section with their stratigraphic position given in meters. Fossils were considered to be in a single horizon when they were within one meter of each other stratigraphically. Average ammonite and benthic molluscan  $\delta^{13}\text{C}$  values were calculated at each horizon, and their differences (defined here as  $\Delta\delta^{13}\text{C}_{\text{ben} - \text{amm}}$ ) are plotted in Fig. 4 and Table 1. In every case, the ammonite mean  $\delta^{13}\text{C}$  value is lower than the mean benthic  $\delta^{13}\text{C}$  values, though there is substantial variation in magnitude. At some horizons, there is only one representative ammonite or benthic mollusk, which is reflected in Fig. 4 by the point overlying the benthic or nektonic mean. The average  $\Delta\delta^{13}\text{C}_{\text{ben} - \text{amm}}$  for the selected horizons is  $4.7\text{‰}$  for the PRI collection,  $2.7\text{‰}$  for the UW collection and  $3.8\text{‰}$  for the combined data set. These values are similar to those obtained by averaging all the available data.

Separating the  $\delta^{13}\text{C}$  values for the ammonites and benthic mollusks also reveals the previously unrecognized  $\delta^{13}\text{C}$  anomaly at the K–Pg boundary. A negative  $\sim 3\text{‰}$  excursion has long been observed globally at the boundary (e.g. Molina et al., 2006; Schulte et al., 2010). This pattern is not observed in our data if ammonite  $\delta^{13}\text{C}$  values are included, as they bias average Cretaceous  $\delta^{13}\text{C}$  values in a negative direction. The boundary negative excursion is disguised by their disappearance. Fig. 5 shows the benthic  $\delta^{13}\text{C}$  record for the PRI collection with a seven point running average showing a negative  $3\text{‰}$  excursion. The running average was calculated using horizon averages of benthic values, weighted by the number of samples at each horizon; excursion

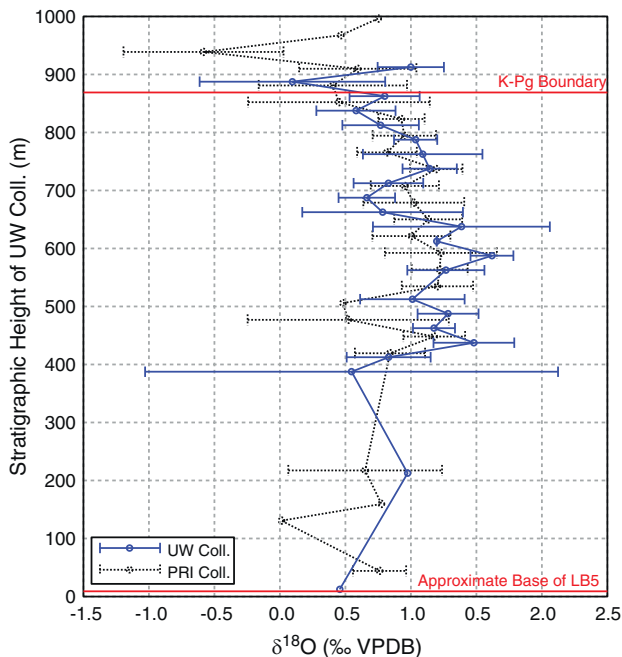


Fig. 2. Oxygen isotopic ( $\delta^{18}\text{O}$ ) records for the UW and PRI sample collections. The data are plotted in the UW collection stratigraphic framework, and the PRI collection is correlated and overlain by being linearly stretched, using the K–Pg boundary and the base of informal unit 5 from Macellari (1988). Apart from the two tie points, the stratigraphic relationship between the two collections has unquantifiable uncertainty. Overall good correspondence suggests that there are no diagenetic differences between the two collections.

