



# Rapid rates of aerobic methane oxidation at the feather edge of gas hydrate stability in the waters of Hudson Canyon, US Atlantic Margin

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## Abstract

Aerobic oxidation is an important methane sink in seawater overlying gas seeps. Recent surveys have identified active methane seeps in the waters of Hudson Canyon, US Atlantic Margin near the updip limit of methane clathrate hydrate stability. The close proximity of these seeps to the upper stability limit of methane hydrates suggests that changing bottom water temperatures may influence the release rate of methane into the overlying water column. In order to assess the significance of aerobic methane oxidation in limiting the atmospheric expression of methane released from Hudson Canyon, the total extent of methane oxidized along with integrated oxidation rates were quantified. These calculations were performed by combining the measurements of the natural levels of methane concentrations, stable carbon isotopes, and water current velocities into kinetic isotope models yielding rates ranging from  $22.8 \pm 17$  to  $116 \pm 76$  nM/day with an average of  $62.7 \pm 37$  nM/day. Furthermore, an average of 63% of methane released into the water column from an average depth of 515 m was oxidized before leaving this relatively small study area (6.5 km<sup>2</sup>). Results from the kinetic isotope model were compared to previously-published but concurrently-sampled ex situ measurements of oxidation potential performed using <sup>13</sup>C-labeled methane. Ex situ rates were substantially lower, ranging from 0.1 to 22.5 nM/day with an average of  $5.6 \pm 2.3$  nM/day, the discrepancy likely due to the inherent differences between these two techniques. Collectively, the results reveal exceptionally-rapid methane oxidation, with turnover times for methane as low as 0.3–3.7 days, indicating that methane released to the water column is removed quantitatively within the greater extent of Hudson Canyon.

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## 1. INTRODUCTION

Atmospheric methane (CH<sub>4</sub>) has a strong radiative forcing and is sustained by significant natural and anthropogenic sources (Ciais et al., 2013). The largest global reservoir of CH<sub>4</sub> occurs within the seafloor (Milkov, 2004) and paleoclimate evidence suggests that CH<sub>4</sub>

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emissions from oceanic sediments have impacted global climate during events such as glacial-interglacial cycles (Kennett et al., 2000) and the Paleocene-Eocene Thermal Maximum (Dickens et al., 1997). In the modern ocean, recent acoustic surveys along continental margins (e.g. US Atlantic Margin, northern Gulf of Mexico, and Svalbard) have identified an abundance of CH<sub>4</sub> seep fields, many of which lie at or up dip of the stability of methane hydrates, thus making their flux susceptible to changing ocean temperature (e.g. Ruppel, 2011; Skarke et al., 2014; Weber et al., 2014; Graves et al., 2015).

While CH<sub>4</sub> production is nearly ubiquitous in anaerobic oceanic sediments, the microbial oxidation of CH<sub>4</sub> in the water column is so efficient that only a small fraction escapes to the atmosphere (Reeburgh, 2007). Along continental shelves where CH<sub>4</sub> production is greatest and the water depth is the shallowest, modern fluxes of CH<sub>4</sub> from sediments into the water column have been estimated to at 8–65 Tg/yr (Hovland et al., 1993). Offshore releases of CH<sub>4</sub> to the atmosphere have been estimated at 6.6–19.5 Tg/yr, suggesting that CH<sub>4</sub> is actively removed from the water column before it reaches the atmosphere (Judd et al., 2002). Since CH<sub>4</sub> is either oxidized by bacteria, emitted to the atmosphere, or retained in ocean water, the efficiency of microbial oxidation determines the partitioning of dissolved CH<sub>4</sub> between atmospheric exchange and conversion into oceanic dissolved inorganic carbon (DIC) and organic carbon pools (Hanson and Hanson, 1996).

