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Insights into methane dynamics from analysis of authigenic carbonates and chemosynthetic mussels at newly-discovered Atlantic Margin seeps

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A B S T R A C T

The recent discovery of active methane venting along the US northern and mid-Atlantic margin represents a new source of global methane not previously accounted for in carbon budgets from this region. However, uncertainty remains as to the origin and history of methane seepage along this tectonically inactive passive margin. Here we present the first isotopic analyses of authigenic carbonates and methanotrophic deep-sea mussels, *Bathymodiolus* sp., and the first direct constraints on the timing of past methane emission, based on samples collected at the upper slope Baltimore Canyon (∼385 m water depth) and deepwater Norfolk (∼1600 m) seep fields within the area of newly-discovered venting. The authigenic carbonates at both sites were dominated by aragonite, with an average $\delta^{13}C$ signature of −47‰, a value consistent with microbially driven anaerobic oxidation of methane-rich fluids occurring at or near the sediment–water interface. Authigenic carbonate U and Sr isotope data further support the inference of carbonate precipitation from seawater-derived fluids rather than from formation fluids from deep aquifers. Carbonate stable and radiocarbon ($\delta^{13}C$ and $\Delta^{13}C$) isotope values from living *Bathymodiolus* sp. specimens are lighter than those of seawater dissolved inorganic carbon, highlighting the influence of fossil carbon from methane on carbonate precipitation. U–Th dates on authigenic carbonates suggest seepage at Baltimore Canyon between 14.7 ± 0.6 ka to 15.7 ± 1.6 ka, and at the Norfolk seep field between 1.0 ± 0.7 ka to 3.3 ± 1.3 ka, providing constraint on the longevity of methane efflux at these sites. The age of the brecciated authigenic carbonates and the occurrence of pockmarks at the Baltimore Canyon upper slope could suggest a link between sediment delivery during Pleistocene sea-level lowstand, accumulation of pore fluid overpressure from sediment compaction, and release of overpressure through subsequent venting. Calculations show that the Baltimore Canyon site probably has not been within the gas hydrate stability zone (GHSZ) in the past 20 ka, meaning that in-situ release of methane from dissociating gas hydrate cannot be sustaining the seep. We cannot rule out updip migration of methane from dissociation of gas hydrate that occurs farther down the slope as a source of the venting at Baltimore Canyon, but consider that the history of rapid sediment accumulation and overpressure may play a more important role in methane emissions at this site.

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1. Introduction

The distribution of newly discovered seafloor methane seeps along the US Atlantic margin (USAM) (Skarke et al., 2014) has important implications for ocean carbon dynamics (Boetius and Wenzhöfer, 2013), continental slope stability and related hazards (Dugan and Flemings, 2000; ten Brink et al., 2014), and also the geographic extent of chemosynthetic communities (Quattrini et al., 2015). Whereas seafloor methane venting typically occurs in major hydrocarbon basins such as the Gulf of Mexico or on active mar-

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gins such as Cascadia, the northern USAM passive margin had long been considered relatively inactive (Skarke et al., 2014). Methane seeps have been documented on the southern USAM, at Cape Fear (L.L. Brothers et al., 2013) and Blake Ridge (Paull et al., 1995; Van Dover et al., 2003), where they occur at a depth range of 2155 to 2600 m above rising salt diapirs that perturb that gas hydrate stability field (Hornbach et al., 2005), but no such features were known on the northern part of the margin. This assessment was revised when geophysical surveys conducted between 2011 and 2013 identified ∼570 gas plumes at water depths of 50–1700 m between Cape Hatteras and Georges Bank (Skarke et al., 2014). Observations at a few of the sites from remotely operated vehicles (ROV) included bubble streams, bacterial mats, chemosynthetic communities, authigenic carbonates, deep-sea corals, and gas hydrate (Skarke et al., 2014; Quattrini et al., 2015). Average contemporary methane emissions from seeps along the entire northern USAM are estimated at ∼15 to 90 $Mg\,yr^{-1}$ (equivalent to 0.95 to 5.66×10^6 $mol\,yr^{-1}$) based on analysis of ROV bubble observations (Skarke et al., 2014), versus 2.15 to 8.65×10^6 $mol\,yr^{-1}$ in a seep field of Hudson Canyon based on the water column methane concentrations (Weinstein et al., submitted for publication).

The origin and characteristics of the methane seeps north of Cape Hatteras remain elusive. No underlying salt diapirs have been documented in the seeping areas, and Skarke et al. (2014) postulate that dissociation of gas hydrate and possibly submarine groundwater discharge may play a role in feeding seeps between the outer continental shelf and uppermost continental slope, while the deeper seeps represent leakage of methane through fractured Eocene rocks. Distinguishing among these and other processes that may be responsible for the methane emissions requires direct study of seep fluids, rocks, and organisms. To acquire samples for such studies, the Bureau of Ocean Energy Management (BOEM), the U.S. Geological Survey (USGS), the National Oceanic and Atmospheric Administration (NOAA), and their academic partners initiated a 5-year multi-disciplinary "Atlantic Deepwater Canyons" study focusing on ecologically significant habitats (canyons, cold seeps, hard-bottoms and shipwrecks) in Norfolk Canyon (off Virginia) and overlooking Baltimore Canyon (off Maryland) (Fig. 1). Of the two sites, Baltimore Canyon had been previously investigated in the early 1980s with photographs of a dense community of mussels at ∼400 m obtained using a towed camera sled (B. Hecker, pers. comm.), but no further work was conducted in the area until recently. During the Atlantic Deepwater Canyons cruises, we used ROVs designed to support physical and biological sampling to confirm the location of a shallow (∼400 m) seep site overlooking Baltimore Canyon in 2012 and, following the discovery of deep-sea gas plumes (NOAA, 2012), identified a new chemosynthetic community at ∼1600 m water depth south of Norfolk Canyon in 2013.