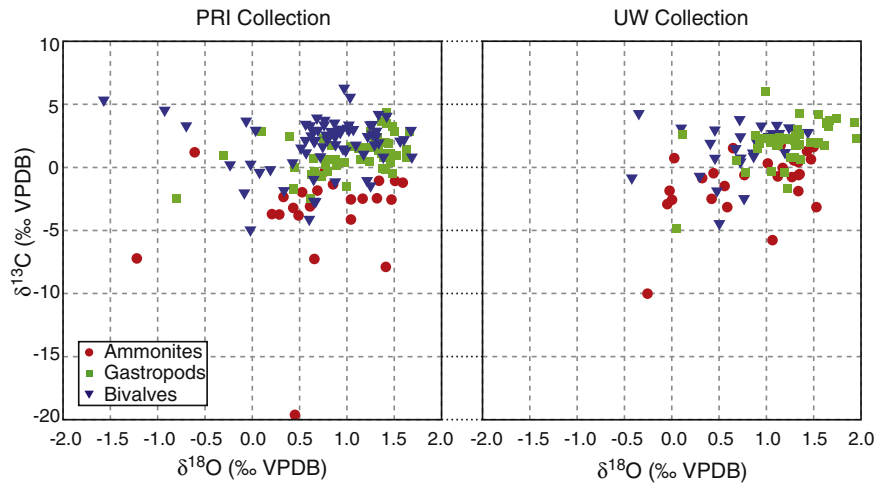


Fig. 3. Crossplots of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for both the UW and PRI collections, separated by taxonomic group. No significant or strong correlations were found between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for any subset or the total data set.

