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Chemostratigraphy of deep-sea Quaternary sediments along the Northern Gulf of Mexico Slope: Quantifying the source and burial of sediments and organic carbon at Mississippi Canyon 118

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A B S T R A C T

This study investigates late Pleistocene to Holocene sedimentation, sedimentary geochemistry, and organic-carbon burial near the Mississippi Canyon 118 (MC118) gas-hydrate and cold-seep field at 890 m water depth – the first National Gas Hydrate Seafloor Observatory. The depositional history is reconstructed, producing a paleoenvironmental context for ongoing geochemical and geophysical monitoring at MC118. A chemostratigraphy is established from sediments that were recovered in 10 shallow gravity cores surrounding the MC118 field on the Northern Gulf of Mexico Slope. Geochemical data (from X-ray fluorescence core scanning, CO_2 coulometry, and inductively coupled plasma emission spectrometry) are evaluated within the context of a detailed chronostratigraphy to map geochemical burial fluxes across MC118 during distinct stratigraphic intervals, each of which represents substantial changes in the depositional environment. These measurements are accompanied by Rock Eval pyrolysis data to aid in the evaluation of organic matter source contributions.

The new dataset provides a means to quantitatively assess temporal and spatial changes in geochemistry and deposition surrounding the MC118 field. Results indicate that terrigenous sediment burial flux is the primary control on temporal changes in sediment composition and organic carbon burial, which are linked to sea level change and Mississippi delta lobe switching. Terrigenous proxy burial fluxes (titanium and insoluble residue) and organic carbon accumulation (primarily "type III" organic matter) are elevated during the interval spanning 14 to 9.5 kilo-years BP, compared to more recent deposition at MC118. Conversely, $CaCO_3$ accumulation (due to pelagic biogenic sources) is more consistent through time, although $CaCO_3$ concentration displays pronounced changes due to variable dilution by clay. The gas-hydrate and cold-seep field itself forms a bathymetric high due to salt diapirism, which is reflected in spatial patterns recorded in the chemostratigraphy. Analyses of geochemical burial fluxes indicate an increase of all sedimentary components (pelagic and terrigenous, including total organic carbon) with increased distance from the field. The results suggest a relatively stable spatial pattern of sedimentation with respect to MC118 during the latest Pleistocene and Holocene, but also a dynamic nature of deposition near the salt diapirism-induced bathymetric high, which contains the present day gas-hydrate deposits and active cold seeps.

1. Introduction

The Mississippi Canyon 118 (MC118) gas-hydrate and cold-seep field is situated on the northern Gulf of Mexico slope in approximately 890 m water depth, 150 km south of Gulfport Mississippi (Fig. 1). This study investigates the chemistry of late Pleistocene to Holocene deep-sea sediments surrounding the MC118 field, to evaluate controls on organic matter burial, reconstruct depositional history, and provide a paleoenvironmental context for ongoing geochemical and geophysical monitoring (Macelloni et al., 2010, 2012; Lapham et al., 2008; McGee, 2006). This new geochemical dataset is integrated with a recently published chronostratigraphy at MC118 (Ingram et al., 2010) to specifically address the following inter-related research questions: (1) How have terrigenous and pelagic inputs, including organic matter burial,

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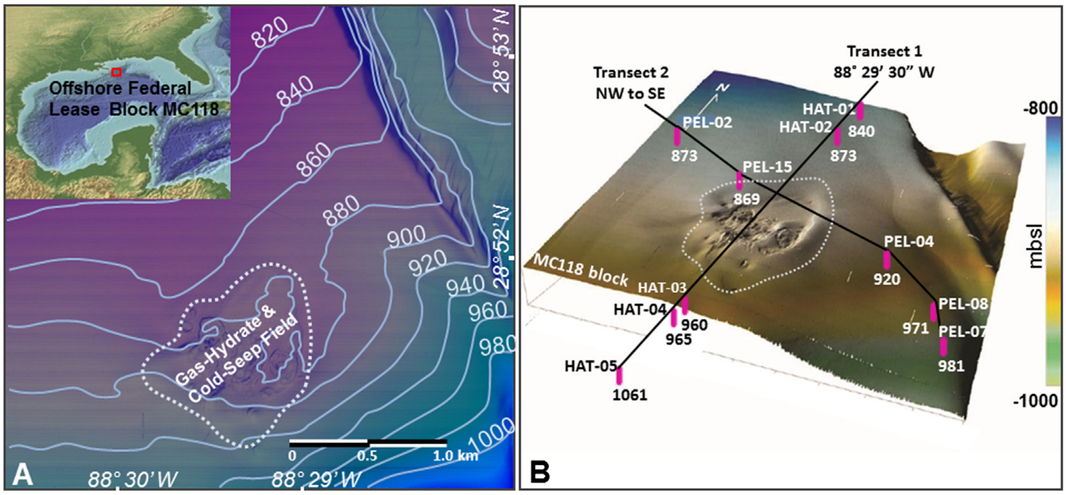

