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# Tracing the incorporation of carbon into benthic foraminiferal calcite following the Deepwater Horizon event \*



<sup>a</sup> University of South Florida, College of Marine Science, 140 7th Ave. S., Saint Petersburg, FL 33701, USA

<sup>b</sup> Florida State University, Department of Earth, Ocean and Atmospheric Science, P.O. Box 3064520, Tallahassee, FL 32306, USA

<sup>c</sup> Eckerd College, 4200 54th Ave. S., Saint Petersburg, FL 33711, USA

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## ABSTRACT

Following the Deepwater Horizon (DWH) event in 2010, hydrocarbons were deposited on the continental slope in the northeastern Gulf of Mexico through marine oil snow sedimentation and flocculent accumulation (MOSSFA). The objective of this study was to test the hypothesis that benthic foraminiferal  $\delta^{13}$ C would record this depositional event. From December 2010 to August 2014, a time-series of sediment cores was collected at two impacted sites and one control site in the northeastern Gulf of Mexico. Short-lived radioisotopes (<sup>210</sup>Pb and <sup>234</sup>Th) were employed to establish the pre-DWH, DWH, and post-DWH intervals. Benthic foraminifera (*Cibicidoides* spp. and *Uvigerina* spp.) were isolated from these intervals for  $\delta^{13}$ C measurement. A modest (0.2–0.4‰), but persistent  $\delta^{13}$ C depletion in the DWH intervals of impacted sites was observed over a two-year period. This difference was significantly beyond the pre-DWH (background) variability and demonstrated that benthic foraminiferal calcite recorded the depositional event. The longevity of the depletion in the  $\delta^{13}$ C record suggested that benthic foraminifera may have recorded the change in organic matter caused by MOSSFA from 2010 to 2012. These findings have implications for assessing the subsurface spatial distribution of the DWH MOSSFA event.

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# 1. Introduction

The Deepwater Horizon (DWH) event in 2010 released 4.0 million barrels of petroleum into the northeastern Gulf of Mexico (nGoM) (U.S. District Court, 2015). The delivery of DWH-derived hydrocarbons to the sediments of the nGoM was caused primarily by a pulse of oil-mineral-biota aggregates which settled from the surface (Marine Oil Snow, Sedimentation, and Flocculent Accumulation, MOSSFA) onto continental slope sediments (Thibodeaux et al., 2011; Kessler et al., 2011; Passow et al., 2012; Ziervogel et al., 2012; Paris and Henaff, 2012; Passow, 2014; Brooks et al., 2015; Daly et al., 2016; Romero et al., 2017; Schwing et al., 2017). Assessment of the incorporation of oil-derived carbon (petrocarbon) by benthic organisms requires the development of accurate geochemical tracers to improve our understanding of the intensity and duration of impacts caused by accidental releases of oil on deep

benthic environments.

Effects of accidental submarine petroleum releases on benthic foraminiferal stable and radioisotope signatures have not been well studied. Several studies have measured the effects of natural methane seeps on benthic foraminiferal stable carbon isotopes. Hill et al. (2004) contrasted the  $\delta^{13}$ C of three species of benthic foraminifera (Uvigerina peregrina, Cibicidoides mckannai, and Globobulimina auriculata) at a natural methane seep (Hydrate Ridgeoffshore Oregon, USA) and at a control (non-seep) site. The mean benthic foraminiferal  $\delta^{13}$ C from the seep site indicated depletion in  $\delta^{13}C_{DIC}$  and ranged from -1.28% to -5.64%, whereas the mean  $\delta^{13}$ C from the control site ranged from -0.81% to 0.85%. Sen Gupta and Aharon (1994) compared the  $\delta^{13}$ C of Uvigerina peregrina from natural methane seeps in the nGoM with the  $\delta^{13}C$  from non-seep sites reported by Aharon et al. (1992). The mean  $\delta^{13}$ C of benthic for a from the seep sites ranged from -1.3% to -3.6%, while the  $\delta^{13}$ C of benthic foraminifera at the non-seep sites ranged from -0.9% to 0.4%.

The  $\delta^{13}$ C of benthic foraminiferal calcite is primarily affected by environmental changes to bottom water and/or porewater  $\delta^{13}$ C of





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<sup>\*</sup> This paper has been recommended for acceptance by Maria Cristina Fossi.

<sup>\*</sup> Corresponding author.