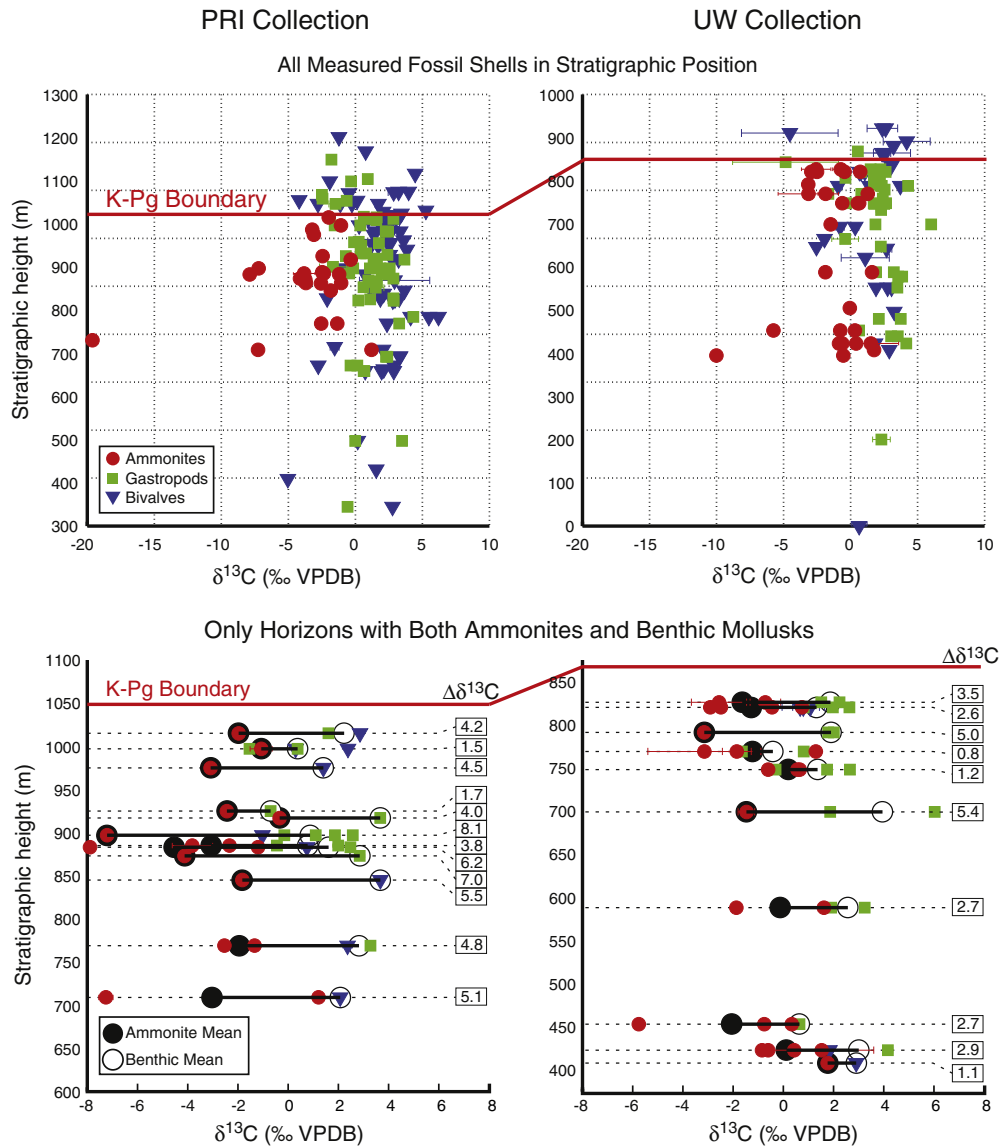


Fig. 4. (Top) Carbon isotopic ( $\delta^{13}\text{C}$ ) records in stratigraphic context, separated by taxonomic group, for both UW and PRI collections. Average ammonite and benthic populations for each collection are statistically distinct. (Bottom) Average  $\delta^{13}\text{C}$  values for horizons (see text for definition) with both ammonites and benthic mollusks present. Every horizon has lower  $\delta^{13}\text{C}$  values for ammonites than benthic mollusks, and the difference is indicated by  $\Delta\delta^{13}\text{C}$ .

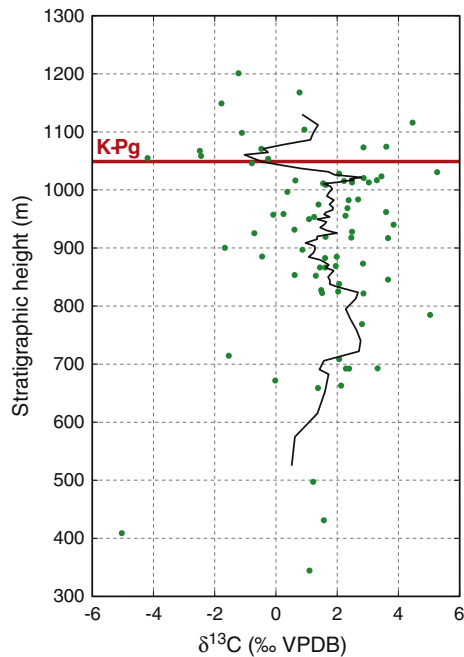


**Table 1**  
Summary of horizon data used in Fig. 4 (bottom) and calculated water  $\delta^{13}\text{C}_{\text{DIC}}$  and ammonite metabolic carbon contribution to  $\delta^{13}\text{C}_{\text{shell}}$  values. Values for both were calculated for cases when bivalves incorporated either 10% or 0% respired  $\text{CO}_2$ .

