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Diverse origins of Arctic and Subarctic methane point source emissions identified with multiply-substituted isotopologues

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Abstract

Methane is a potent greenhouse gas, and there are concerns that its natural emissions from the Arctic could act as a substantial positive feedback to anthropogenic global warming. Determining the sources of methane emissions and the biogeochemical processes controlling them is important for understanding present and future Arctic contributions to atmospheric methane budgets. Here we apply measurements of multiply-substituted isotopologues, or clumped isotopes, of methane as a new tool to identify the origins of ebullitive fluxes in Alaska, Sweden and the Arctic Ocean. When methane forms in isotopic equilibrium, clumped isotope measurements indicate the formation temperature. In some microbial methane, however, non-equilibrium isotope effects, probably related to the kinetics of methanogenesis, lead to low clumped isotope values. We identify four categories of emissions in the studied samples: thermogenic methane, deep subsurface or marine microbial methane formed in isotopic equilibrium, freshwater microbial methane with non-equilibrium clumped isotope values, and mixtures of deep and shallow methane (i.e., combinations of the first three end members). Mixing between deep and shallow methane sources produces a non-linear variation in clumped isotope values with mixing proportion that provides new constraints for the formation environment of the mixing end-members. Analyses of microbial methane emitted from lakes, as well as a methanol-consuming methanogen pure culture, support the hypothesis that non-equilibrium clumped isotope values are controlled, in part, by kinetic isotope effects induced during enzymatic reactions involved in methanogenesis. Our results indicate that these kinetic isotope effects vary widely in microbial methane produced in Arctic lake sediments, with non-equilibrium Δ_{18} values spanning a range of more than 5‰.

Keywords: Methane; Clumped isotope geochemistry; Arctic; Carbon cycle; Greenhouse gases

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1. INTRODUCTION

Methane (CH_4) is a critical atmospheric greenhouse gas, with 28 times (on a molar basis) the global warming potential of CO_2 on a 100-year timescale (Myhre et al., 2013). Due to its importance to the climate state of the Earth, the sources of methane to the atmosphere and how they might respond to future climate change are of key concern. One region where natural (i.e., non-anthropogenic) methane emissions are of interest and concern is the Arctic, which has been predicted to experience pronounced warming in the future (Holland and Bitz, 2003; Comiso and Hall, 2014). Methane emissions from Arctic environments have been predicted to increase under a warmer climate (Christensen et al., 2004; Walter et al., 2006; O'Connor et al., 2010; Walter Anthony et al., 2012; Thornton et al., 2015; Wik et al., 2016), thus acting as a positive feedback to global warming (Anisimov, 2007; Schuur et al., 2008, 2015; Isaksen et al., 2011; Koven et al., 2011).

Microbial methanogenesis in wetland and lake sediments is thought to be the dominant source of natural methane emissions originating in the Arctic, contributing up to 90% of emissions during the boreal summer (Fisher et al., 2011). Consequently, this source has been the primary focus of studies of Arctic methane emissions (Walter et al., 2006; Schuur et al., 2008; Fisher et al., 2011; Isaksen et al., 2011). However, recent studies have identified two additional and potentially important sources of natural Arctic methane emissions. First, analyses of the isotopic and molecular composition of gases from ebullitive seeps in Alaskan lakes have suggested that many of these seeps emit methane from thermogenic or deep subsurface microbial sources. Such gases are thought to be transported to the surface by faults, and stored in shallow reservoirs underlying permafrost and glaciers (Walter Anthony et al., 2012). The emission of methane from these deep sources could be enhanced as permafrost thaws and glaciers melt, which could increase the number of conduits from subsurface reservoirs to the atmosphere (Formolo et al., 2008; Walter Anthony et al., 2012).

