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Research paper

Influence of total organic carbon deposition on the inventory of gas hydrate in the Indian continental margins

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ABSTRACT

Total organic carbon (TOC) content of marine sediments represents residual carbon, originally derived from terrestrial and marine sources, which has survived seafloor and shallow subseafloor diagenesis. Ultimately, its preservation below the sulfate reduction zone in marine sediments drives methanogenesis. Within the gas hydrate stability zone (GHSZ), methane production along continental margins can supersaturate pore fluids and lead to the formation of gas hydrate. In this paper we examine the inventory and sources of TOC in sediments collected from four regions within the GHSZ along the Indian continental margins. The recovered sediments vary in age from Oligocene to recent. Mean TOC abundance is greatest in the Krishna–Godavari (K–G) Basin and decreases progressively to the Mahanadi basin, Andaman wedge, and Kerala–Konkan (K–K) Basin. This decrease in TOC is matched by a progressive increase in biogenic $CaCO_3$ and increasing distance from terrestrial sources of organic matter and lithogenic materials. Organic carbon sources inferred from C/N and $\delta^{13}C_{TOC}$ range from terrestrial (K–G Basin) to mixed marine and terrestrial (Mahanadi Basin), to marine dominant (Andaman wedge and K–K Basin). In the K–G Basin, variation in the bulk $\delta^{13}C_{TOC}$ is consistent with changes in C_3 and C_4 vegetation driven by monsoon variability on glacial-interglacial timescales, whereas in the Mahanadi Basin a shift in the $\delta^{13}C_{TOC}$ likely reflects the onset of C_4 plant deposition in the Late Miocene. A large shift the $\delta^{13}C_{TOC}$ in the K–K basin is consistent with a change from C_3 to C_4 dominated plants during the middle Miocene. We observe a close relationship between TOC content and gas hydrate saturation, but consider the role of sedimentation rates on the preservation of TOC in the zone of methanogenesis and advective flow of methane from depth. Although TOC contents are sufficient for *in situ* methanogenesis at all the sites where gas hydrates were observed or inferred from proxy data, seismic, borehole log, pressure core, and gas composition data coupled with relatively high observed gas hydrate saturations suggest that advective gas transport may also play a role in the saturation of methane and the formation of gas hydrates in these regions. Although TOC content may be a first order indicator for gas hydrate potential, the structural and stratigraphic geologic environment along a margin will most likely dictate where the greatest gas hydrate saturations will occur.

1. Introduction

Marine gas hydrates form and accumulate within the gas hydrate stability zone (GHSZ) in continental margin sediments with sufficient methane concentrations. Methane is generated from microbial degradation of organic carbon (<50 °C), from thermogenic decomposition of organic carbon at depth (80–150 °C) or from the conversion of heavier hydrocarbons to methane at temperatures >150 °C (Claypool and Kvenvolden, 1983). Gas hydrates, or methane hydrates, are most commonly formed from microbial methane, which is generated by methanogenesis from sedimentary organic carbon (Kvenvolden, 1993), and have been sampled and/or inferred in all of the global oceans (Collett et al., 2009). Thermogenic gas hydrates are less common, but have been observed for

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example in the Gulf of Mexico (Brooks et al., 1984), Caspian Sea (Ginsburg and Soloviev, 1998), on the Northern Cascadia margin (Pohlman et al., 2005), and in the Arctic Fram Strait (Smith et al., 2014). In addition, abiotic marine gas hydrates derived from the serpentinization of ultramafic rocks in oceanic crust may also exist in the Arctic Ocean (Rajan et al., 2012).

Methane migration into and within the GHSZ occurs through diffuse intragranular flow and/or advective flow through fractures, faults, or stratigraphic conduits (e.g. Carson and Screaton, 1998; Tréhu et al., 2004). Gas hydrates may persist through time along continental margins as long as (1) there is a source of methane, (2) short term pertubations (e.g. T, P, or salinity changes; Sloan and Koh, 2008) are recoverable (methane losses are balanced by inputs from depth), and (3) there is some holding capacity for methane to accumulate as gas hydrate in the GHSZ (e.g. significant host porosity and permeability; Lorenson, 2000; Xu and Ruppel, 1999). Gas hydrates can form and accumulate in unconsolidated to semi-lithified marine sediments of various stratigraphic ages, but are restricted to and maintained in the uppermost few hundred meters of sediment within the GHSZ along continental margins. In this environment high sedimentation and subsidence rates can result in the efficient burial and conversion of organic carbon to hydrocarbons and the continued upward migration of the GHSZ with time.