	Amm. $\delta^{13}\text{C}$ (‰)	n	Ben. $\delta^{13}\text{C}$ (‰)	n	$\Delta\delta^{13}\text{C}_{\text{ben} - \text{amm}}$ (‰)	Strat (m)	Benthic R = 10%		Benthic R = 0%	
							DIC $\delta^{13}\text{C}$ (‰)	Amm. $C_{\text{meta}}$ (%)	DIC $\delta^{13}\text{C}$ (‰)	Amm. $C_{\text{meta}}$ (%)
PRI collection individual horizons	−3.0	2	2.1	1	5.1	709	1.4	39	−0.6	31
	−1.9	2	2.8	2	4.8	769	2.2	36	0.1	28
	−1.8	1	3.7	1	5.5	845	3.2	38	1.0	31
	−4.1	1	2.8	1	7.0	873	2.3	47	0.1	41
	−4.5	4	1.6	2	6.2	883	0.9	45	−1.1	39
	−3.1	1	0.8	2	3.8	885	0.0	34	−1.9	26
	−7.2	1	0.9	4	8.1	897	0.1	58	−1.8	53
	−0.3	1	3.7	1	4.0	917	3.2	31	1.0	22
	−2.4	1	−0.7	1	1.7	925	−1.7	23	−3.4	13
	−3.1	1	1.4	1	4.5	975	0.7	37	−1.3	29
	−1.1	1	0.4	4	1.5	997	−0.5	20	−2.3	10
	−2.0	1	2.2	2	4.2	1015	1.6	34	−0.5	25
Average =	−2.9	17	1.8	22	4.7	–	1.1	36.8	−0.9	28.9
UW collection individual horizons	1.8	1	2.9	1	1.1	408	2.3	17	0.2	7
	0.1	4	3.0	2	2.9	423	2.4	26	0.3	17
	−2.1	3	0.6	1	2.7	453	−0.2	27	−2.1	18
	−0.1	2	2.6	2	2.7	588	2.0	25	−0.1	16
	−1.5	1	3.9	2	5.4	699	3.5	37	1.2	30
	0.2	2	1.4	3	1.2	748	0.6	18	−1.3	7
	−1.2	3	−0.4	2	0.8	769	−1.4	16	−3.1	6
	−3.0	1	1.9	2	4.9	791	1.3	38	−0.8	30
	−1.3	4	1.3	5	2.6	820	0.5	26	−1.4	16
	−0.8	2	2.1	2	2.9	826	1.4	27	−0.6	18
Average =	−0.8	23	1.9	22	2.7	–	1.2	25.8	−0.8	16.5
UW & PRI horizons =	−1.9	40	1.9	44	3.8	–	1.2	31.8	−0.8	23.2

presence is insensitive to the weighting or the length of the running average (anywhere from 3 to 15 point running averages reveal a  $>2\%$  excursion). A (one-tailed, unequal variance) student's t-test comparing all data from the interval above the boundary ( $\delta^{13}\text{C} = -0.1\%$ ) and all data in the well-sampled interval (above 800 m) below the boundary ( $\delta^{13}\text{C} = 1.7\%$ ) suggest that the mean of two intervals is significantly

different ( $p < 0.001$ ). Standard models of this carbon isotope anomaly (see Alegret et al., 2012) interpret the excursion as abrupt with a gradual return to pre-boundary levels over the next 500 kyr. The Danian interval sampled here represents less than 500 kyr (see Tobin et al., 2012 for age model) and a t-test is appropriate (abrupt change creates two data populations) and conservative (Danian fossils incorporate return to background  $\delta^{13}\text{C}$  values into the average) as a testing tool.



**Fig. 5.** Seven point running average (black line) of benthic  $\delta^{13}\text{C}$  values averaged at the horizon level (green circles) revealing carbon isotope excursion ( $-3\%$ ) at the K-Pg boundary that is not present when ammonites and benthic mollusks are included due to depleted ammonite  $\delta^{13}\text{C}$  values present only below the boundary.  $\delta^{13}\text{C}$  values above the boundary are statistically different than those below the boundary (see text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 5. Discussion

The stable isotopic data show that ammonites have comparable  $\delta^{18}\text{O}$  values but lower  $\delta^{13}\text{C}$  values than benthic mollusks. With similar  $\delta^{18}\text{O}$  values it is most likely that these organisms are living in water of similar temperature, if not living in precisely the same environment. Three hypotheses, outlined below, are capable of explaining this offset under the assumption that mollusks secrete their shell under equilibrium conditions. Two are based on different living environments, specifically ammonites exploring  $\delta^{13}\text{C}$  – water-depth gradients or methane seep localities, while the third involves the incorporation of metabolic, or respired,  $\text{CO}_2$  into the extra-palial fluid (EPF) used to generate shell material. Kinetic isotopic effects could plausibly explain differences in  $\Delta\delta^{13}\text{C}_{\text{ben} - \text{amm}}$ , but would usually influence  $\delta^{18}\text{O}$  values as well, which is not observed in our data sets (McConnaughey, 1989a,b). Most mollusks are thought to precipitate shell in equilibrium with surrounding water, though it may be more accurate to say they secrete their shell in equilibrium with the EPF, which may be significantly altered from seawater by respired  $\text{CO}_2$  (Gillikin et al., 2007). It is unlikely that the lower  $\delta^{13}\text{C}$  values are a consequence of diagenesis, as the  $\delta^{18}\text{O}$  values are much more prone to alteration due to the relative amounts of carbon and oxygen in diagenetic fluids (Banner and Hanson, 1990).