Second, methane ebullition has been observed in several locations on the continental shelf and slope of the Arctic Ocean (Paull et al., 2007; Westbrook et al., 2009; Shakhova et al., 2010). The sources of these bubbles may be from either the dissociation of gas hydrates or the thawing of permafrost inundated by sea level rise following the last deglaciation (Paull et al., 2007; Westbrook et al., 2009; Portnov et al., 2013; Frederick and Buffett, 2014). Methane emitted from the Arctic Ocean shelf may not have a significant influence on atmospheric budgets, given evidence for its efficient oxidation in sediments and the water column (Graves et al., 2015; Overduin et al., 2015). Nevertheless, the source and distribution of methane emissions from the Arctic Ocean remain poorly constrained (Kort et al., 2012; Schuur et al., 2015), making it difficult to quantitatively evaluate the importance of these sources to the atmospheric methane budget.

Carbon and hydrogen stable isotope measurements are an important tool for fingerprinting different sources of methane (Schoell, 1980; Whiticar et al., 1986; Whiticar, 1999). For example, thermogenic methane typically contains greater $^{13}C/^{12}C$ and D/H ratios relative to microbial methane (Schoell, 1980). Additionally, stable isotope measurements can in some cases differentiate between pathways of microbial methanogenesis (Whiticar et al., 1986; Krzycki et al., 1987; Hornibrook et al., 1997, 2000; Whiticar, 1999; Conrad et al., 2002; Krüger et al., 2002; Walter et al., 2008; Brosius et al., 2012). In particular, hydrogenotrophic methanogenesis (i.e., methanogens that reduce CO_2 with H_2) is thought to produce methane with lower $^{13}C/^{12}C$ and higher D/H relative to fermentative methanogenesis (i.e. methanogens that metabolize acetate or other methylated compounds) (Whiticar et al., 1986; Whiticar, 1999). However, ambiguities in the isotopic composition of methane can preclude accurate source assignment (Martini et al., 1996; Prinzhofer and Pernaton, 1997; Waldron et al., 1998, 1999; Valentine et al., 2004; Conrad, 2005). For example, microbial methanogenesis in some environments can produce stable isotope compositions resembling thermogenic methane (Martini et al., 1996; Valentine et al., 2004). Additionally, multiple factors in addition to methanogenic pathway can substantially influence the stable isotope composition of microbial methane, including substrate isotopic composition, substrate limitation, the kinetics of methane production, transport, and oxidation (Sugimoto and Wada, 1995; Waldron et al., 1998, 1999; Whiticar, 1999; Valentine et al., 2004; Conrad, 2005; Penning et al., 2005). These multiple influences on methane stable isotope values can complicate inferences regarding the pathway of methanogenesis in natural samples (Conrad, 2005).

Recently the analysis of multiply-substituted isotopologues, or 'clumped isotopes', has emerged as an additional isotopic constraint on the sources of methane (Tsuji et al., 2012; Ono et al., 2014; Stolper et al., 2014a,b; Inagaki et al., 2015; Stolper et al., 2015; Wang et al., 2015). Clumped-isotope geochemistry refers to the analysis of the abundances of molecules containing multiple rare, heavy isotopes (e.g. $^{13}CH_3D$ and $^{12}CH_2D_2$). Clumped isotope analyses are of interest in part because the proportions of clumped isotope species in equilibrated systems are solely a function of temperature-dependent homogeneous phase equilibria (Urey and Rittenberg, 1933; Wang et al., 2004) and can be used to determine formation or re-equilibration temperatures of a molecule using only a single phase, as opposed to multiple phases as is typical in stable-isotope-based geothermometry (Eiler and Schauble, 2004; Ghosh et al., 2006; Stolper et al., 2014a,b). See Eiler (2007, 2011, 2013), and references therein for detailed reviews of clumped-isotope geochemistry.

The first accurate and precise clumped isotope measurements of methane were achieved on a prototype high-resolution isotope ratio mass spectrometer—the Thermo Fisher IRMS 253 Ultra (hereafter the 'Ultra') (Eiler et al., 2013). Most measurements of methane clumped isotopes performed with the Ultra report variations in the sum of $^{13}CH_3D$ and $^{12}CH_2D_2$, as measured by the quantity Δ_{18} (Stolper et al., 2014a). $\Delta_{18\ \text{values}}$ represent the relative deviation in a sample from the amount of mass-18 methane predicted for a random distribution of isotopes among all