E-mail address: pschwing@mail.usf.edu (P.T. Schwing).

dissolved inorganic carbon (DIC), the isotopic composition of food sources (e.g. microbial biomas and phytodetritus) and total organic carbon (TOC) flux (Rathburn et al., 2003; Torres, 2003; Hill et al., 2004; Nomaki et al., 2006; Panieri, 2006; Panieri and Sen Gupta, 2008; Zariess and Mackensen, 2011; Panieri et al., 2014; Theodor et al., 2016; Schneider et al., 2017). Zariess and Mackensen (2011) reported that seasonal increases in phytodetritus deposition caused depletion in *Cibicidoides wuellerstorfi*  $\delta^{13}C_{CaCO3}$  from 0.1% to 0.4‰. Theodor et al. (2016) were able to construct a TOC flux transfer function for the Mediterranean Sea based on the difference between  $\delta^{13}$ C of epifaunal taxa (*Planulina ariminensis*, *Cibicidoides* pachydermus, Cibicides lobatulus) and the  $\delta^{13}$ C of shallow infaunal species (Uvigerina mediterranea). This relationship is based on the increased microbial respiration rates and trophic conditions induced by TOC flux, which in turn depletes the  $\delta^{13}$ C of dissolved inorganic carbon in the bottom water and sedimentary pore water. This relationship also indicates that increased TOC flux may have resulted in  $\delta^{13}C$  depletion in benthic foraminiferal stable carbon isotope signatures following the DWH event. MOSSFA increased sedimentary mass accumulation rates (up to 4-10 fold; Brooks et al., 2015) and total organic carbon (TOC) flux (Romero et al., 2015: Schwing et al., 2015).

The objective of this study was to test the hypothesis that benthic foraminiferal  $\delta^{13}$ C would record changes in organic carbon fluxes and sources observed in the aftermath of the DWH event by documenting the pre-DWH baseline stable carbon ( $\delta^{13}$ C) of benthic foraminiferal CaCO<sub>3</sub> and how it was affected during and after the event.

#### 2. Methods

Sediment cores were collected from impacted sites PCB06 ( $29^{\circ}$  5.99' N, 87° 15.93 W, 1043 m depth) and DSH08 ( $29^{\circ}$  7.25' N, 87° 51.93' W, 1143 m depth) in December 2010, February 2011, September 2011, August 2012 and August 2014 (Fig. 1) using an Ocean Instruments MC-800 multicorer. These sampling sites provide a record of increased oil-mineral-biota aggregate accumulation (MOSSFA) following the DWH event (Brooks et al., 2015; Romero et al., 2015). These sites also document a region-wide decline in benthic foraminiferal density and diversity following the DWH event (Schwing et al., 2015, 2016A). Due to the lack of sediment cores from before 2010 at these sites, it was necessary to use the down-core record as an indicator of sedimentary conditions prior to the DWH event. In addition, a core at NT1200 ( $27^{\circ}$  57.98' N,

86° 1.39′ W, 1200 m depth) was collected in June 2011, which provided a baseline control record on the West Florida Slope. This site is outside of the area influenced by the DWH event.

Each sediment core was refrigerated (~4 °C) until it was subsampled using a calibrated, threaded rod extrusion device at 2 mm and 5 mm intervals (Schwing et al., 2016B). Subsamples were freeze-dried, weighed and washed with a sodium hexametaphosphate solution through a 63- $\mu$ m sieve to disaggregate clay particles from foraminifera tests. The fraction remaining on the sieve (coarse fraction) was dried, weighed again, and stored at room temperature.

#### 2.1. Geochronology

Short-lived radioisotope geochronologies, based on excess <sup>210</sup>Pb and <sup>234</sup>Th (<sup>210</sup>Pb<sub>xs</sub> and <sup>234</sup>Th<sub>xs</sub>) from Brooks et al. (2015) were used to establish pre-DWH and post-DWH intervals. Freeze-dried samples were counted on a Canberra HPGe (high-purity germanium) coaxial planar photon detector to determine <sup>210</sup>Pb<sub>xs</sub> activity. Activities were corrected for counting time, detector efficiency, and self-absorption using the IAEA-447 standard. The constant rate of supply (CRS) model was used to establish a chronology and mass accumulation rates (Table S2) for each core.

#### 2.2. Stable carbon isotope measurements

Hill et al. (2004) and McCorkle et al. (1990) found no significant difference in  $\delta^{13}$ C of stained (living) and unstained (dead) benthic foraminifera specimens, while Mackensen et al. (2006) found significant differences between stained and unstained specimens at cold methane seeps off northern Norway. The post-DWH depletions in benthic foraminiferal  $\delta^{13}$ C in this study should be considered conservative estimates considering that both live and dead specimens were included in these measurements.

*Cibicidoides* spp. was chosen as the most appropriate benthic taxa for this study based on the findings of Grossman (1987), McCorkle et al. (1990), and Linke and Lutze (1993). McCorkle et al. (1990) suggest that *Cibicidoides* spp. is the best taxa for paleoceanographic reconstructions of  $\delta^{13}C_{DIC}$  of bottom water, due to their preferred epifaunal niche. However, Gottschalk et al. (2016) found significant variability of  $\delta^{13}C$  between *Cibicidoides* spp. Considering the potential variability between species, any consistent and significant depletion in *Cibicidoides* spp.  $\delta^{13}C$  in this study should be considered conservative estimates. *Cibicidoides* spp.



Fig. 1. Location map of each sampling site including the DWH impacted sites (DSH08, PCB06) and the control site in relation to the location of the DWH wellhead.

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