



High benthic methane flux in low sulfate oceans: Evidence from carbon isotopes in Late Cretaceous Antarctic bivalves

Joanna L.O. Hall^{a,*}, Robert J. Newton^a, James D. Witts^{a,1}, Jane E. Francis^b,
Stephen J. Hunter^a, Robert A. Jamieson^a, Elizabeth M. Harper^c, J. Alistair Crame^b,
Alan M. Haywood^a

^a School of Earth and Environment, University of Leeds, West Yorkshire, LS2 9JT, United Kingdom

^b British Antarctic Survey, Madingley Road, Cambridge, CB3 0ET, United Kingdom

^c Department of Earth Sciences, University of Cambridge, Downing Site, Cambridge, CB2 3EQ, United Kingdom

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ABSTRACT

The shell material of marine benthic bivalves provides a sensitive archive of water chemistry immediately above the sediment–water interface, which in turn is affected by sedimentary geochemistry and redox reactions. Sulfate has a major controlling effect on sedimentary carbon cycling, particularly the processes of methane production and oxidation, with lower concentrations of sulfate likely resulting in an increase in sedimentary methane production. Whilst it is accepted that ocean sulfate varied markedly across the Phanerozoic, evidence of changes in methane production in sediments has so far been lacking. There is potential for the oxidation products of sedimentary methane to be preserved and detected in marine fossils. Here we present the results of high resolution carbonate isotope records from two taxa of well-preserved shallow-infaunal bivalve (*Lahillia* and *Cucullaea*) collected from the marine shelf succession across the Cretaceous–Paleogene (K–Pg) boundary in Seymour Island, Antarctica. The succession has pre-existing subtle indications of more abundant methane, and the time period is characterized by much lower marine sulfate concentrations than modern.

These shell carbonate–carbon isotope records vary widely: at one extreme, shells have typical average values and small ranges compatible with a contemporaneous marine dissolved inorganic carbon (DIC) source and modern-style sedimentary carbon cycling. At the other, the shells have large-amplitude annual cycles of carbon isotopic variability of up to 23.8‰ within a single year of growth and shell carbonate $\delta^{13}\text{C}$ compositions as negative as -34‰ . Shells with these increased ranges and unusually negative values are found at discrete intervals and across both bivalve taxa. The contribution of methane required to explain the most negative carbonate–carbon isotopic values in the bivalve shells is extremely high (between 30 to 85% of bottom-water DIC based on mass balance calculations). Records of organic–carbon isotopes from the same succession remained between -26.1 and -21.7‰ throughout, suggesting that methane influence was restricted to bottom-waters. A lack of authigenic carbonate in the section indicates that methane oxidation progressed aerobically and may have provided a significant driver for transient bottom water de-oxygenation.

Where methane addition is indicated, the seasonal sensitivity precludes control by methane hydrates. We argue that these data represent the increased importance and sensitivity of methanogenesis in the sediments, enabled by lower ocean sulfate concentrations during the Late Cretaceous. The tendency towards a more dynamic role for marine methane production and oxidation is likely to apply to other times of low marine sulfate in Earth's history.

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1. Introduction

Marine bivalves can be sensitive recorders of past bottom-water redox reactions, which are themselves conditioned by major seawater chemistry. In particular, records of marine dissolved inorganic carbon (DIC) can be preserved in the fossil record by

* Corresponding author.

E-mail address: eejlh@leeds.ac.uk (J.L.O. Hall).

¹ Present address: American Museum of Natural History, Central Park West at 79th Street, New York, NY, 10024.

biomineralizing organisms which incorporate carbon from the ambient DIC pool into biological compounds such as shell carbonate (McConnaughey and Gillikin, 2008). High resolution carbon isotope analysis was performed on specimens of Late Cretaceous and early Paleocene infaunal bivalves from a marine shelf succession cropping out on Seymour Island, Antarctica. This analysis was undertaken to examine variation in the composition of the marine DIC pool within lifetime growth cycles. In turn, this provides the potential for insight into changes in past productivity and redox conditions including methane oxidation.

The shells of infaunal bivalves are ideal archives in which to search for signals of methane oxidation in the benthic boundary layer of the water column. The active pumping of water by bivalves to supply food particles, oxygen, and ions for biomineralization means that the isotope signatures produced in modern shells are dominated by bottom water rather than sedimentary pore-water signatures (Klein et al., 1996). Some species do incorporate a small amount of respired organic carbon into their shell carbonate; however, most is precipitated from the DIC in inhaled seawater with little carbon isotope fractionation (McConnaughey et al., 1997; Poulain et al., 2010).