The global predominance of microbial methane in marine gas hydrate systems suggests that low temperature diagenetic alterations of organic matter in continental margin sediments plays a critical role in methanogenesis and the accumulation of gas hydrate within the gas hydrate stability zone (Kvenvolden, 1995). Methane in gas hydrates can be formed *in situ* from methanogenesis of the local organic carbon and/or be formed *ex situ* by either microbial or thermogenic gas generated at depth and advected upward toward or within the GHSZ. In a comparison study of TOC content and observed gas hydrate from several Pacific and Atlantic Ocean continental margins, Waseda (1998) suggests a minimum of 0.5 wt. % TOC is needed to fuel methanogenesis sufficiently to produce methane in excess of saturation and precipitate *in situ* gas hydrate. Using the modeling approach of Davie and Buffett (2001), Klauda and Sandler (2005) suggest a similar minimum TOC (>0.4 wt. %) to form *in situ* gas hydrates. Although Clayton (1992) also suggests significant microbial gas generation occurs at TOC contents >0.5 wt. %, he notes that only 0.2 wt. % is required to result in a free gas phase in sediments with 30% porosity at a 1 km burial depth. Kastner (2001) also suggests marine organic matter dominated settings with only 0.1 wt. % TOC could generate significant (~200 mM) methane concentrations in pore waters. Using data and observations from the northern Cascadia margin, Pohlman et al. (2009) suggests rather than the amount of TOC, it is the bioavailability of that TOC that may be important for *in situ* methanogenesis and gas hydrate formation. The bioavailability of organic carbon for methanogenesis in marine sediments is a function of the sedimentation (burial) rate (Stein, 1990), which affects the exposure time of the organic carbon to aerobic oxidation and sulfate reduction, and the type of organic carbon, with marine organic matter more labile than terrestrial (Burdige, 2005). Consistent with these observations, pore water data and numerical modeling show that elevated saturations of >1% observed in the Krishna–Godavari Basin offshore India, at sites with no evidence for fluid advection, may be the result of higher rates of *in situ* organic matter degradation and methanogenesis related to the high, non-steady state sedimentation rates across the basin (Solomon et al., 2014). In addition, sediments with low TOC content could host gas hydrates if the source of the gas is *ex situ* and delivered to the host via advective flow. Waseda and Uchida (2004) argue that passive margin environments like the Blake Ridge on the U.S. margin, may be dominated by *in situ* formed gas hydrate, due to the fine grained nature of the sediments and pervasive, diffuse fluid flow, resulting from the lack of significant deformation to focus gas migration upward and into the GHSZ. Paull et al. (1994), however, suggested some migration of gas from depth could occur at Blake Ridge and along other margins via gas hydrate recycling through time, which could resupply the GHSZ with *ex situ* microbial methane and precipitate gas hydrate. In active margin accretionary wedge environments (e.g. Cascadia, Nankai Trough, Chile) and on deformed passive margins, such as those influenced by salt or shale tectonics (e.g. Gulf of Mexico, Krishna–Godavari Basin), deformation and abundant stratigraphic and structural conduits for fluid flow help supply the GHSZ with deeper sources of methane, both of biogenic and thermogenic origins (e.g. Liu and Flemings, 2006; Tréhu et al., 2004). In these active margin/deformed margin settings, gas hydrate saturations locally can be very high, due to the concentrating effect of supplying the GHSZ with methane beyond that produced by *in situ* methanogenesis. For this reason, the highest gas hydrate saturation identified to date (near 100% for seafloor gas hydrate mounds), typically involve advection of methane in the gas phase along faults, fractures, or high porosity and permeability lithologic facies (Torres et al., 2008, 2011). In many of these advection-dominated environments, some of the excess advective methane can also bypass the GHSZ (Liu and Flemings, 2006; Smith et al., 2014), and be vented into the ocean, producing bubble plumes commonly imaged acoustically in the water column along many continental margins (e.g. Heeshen et al., 2003; Gardner et al., 2009; Weber et al., 2014).

If TOC preservation within the seafloor has been relatively constant over geologic timescales (i.e. the depositional environment has not changed significantly) the TOC content of shallow sediments within the GHSZ could be representative of deeper source TOC for *ex situ* produced gas and thus be a good first order indicator for overall (microbial or thermogenic) gas hydrate potential. On continental margins with consistent and high wt % TOC preserved in the sediments over geologic timescales, hydrocarbon (petroleum and gas) systems develop from this TOC (e.g. Gulf of Mexico, USA, Krishna–Godavari Basin, India). Advection of microbial and/or thermogenic gas along faults or stratigraphic conduits sourced in deeper reservoirs is often responsible for significant accumulations of gas hydrate in the subsurface (e.g. Tréhu et al., 2004; Riedel et al., 2010) and escape of gases through the GHSZ (Liu and Flemings, 2006, 2007; Torres et al., 2004, 2011). Integration of several variables, including TOC content (0.2–5 wt %), rates of sedimentation and methanogenesis, and host porosity and permeability, into the geochemical reaction transport model of Wallmann et al. (2012) suggest that gas hydrate saturations greater than 3% pore volume must be generated by advective delivery of dissolved or gaseous methane from depth.

In this paper we document the spatial and temporal variability of bulk TOC and organic carbon sources from C/N ratios and $\delta^{13}C_{TOC}$ from long sediment cores collected within the GHSZ along the continental margins of peninsular India and in the Andaman Sea during the 2006 National Gas Hydrate Program of India (NGHP) Expedition 01. We integrate these data with core lithology and sedimentation rates in order to assess the role of TOC in the documented gas hydrate occurrence at these sites. Our results show the general trend that higher TOC contents track with greater gas hydrate saturations. However, the sedimentation patterns, specifically rapid deposition of mass transport deposits (MTDs), regulates the amount of time TOC spends in the sulfate