### 5.1. Environmental differences

In the modern ocean there are vertical gradients in dissolved inorganic carbon (DIC)  $\delta^{13}\text{C}$  values where the surface can range up to 3‰ higher than at ~500 m depth, though the magnitude of the difference is more commonly less than 2‰ for the last million years (Hodell et al., 2003). Given that the average  $\Delta\delta^{13}\text{C}_{\text{ben} - \text{amm}}$  observed was

3.7‰, it is possible that a greater-than-modern  $\delta^{13}\text{C}_{\text{DIC}}$  gradient existed during the Late Cretaceous in this specific location, but foraminiferal differences in the South Atlantic for the latest Cretaceous record a 2‰ maximum carbon isotope gradient (D'Hondt, 2005). The western interior of North America may have had a higher  $\delta^{13}\text{C}_{\text{DIC}}$  gradient of 3‰ (Fisher and Arthur, 2002) but is likely to have been more stratified. Higher gradients may still exist, and have been recorded in the past, including at the Permo-Triassic boundary (Song et al., 2013). Given the range of  $\Delta\delta^{13}\text{C}_{\text{ben-amm}}$  values, some of the smaller differences could reasonably be explained by a lower  $\delta^{13}\text{C}_{\text{DIC}}$  values in the ammonite habitat, but the larger differences present a significant challenge to this hypothesis. Additionally, we do not see higher  $\delta^{18}\text{O}_{\text{shell}}$  values in ammonites that would reflect them living in a cooler, deeper environment. In the interest of completeness, it is theoretically possible that ammonites could be living in brackish water heavily influenced by terrestrial runoff, but there is no reliable evidence to date of ammonites living in anything but truly marine environments.

## 5.2. Metabolic $\text{CO}_2$

Modern mollusks have occasionally been recorded as incorporating significant amounts of depleted carbon in the form of metabolic  $\text{CO}_2$  into their EPF, where it mixes with the DIC pool of the EPF reducing the overall  $\delta^{13}\text{C}_{\text{shell}}$  value. This effect may occur in most marine mollusks, but if so, it is likely a small contribution, usually less than ten percent (McConnaughey and Gillikin, 2008). There are often fluid pathways connecting the EPF with ambient water, reducing the impact of respired  $\text{CO}_2$ , but in some cases it appears water, and consequently DIC, exchange across these pathways can be reduced or the relative metabolic rate increased (Gillikin et al., 2005, 2009). In this situation the percentage of respired  $\text{CO}_2$  contributing to the DIC pool can grow substantially larger than 10%, allowing the low  $\delta^{13}\text{C}$  value of respired  $\text{CO}_2$  to significantly reduce  $\delta^{13}\text{C}_{\text{DIC}}$  of the EPF, and consequently the shell material precipitated from it.

If we assume that the high  $\Delta\delta^{13}\text{C}_{\text{ben-amm}}$  is a consequence of respired  $\text{CO}_2$  contribution, it is straightforward to model the percentage contribution of respired  $\text{CO}_2$  ( $C_{\text{meta}}$ ) if the  $\delta^{13}\text{C}_{\text{DIC}}$  value of ambient seawater is known. A reasonable assumption is to use the  $\delta^{13}\text{C}_{\text{shell}}$  of bivalves and gastropods as a proxy for the oceanic  $\delta^{13}\text{C}_{\text{DIC}}$  value, either by assuming there is no respired  $\text{CO}_2$  contribution, or assuming that there is an average 10% contribution of respired  $\text{CO}_2$  as McConnaughey and Gillikin (2008) demonstrate may be common for mollusks. Eq. (1) below (McConnaughey and Gillikin, 2008; McConnaughey et al., 1997), describes the relationship between these components:

$$C_{\text{metabolic}} = \frac{\delta^{13}\text{C}_{\text{shell}} - \varepsilon_{\text{aragonite}} - \delta^{13}\text{C}_{\text{DIC}}}{\delta^{13}\text{C}_{\text{metabolic}} - \delta^{13}\text{C}_{\text{DIC}}} \quad (1)$$

where  $\varepsilon_{\text{aragonite}}$  is the  $\delta^{13}\text{C}$  fractionation between DIC and aragonite (+2.7‰, Romanek et al., 1992). The value of  $\delta^{13}\text{C}_{\text{metabolic}}$  in the benthic mollusks can be estimated by examining modern examples, usually between -18‰ and -20‰ (e.g. Gillikin et al., 2007). Modern *Nautilus*, a potential analog for ammonites, has been recorded with a similar value, -17 ± 2‰ (Crocker et al., 1985). Given these values for benthic mollusks, we can solve for the  $\delta^{13}\text{C}_{\text{DIC}}$  value, rearranging Eq. (1) to Eq. (2):

$$\delta^{13}\text{C}_{\text{DIC}} = \frac{\delta^{13}\text{C}_{\text{shell}} - \varepsilon_{\text{aragonite}} - (C_{\text{metabolic}} \times \delta^{13}\text{C}_{\text{metabolic}})}{1 - C_{\text{metabolic}}} \quad (2)$$

When  $C_{\text{meta}}$  is equal to 0, Eq. (1) simplifies to  $\delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{shell}} - \varepsilon_{\text{aragonite}}$ . Estimated  $\delta^{13}\text{C}_{\text{DIC}}$  values using this method are recorded in Table 1, for both benthic  $C_{\text{meta}} = 0\%$  and 10% cases. This  $\delta^{13}\text{C}_{\text{DIC}}$  value can be used with Eq. (1) for ammonites to determine the metabolic carbon contribution necessary to generate the measured  $\Delta\delta^{13}\text{C}_{\text{ben-amm}}$  at

any stratigraphic horizon. Cases where  $C_{\text{meta}} = 0\%$ , instead of 10%, for benthic organisms produce lower estimates of  $C_{\text{meta}}$  for ammonites.

Calculated values of  $C_{\text{meta}}$  for ammonites were variable when values for individual horizons were examined (~10–50%, see Table 1), but averages were between 17% and 37% for the two collections. Using the averages for all data in both collections ammonite  $C_{\text{meta}}$  was calculated as between 24% and 33% for benthic  $C_{\text{meta}}$  values ranging from 0 to 10%. All of these ammonite  $C_{\text{meta}}$  values are within published ranges for vital effects in marine mollusks, suggesting that the contribution of respired carbon to ammonite shell material is a plausible explanation for the discrepancy between ammonites and benthic mollusks. Only two fossil samples had  $\delta^{13}\text{C}$  values that would necessitate  $C_{\text{meta}}$  values greater than 50%, we attribute these values as likely due to diagenetic alteration given they are in the less-well-tested PRI collection, though they could also be indicative of methane seep contribution (see Section 5.3).

A potential modern analog, *Nautilus*, does not show a significant difference between their  $\delta^{13}\text{C}_{\text{shell}}$  values and that of other benthic organisms (Crocker et al., 1985; Taylor and Ward, 1983; Zakharov et al., 2006). As described above, modern benthic mollusks have, in some cases, been shown to display substantially negative  $\delta^{13}\text{C}_{\text{shell}}$  values that are attributed to higher  $C_{\text{meta}}$  contributions. Some modern bivalves have shown a dependence of  $\delta^{13}\text{C}_{\text{shell}}$  value on body size or age (Lorrain et al., 2004; Gillikin et al., 2007, 2009) which can be explained by some combination of an increased production of metabolic carbon from increased tissue volume and a decrease in mixing between EPF and ambient ocean water. It is possible that ammonites generate greater amounts of respired  $\text{CO}_2$  due to increased metabolic activity, possibly due to an active swimming and feeding lifestyle when compared with benthic mollusks. Due to the morphology and sampling restrictions on the ammonites, samples were generally obtained from later in life positions on the shells, in contrast to fossil bivalves, which were sampled toward the earliest life stages (near the umbo). This potential age difference, and the generally larger ammonite body size, could also explain the higher  $C_{\text{meta}}$  values inferred from the lower  $\delta^{13}\text{C}_{\text{shell}}$  values. However, ontogenetic stable isotope studies of ammonites have generally not shown decreasing patterns of  $\delta^{13}\text{C}_{\text{shell}}$  values, and in some cases record an increase in  $\delta^{13}\text{C}_{\text{shell}}$  values (Fatherree et al., 1998; Lukeneder et al., 2010).

