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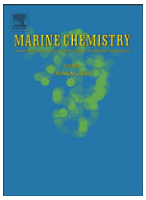

Detection of cold seep derived authigenic carbonates with infrared spectroscopy

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ABSTRACT

Infrared attenuated total reflection (IR-ATR) spectroscopy was applied to analyze carbonates in sediment samples collected at a cold seep site in Mississippi Canyon 118, Gulf of Mexico. Previously, these samples were grouped into low, moderate, and high microbial activity based on sulfate and methane down-core profiles. We have hypothesized that within these groups, IR-ATR spectroscopy could differentiate between cold seep derived microbially mediated authigenic carbonates found in high and moderate microbially active sediments, and biogenically produced carbonates representative for low microbially active sediments. Within the respective IR spectroscopic absorption profiles, the ν_3 *antisymmetric* carbonate stretching vibration was identified as a suitable indicator within these diverse geochemical groupings. Low microbial activity cores revealed absorption profiles that are significantly different from those of high and moderate microbial activity cores. To verify the IR-ATR results, the obtained spectral profiles were compared to stable isotopic values of *in situ* bulk carbonate signals. It is shown that for carbonates depleted in δ^{13}C (negative values), the IR ν_3 profiles are uniquely different. To semi-quantify this method, the obtained IR profiles were utilized for deriving an IR indicator (F) for establishing an analytical model suitable for the identification of cold seep derived authigenic carbonate. The sediment samples characterized by cold seep derived authigenic carbonates have an average indicator F value of 104.3 ± 15.8, whereas biogenic carbonates show F values of 53.5 ± 11.4. The obtained results demonstrate that IR-ATR spectroscopy may be applied as a shipboard and potentially *in situ* research tool for rapid and cost-effective characterization of carbonate formations in cold seep ecosystems.

1. Introduction

Cold seeps, which are also referred to as methane or hydrocarbon seeps, are ubiquitous features found at many active and passive continental margins (Formolo et al., 2004). They are essential reservoirs of methane and other hydrocarbons. At appropriate temperature and pressure conditions, small hydrocarbons (mostly methane) are incorporated into gas hydrates, which are recognized as an important potential energy source (Sloan, 1998). Microbial respiration of organic compounds sequesters this carbon as authigenic ("formed-in-place") carbonates. Thus, the overall magnitude of hydrocarbons and greenhouse gases trapped within hydrate-bearing and cold seep carbonate formations indicates the biogeochemical significance of these ecosystems within the global carbon cycle (Formolo et al., 2004; Sassen et al., 2006).

Numerous hydrocarbon seeps have been found in the Gulf of Mexico, where hydrocarbons usually originate from deeply seeded petroleum reservoirs (Roberts and Aharon, 1994; Sassen et al., 1999; Naehr et al., 2000; Sassen et al., 2004). One such seep site is Mississippi Canyon (MC118), Fig. 1a (McGee and Woolsey, 2000; Woolsey et al., 2005; Lutken et al., 2006; Sassen et al., 2006; Lapham et al., 2008a,b). The site is an exemplary natural laboratory that exhibits the diverse and complex biogeochemical characteristics of cold seep ecosystems (Sassen et al., 2004; Lapham et al., 2008b). Two active hydrocarbon vents, characterized by outcropping gas hydrate, bubble vents, and carbonate formations are located in the northwest and southwest portion of the seep, which is approximately one kilometer in diameter (blue circles in Fig. 1b). The goal of the present study was to develop a measurement technique enabling direct and rapid discrimination between authigenic and biogenic carbonate formations including the option to transition this method toward shipboard and potentially *in situ* analysis.

Carbonates form from the local saturation of alkaline earth metal ions (i.e., Ca^{2+}, Mg^{2+}, etc.) in combination with bicarbonate (HCO_3^-) (Formolo et al., 2004; Naehr et al., 2007). Biogenic carbonates are formed in surface waters and within surficial sediments, and eventually accumulate at the seafloor. These carbonates are primarily calcite products of planktonic foraminifera and coccolithophore algae (Milliman, 1974; Pierce and Hart, 1979; Balsam and Beeson, 2003; Sassen et al., 2004; Stanley et al., 2005). The primary carbon source of biogenic carbonates is bicarbonate from carbon dioxide dissolved in