Examples of the infaunal genera *Lahillia* and *Cucullaea* were chosen for this study due to their abundance in the Seymour Island study section. Many specimens were collected in an intact or near-intact condition, and their large aragonitic shells and prominent internal or external shell growth lines make them ideal for high resolution geochemical studies. The visible growth lines were used to identify the cyclicity of shell growth; many species of bivalve produce these lines with distinct periodicity (i.e. annual, monthly, daily; Schöne et al., 2005b; Immenhauser et al., 2016). Each growth line represents a pause in the shell accretion, and the growth increment between consecutive lines records a period of active shell growth that can be used to identify the relative timing of geochemical signals incorporated into shell material from the ambient water. The large shell size (typically up to 10 cm in length) enabled microsampling for stable carbon and oxygen isotopic analysis within growth increments. A similar method was used by Buick and Ivany (2004) to analyze material from Eocene *Cucullaea raea* from Seymour Island and determine that shell production occurred with annual periodicity and growth lines were produced during each summer.

Muted indicators of methane production and oxidation have also been observed at discrete levels within the Cretaceous sediments on Seymour Island. They include the occurrence of thyasirid, lucinid and solemyid bivalves, which are taxa known to host chemosymbiotic bacteria and occur at modern and Cretaceous sites of methane seepage (Kauffman et al., 1996). Burrow-filling carbonates are also sometimes present within these levels and have distinctly negative carbon isotope compositions (−24 to −58‰, Little et al., 2015). However, the Maastrichtian–Paleocene López de Bertodano Formation on Seymour Island lacks the abundant authigenic carbonate which characterizes many modern marine methane seeps, and which can also be found in stratigraphically older early Maastrichtian sediments on nearby Snow Hill Island

(Little et al., 2015). This lack of authigenic carbonate (typically the burial product of sedimentary methane oxidation) suggests that the methane production and oxidation system in the Seymour Island region may have differed substantially from modern marine systems. One potential difference may have been the concentration of marine sulfate which plays a particularly important role in the marine methane cycle as discussed below.

The sedimentary production and release of methane is largely a function of the depth of penetration of various oxidants into marine sediments. In the modern ocean, sulfate plays a key role in the oxidation of organic carbon in ocean sediments via microbial sulfate reduction (MSR), which can account for up to ~80% of organic carbon oxidation (Jørgensen and Kasten, 2006). Only organic carbon that survives oxidation by MSR at sedimentary depths where sulfate concentrations have been reduced to zero is then available for methanogenesis. Once methane is produced it diffuses upwards until it encounters dissolved sulfate in porewaters where it is almost wholly consumed via sulfate fueled anaerobic oxidation of methane (AOM, Knittel and Boetius, 2009). Ocean sulfate concentrations will, therefore, exert a first order control on sedimentary methane production by affecting both the amount of organic carbon available for methanogenesis, and the depth in the sediment at which methanogenesis becomes the dominant fate for this carbon.

Estimates of marine sulfate concentrations from halite fluid inclusions, sulfur isotope rate of change calculations and geochemical models suggest that the Maastrichtian–early Paleocene time period (approximately 69 to 65 Ma) examined in this study was likely to have been characterized by ocean sulfate concentrations far lower than modern seawater (Table 1; modern seawater = 29 mM). Of particular note is the estimate from sulfate isotope rate of change calculations performed on a carbonate associated sulfate–sulfur isotope record derived from the same Seymour Island succession used in this study, which indicates that the maximum sulfate concentration for this time interval was ~2 mM (Witts et al., 2018). This is at the bottom end of the range of estimates produced by other methods, although there are no data from Maastrichtian halite fluid inclusions for a direct comparison. The temporally closest halite fluid records are of Aptian and Albian–Cenomanian age (125 to 93.9 Ma) with a range of sulfate concentrations between 5 and 16 mM (Lowenstein et al., 2003; Timofeeff et al., 2006), and the Eocene and Oligocene (56 to 23 Ma) with sulfate concentrations between 14 and 23 mM (Horita et al., 2002). This suggests that marine sulfate concentrations began to rise significantly after the K–Pg boundary. Modeling studies also give similar intermediate marine sulfate concentrations for the Maastrichtian with estimates from ~5 to ~15 mM (Wortmann and Paytan, 2012; Berner, 2004; Demicco et al., 2005). Taken together, this evidence strongly suggests that, while the exact concentration of sulfate in the Late Cretaceous is uncertain, concentrations were likely to have been less than half that of modern seawater (i.e. ~14 mM).

It is therefore reasonable to hypothesize that lower sulfate oceans of the Late Cretaceous would have been characterized by greater methane production, with methanogenesis occurring at

Table 1

A compilation of marine sulfate concentration estimates for the Maastrichtian and additional temporally closest data sets using a variety of methods.

Age (Ma)	SO ₄ (mmol/kg H ₂ O)	Method	References
37–35	12–23	Halite fluid inclusion	Horita et al. (2002)
69–65	~5	Modeling	Wortmann and Paytan (2012)
69–65	~11	Modeling	Berner (2004)
69–65	~15	Modeling	Demicco et al. (2005)
69–65	≤2	S-isotope rate of change	Witts et al. (2018)
100.5–89.8	2–7	S-isotope rate of change	Adams et al. (2010), Owens et al. (2013)
125–93.9	5–16	Halite fluid inclusion	Lowenstein et al. (2003), Timofeeff et al. (2006)

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