## 5.3. Methane seep influence

Cold methane seeps bring depleted ( $\delta^{13}\text{C}$ ) organic carbon to the ocean floor, which can influence the local DIC pool around the seep. This negative  $\delta^{13}\text{C}$  value source could plausibly explain a depleted ammonite  $\delta^{13}\text{C}_{\text{shell}}$  values. Landman et al. (2012) observed that ammonite shells have been found in direct association with methane seep environments. Geologic and paleobiological data both support their interpretation of that environment as a cold methane seep, as does the depleted carbon signal from the inorganic carbonates. Lower  $\delta^{13}\text{C}_{\text{shell}}$  values for the seep associated ammonites, when compared with nearby non-seep ammonites could be explained by the seep ammonites actively participating in the chemoautotrophically driven ecosystem. The range of ammonite  $\delta^{13}\text{C}_{\text{shell}}$  values observed in our study is within the upper range of those observed for seep ammonites (-13.7‰ to 0.7‰), but also in lower range of the non-seep ammonites (-1.8‰ to 3.4‰) from Landman et al. (2012). Many of our ammonite samples are more depleted than the non-seep ammonite range from Landman et al. (2012).

On Seymour Island specifically, where all of the measured samples were collected, there is little clear evidence for methane seeps in outcrop, but recent work (Little et al., 2015) provides geochemical evidence that hydrocarbon seeps may be present in at least one place on Seymour Island, though toward the bottom of our section (~400 m in the UW collection). On Snow Hill Island (Fig. 1), bivalves commonly associated with methane seeps have been found in association with well cemented mounds that are typical of preserved methane seep environments. The sediments on Snow Hill Island are stratigraphically equivalent to, or

slightly below, the lowest deposits on Seymour Island, and further demonstrate the potential of cold methane seep production in this area (Little et al., 2015). While methane seeps could have been present in the upper part of the LBF on Seymour Island, there is no geologic evidence that the fossils were preserved in such an environment.

Slight decreases in  $\delta^{13}\text{C}_{\text{shell}}$  values have been observed in modern benthic mollusks (mussels) living exclusively at methane seep environments (Paull et al., 1989). Despite living on the seep itself, and feeding on highly depleted organic matter, the  $\delta^{13}\text{C}_{\text{shell}}$  was only marginally depleted, ranging from -3‰ to -8‰. In contrast, their organic tissues were strongly influenced by the methane seep organic carbon, as almost all sampled tissues were below -70‰. The small effect on the shell isotopic values is likely because the local DIC pool is only marginally influenced by the exchange with the depleted carbon, and dominated by more typical ocean DIC values.

The range of  $\delta^{13}\text{C}$  values observed in these modern bivalves (Paull et al., 1989) is similar to that observed in the Seymour Island ammonites, and could be a potential explanation for the observed  $\Delta\delta^{13}\text{C}_{\text{ben-amm}}$ . For ammonites to preserve depleted  $\delta^{13}\text{C}_{\text{shell}}$  value, but similar  $\delta^{18}\text{O}_{\text{shell}}$  values, they must live in water of similar temperature to the bivalves with which they were preserved, but with different  $\delta^{13}\text{C}_{\text{DIC}}$  values, assuming no metabolic carbon contribution. In this scenario, ammonites could be moving between the depositional area where benthic mollusks are found and a methane seep environment, but spending a substantial portion of their life cycle at the methane seep, as their  $\delta^{13}\text{C}_{\text{shell}}$  values are similar to mollusks living their entire life on the seep. This lifestyle could reflect a feeding preference for methane seeps, but a need to leave for more oxygenated waters. Alternatively, the ammonites could live exclusively at the methane seep, but their empty shells could be transported after their death, leading to their deposition with the benthic mollusks. In either case, large transport distances, either laterally or vertically in the water column, would be unlikely due to the good correspondence in water temperature ( $\delta^{18}\text{O}$ ) with benthic mollusks and the size of the ammonite shells (Wani et al., 2005).