Traditionally, CH<sub>4</sub> oxidation rate measurements are carried out by inoculating a water sample with radiolabeled CH<sub>4</sub>, either <sup>14</sup>C or <sup>3</sup>H, incubating the sample, then quantifying the radiolabeled oxidation products (e.g. Ward et al., 1987; Valentine et al., 2001; Pack et al., 2011; Mau et al., 2012a, 2013; Gentz et al., 2014). This technique is encumbered by strict government regulations controlling the use of radioactive compounds in the lab and at sea. Based on the radioactive abundance of inoculant used, researchers might require special training and the research vessel might require a separate laboratory space for the handling of radioactive compounds. In addition, these ex situ isotopic tracer techniques determine oxidation rates on a specific parcel of water once the sample is removed from the ocean, such that any oxidation of CH<sub>4</sub> that occurs prior to sampling is not quantified. In certain situations where perturbations of CH<sub>4</sub> concentration in ocean waters drive bacterial growth and decline, determining the total extent of CH<sub>4</sub> oxidized and calculating integrated oxidation rates could provide a better measure of the CH<sub>4</sub> dynamics at play. Since these methods have not been developed, the goals of this study are: (1) to establish a new technique to quantify the total extent of CH<sub>4</sub> oxidized and integrated CH<sub>4</sub> oxidation rates and (2) to apply this new technique in an area experiencing active CH<sub>4</sub> release from the seafloor where the seafloor CH<sub>4</sub> fluxes are susceptible to changing ocean temperature.

Rather than determining CH<sub>4</sub> oxidation rates in specific parcels of water, the new technique described here determines the total extent and rate of oxidation from the point where CH<sub>4</sub> bubbles dissolve in seawater to the point where samples are collected. This method is based on quantifying

the natural isotopic fractionation of δ<sup>13</sup>C–CH<sub>4</sub> that occurs during aerobic CH<sub>4</sub> oxidation. More specifically, this procedure uses natural measurements δ<sup>13</sup>C–CH<sub>4</sub>, dissolved CH<sub>4</sub> concentration, and water current velocity in kinetic isotope models to calculate integrated oxidation rates. While several studies have linked concurrent shifts in CH<sub>4</sub> concentrations and natural stable isotopic ratios as resulting from microbial oxidation, or have modeled the distribution of CH<sub>4</sub> in a study area (Grant and Whiticar, 2002; Damm and Budéus, 2003; Kessler et al., 2006; Damm et al., 2007; Keir et al., 2009; Mau et al., 2012b), these data have not been used previously to determine CH<sub>4</sub> oxidation rates and extents. A significant challenge with this approach is the need to also constrain dilution with background seawater and mixing with neighboring sources of CH<sub>4</sub>, which can confuse oxidation results determined from this data. Our approach involves subjecting our natural isotope and concentration measurements to both Rayleigh and open system kinetic isotope models in order to assess and constrain dilution and mixing, as well as oxidation.

This new technique was applied to investigate the oxidation of CH<sub>4</sub> along the US Atlantic Margin where extensive CH<sub>4</sub> seepage was recently discovered (Skarke et al., 2014). The Hudson Canyon seep field was specifically chosen since most seepage lies at the upper limit of clathrate-hydrate stability, not connected to the deeper geosphere (Skarke et al., 2014; Rona et al., 2015; Weinstein et al., 2016). In addition, the restricted seawater circulation caused by the canyon walls allows CH<sub>4</sub> to accumulate to higher concentrations, improving precision of the chemical analyses used here. Thus, this region can serve as a critical testbed where changes in ocean temperature, CH<sub>4</sub> releases from clathrate-hydrates, and CH<sub>4</sub> oxidation can be investigated (Kessler, 2014; Skarke et al., 2014). Aerobic CH<sub>4</sub> oxidation was also measured in this seep field using a procedure involving ex situ isotope labeling. This procedure inoculated samples with pure <sup>13</sup>CH<sub>4</sub>, incubated them for a known period of time, and measured the tracer incorporated into the produced DIC pool. Here, the aerobic CH<sub>4</sub> oxidation results determined by both independent methods are used for technique intercomparison as well as to assess the significance of aerobic CH<sub>4</sub> oxidation in Hudson Canyon.

## 2. MATERIALS AND METHODS

### 2.1. Sample and data collection

Water column samples and data were collected in the thalweg of Hudson Canyon from 9 to 13 July 2014 onboard the R/V *Endeavor*. An area centered on approximately 39° 32.03'N, 72°24.03'W was chosen based on the previous identification of CH<sub>4</sub> seeps at the theoretical limit of gas hydrate stability (Skarke et al., 2014). During this expedition, acoustic surveys were conducted to detect bubble plumes emanating from the seafloor, as described previously (Weinstein et al., 2016). The real-time results of the acoustic surveys were used to guide water column sampling for chemical properties, and seven stations encompassing a 6.5 km<sup>2</sup> study area within Hudson Canyon were selected

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