Authigenic carbonates are common at cold seeps and record a robust fingerprint of hydrocarbon seep activity, including local and regional controls on the source and flux of carbon, the conditions under which carbonates formed, and information regarding fluid–sediment and rock interactions (see reviews in Campbell, 2006; Suess, 2014). Additionally, authigenic carbonates are amenable to uranium (U)-series dating techniques, and can provide key information on the timing and duration of fluid venting at each seep (Teichert et al., 2003; Bayon et al., 2009; Liebetrau et al., 2014). The isotopic composition of shells from chemosynthetic bivalves living close to fluid vents represents an important archive of the nature and variability of the venting. While previous studies have investigated authigenic carbonate formation and cold seeps in other settings (Han et al., 2014; Suess, 2014; Bayon et al., 2015) and fluid flow in passive margins (Berndt, 2005), this is the first study to examine the origin of the authigenic carbonates, the source fluids, and the timing of methane emissions on the northern USAM. This paper explores the geochemistry,

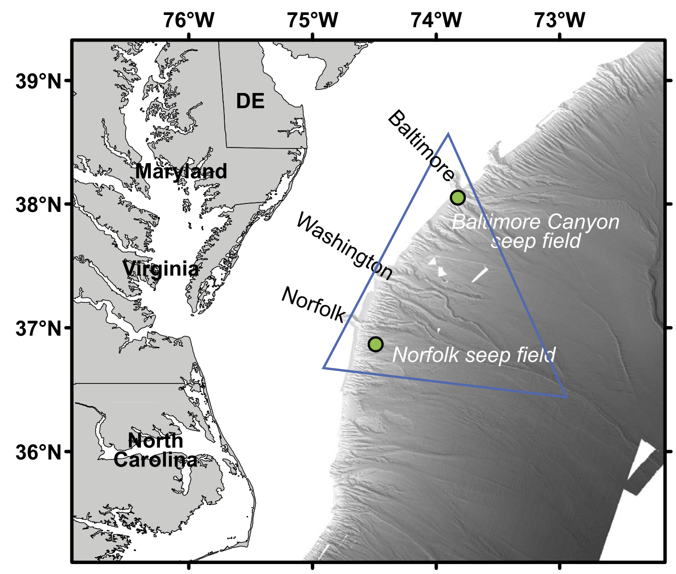

Fig. 1. Location map showing the Norfolk and Baltimore Canyon seep fields (green circles) relative to the major shelf-break canyons (Norfolk, Washington, and Baltimore). The blue triangle outlines the study area for the multi-disciplinary "Atlantic Deepwater Canyons" study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mineralogy, and petrology of authigenic carbonates and bivalve shells recovered by ROVs from both the Norfolk and the Baltimore Canyon seep fields with the aim of tracing the origin and flow pathways of gas and fluids at both sites. Taken together, the geochemical information derived from both authigenic carbonates and bivalve shells collected from seeps in the Baltimore and Norfolk canyons expands our understanding of the origin and occurrence of widespread methane seepage along the US Mid-Atlantic margin.

2. Methods

2.1. Study site

A shallow (∼385 m; Fig. 2) seep site seaward and south of the location where Baltimore Canyon (38°03.086 N, 73°49.379 W) crosses the shelf-break was surveyed and sampled during a 2012 cruise (17 Aug–14 Sep) aboard the NOAA ship *Nancy Foster* using the *Kraken II* ROV (University of Connecticut). This site was sampled again in 2013, along with the deeper (1455–1610 m; Fig. 3) Norfolk seep site (36°51.921 N, 74°29.574 W) during a cruise (2–18 May) onboard the NOAA ship *Ronald H. Brown* using the *Jason II* ROV (Woods Hole Oceanographic Institution). At the Norfolk seep site, gas bubbles can be traced at least ∼600 m above the seafloor (Fig. 3C), as confirmed by USGS surveys on the *R/V Endeavor* in April 2015 (Ruppel et al., 2015a). At the Baltimore Canyon seep field, water column imaging carried out by the USGS in April and September 2015 (Ruppel et al., 2015b) showed that venting is more widespread and diffuse (Fig. 2D). Dense colonies of chemosynthetic mussels, active gas bubbling, and extensive bacterial mats were observed at both seep sites (Fig. 2C and 3D) during the 2012 and 2013 ROV dives. Clams, common at the Blake Ridge seep site (Van Dover et al., 2003), were notably absent, as were tubeworms, a finding that is consistent with a recent survey of chemosynthetic communities from seep sites along the northeastern US continental margin (Quattrini et al., 2015). Seep communities at the Norfolk and Baltimore Canyon seep fields were dominated by the deep-sea mussels of the genus *Bathymodiolus*, which depends on chemosynthetic endosymbiotic bacteria to oxidize sulfur and/or methane for nutrition (Duperron et al., 2011).

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