## 6. Conclusion

Ammonites from Seymour Island show a significant offset in  $\delta^{13}\text{C}_{\text{shell}}$  values when compared with benthic mollusks. Comparable  $\delta^{18}\text{O}_{\text{shell}}$  values also suggest a metabolic carbon contribution is the most parsimonious interpretation. We believe that an elevated  $C_{\text{meta}}$  can, at least partially, explain the results from Landman et al. (2012). We agree that the organisms in their study were likely living in a methane seep environment, but there is also a recognizable  $\delta^{13}\text{C}$  offset between their benthic mollusks and ammonites collected from the seep environment. If the one significant outlier from the ammonite and benthic groups is removed, the populations also have means with statistically significant differences: -3.5‰ (n = 21, s.d. = 2.2‰) and -1.2‰ (n = 6, s.d. 1.1‰) for ammonites and benthic mollusks respectively (Students t-test p-value = 0.003). This signal could be due to more mobile ammonites following the methane seep production more closely, or due to differences in metabolic carbon contribution. As ammonites at seeps appear more negative than benthic mollusks at the same seeps, our results could be explained if Seymour Island was dominated by diffuse methane seepage. Ultimately we cannot rule out that possibility as seeps appear to be present in the lower part of the section (Little et al., 2015). Given that we see currently see no evidence for seeps in the upper part of the section, and that many studies analyzing both ammonites and benthic mollusks also find a notable  $\Delta\delta^{13}\text{C}_{\text{ben-amm}}$  (Malchus and Steuber, 2002; Da Silva, 2006; He et al., 2005; Forester et al., 1977; Henderson and Price, 2012), we believe the most likely cause of this offset is the contribution of metabolic carbon. It would be unlikely, though not impossible, that all of these locations were in unrecognized methane seep environments, but further testing is certainly warranted.

Proposed modern analogs for ammonites are all imperfect, but studies of their isotopic values may still be informative. Modern *Spirula* have

been shown to have an increased metabolic carbon contribution to their shell material despite their small size (Price et al., 2009) as have *Sepia* (Rexfort and Mutterlose, 2006) and possibly fossil belemnites (Wierzbowski, 2002). Their internal shell may slow or reduce the connection between the EPF and the sea water, which one would predict to increase  $C_{\text{meta}}$ . It is unlikely that the shell of ammonites was internal, given the complex shell ornamentation on many species, and lack of fossil evidence, though ammonite soft tissue preservation is very rare. More plausibly, many ammonite species have been interpreted as active swimmers (see Ritterbush et al., 2014 for a review), and an active swimming and feeding lifestyle could substantially increase their metabolic rate and amount of respired  $\text{CO}_2$  produced. This signal would be expected to be recorded as more negative  $\delta^{13}\text{C}$  values in the shell material unless the exchange rate between EPF and ambient sea water was increased. With the exception of a few examples of *Diplomoceras*, ammonites found on Seymour Island are relatively compressed, smooth, planaspiral forms that are more hydrodynamic and more likely to be active swimmers (Ritterbush and Bottjer, 2012; Westermann, 1996). Higher energy demands could increase the susceptibility of adult ammonites to a major event like the end Cretaceous bolide impact when compared with the low energy demands of *Nautilus* (Boutlier et al., 1996). This affect would compound the vulnerability of ammonites planktonic egg forms compared with the benthic embryonic stage of *Nautilus* (Ward, 1996). A better understanding of this  $\delta^{13}\text{C}$  anomaly could help contribute to our understanding of ammonite lifestyle, and possibly their susceptibility to the end Cretaceous mass extinction.

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## Appendix A. Supplementary data

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