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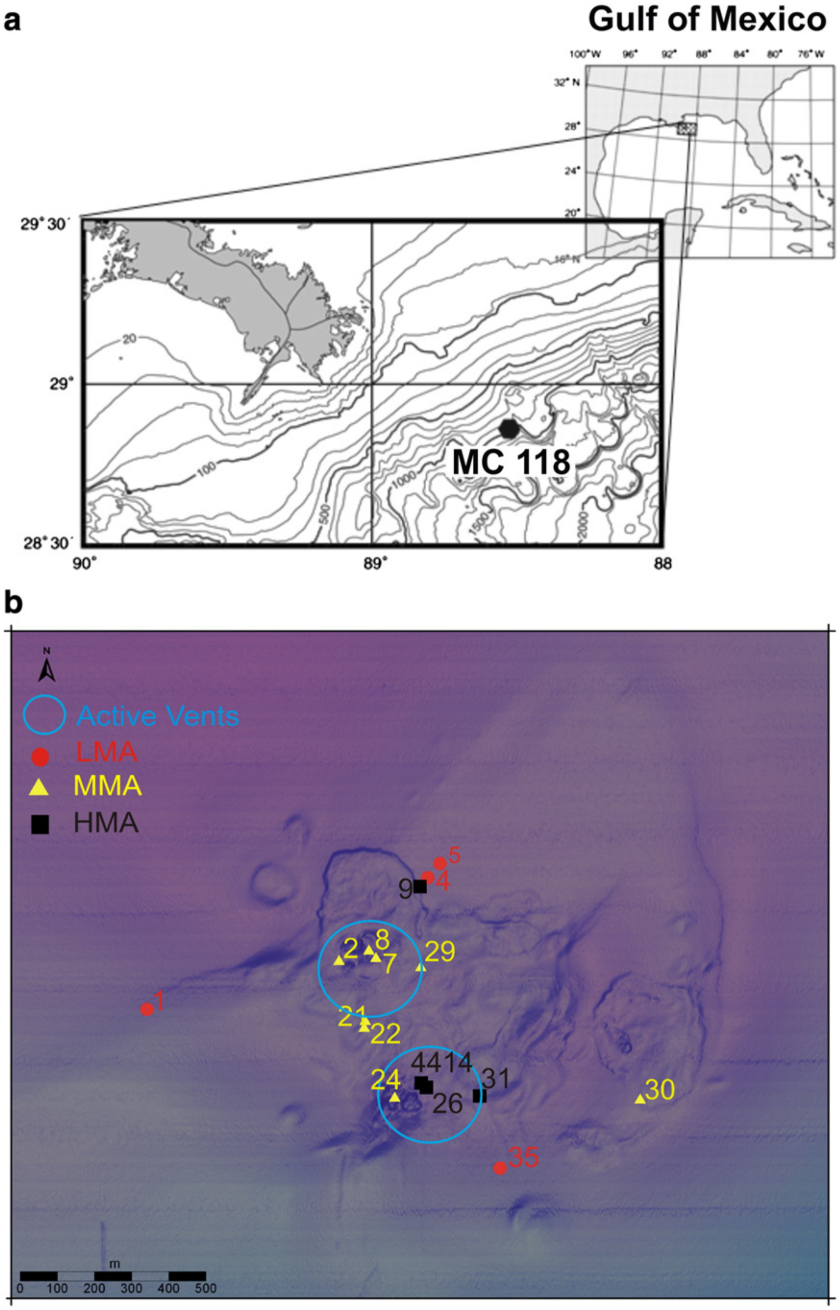

Fig. 1. (a) Map of Gulf of Mexico and close-up of Mississippi Canyon 118 (MC118). (b) MC118 map: red, yellow and black core numbers exhibit microbial activity as low (LMA), moderate (MMA), and high (HMA), respectively. Active vents are shown by blue circle. (Courtesy of Dr. Leonardo Macelloni, Mississippi Mineral Research Institute).

seawater (Fig. 2) (Aharon et al., 1991; Formolo et al., 2004). These biogenic formations are frequently characterized by specific carbon isotopic ratios, which are reported using standard "del" notation $\delta^{13}C$ (‰). The $\delta\ ^{13}C$ isotopic composition of biogenic carbonates is close to 0‰ (Fig. 2) (Aharon et al., 1991; Formolo et al., 2004).

In marine sediments, bicarbonate is a product of microbial oxidation of organic carbon, methane, and hydrocarbons (i.e., petroleum) via anaerobic respiration including bacterial sulfate reduction and anaerobic methane oxidation. These authigenic carbonate formations are imprinted with the stable carbon isotopic composition of their carbon source (Fig. 2; e.g., $\delta^{13}C$ of organic matter = −20‰, $\delta^{13}C$ of non-methane hydrocarbon = −27‰, and $\delta^{13}C$ of methane = −56.5‰) (Roberts and Aharon, 1994; Roberts and Carney, 1997; Naehr et al., 2000). Hence, analyzing carbon isotopic ratios of seep-related minerals provides access to an important geological archive, as these deposits represent one of the few permanent records of an otherwise ephemeral phenomenon (Naehr et al., 2007).

In the deep sea, differentiating between biogenic and authigenic carbonates may elucidate the past seepage history. Standard procedures for such analyses include the determination of bulk carbonate $\delta\ ^{13}C$ values via gas chromatography (GC) coupled with mass spectrometry (MS) (Roberts and Aharon, 1994; Aharon and Fu, 2000; Mazzini et al., 2004). This technique is extremely powerful, however, it may only be used in an appropriate laboratory environment. Consequently, a rapidly responding shipboard or potentially *in situ* research tool, which provides a qualitative and/or semi-quantitative method to characterize carbonate mounds of active or previously active seepage areas is highly demanded. Such a method would work in concert with *in situ* or on-ship/submersible detection and analysis techniques during a field survey to fully characterize a