Figure 1. *Panel A*: Bathymetric map of the study area (Block MC118) with labeled contours (light blue) in meters water depth (base map courtesy of Ken Sleeper) with inset digital elevation and bathymetry map (top left; NOAA geophysical data center image) of the Gulf of Mexico Region. Bathymetry provided by the Gulf of Mexico Hydrate Research Consortium (modified after Sleeper et al., 2006). The location of MC118 offshore federal lease block is indicated by the red box in the inset map. The extent of the studied gas hydrate-cold seep field is outlined by the dotted line and is characterized by an area with gas vents, seafloor pockmark features, petroleum seepage, shallow faults, carbonate hard-grounds and gas hydrate deposits. *Panel B*: Bathymetric map of the study site with the location of cores collected during cruises on the R/V *Hatteras* and R/V *Pelican*; base map image is courtesy of the Gulf of Mexico Hydrate Research Consortium. Cores are indicated as vertical magenta lines, with core identification (above) and water depth (in meters) below the core symbol. The edge of the gas hydrate-cold seep field is outlined by a thin dotted white line, black lines connect core symbols and indicate transects onboard the R/V *Hatteras* ("Hatteras Transect") and R/V *Pelican* ("Pelican Transect"). The color bar on the far right indicates water depth. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

varied during the late Pleistocene and Holocene at MC118?, (2) How have global sea-level changes and regional factors such as delta-lobe switching influenced deposition during this period?, and (3) What is the influence of the gas-hydrate and cold seep field – including seafloor warping associated with salt diapirism – on temporal and spatial changes in pelagic and terrigenous sedimentation over the studied area?

To address these research questions, a multi-proxy geochemical approach is employed. X-ray fluorescence (XRF) core scanning (Richter et al., 2006) is conducted on a total of 10 shallow gravity cores strategically distributed across the seafloor (Ingram et al., 2010, Fig. 1), to generate nearly continuous down-core profiles of Al, Ti, K, Si, Fe and Ca. High resolution (cm scale) XRF core scans (counts) are calibrated to concentration data using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES; wt.% Al, Ti, K, Si, Fe, Ca) and CO_2 Coulometry (wt.% $CaCO_3$; Huffman, 1977). These measurements are supplemented by wt.% Total Organic Carbon (TOC) and wt.% insoluble residue from CO_2 coulometry and Rock Eval pyrolysis data for organic matter typing. This new geochemical dataset is integrated with the MC118 chronostratigraphy established by Ingram et al. (2010), to evaluate spatial and temporal variability of burial fluxes for key geochemical components. The elemental proxies used herein reflect pelagic and terrigenous contributions ($CaCO_3$, Ti, insoluble residue) as well as organic carbon burial (TOC accumulation). In total, the study comprises 33,849 unique geochemical measurements, providing an extensive documentation of sediment geochemistry, and an important context for ongoing monitoring at the first National Gas Hydrate Seafloor Observatory (as designated by the US Department of Energy; McGee, 2006).

1.1. Geologic setting: MC118

The MC118 field is the focus of an extensive multi-disciplinary effort to document physical and biogeochemical processes associated with gas hydrates and marine hydrocarbon systems, as part of a larger consortium effort (Simonetti et al., 2013; Lutken et al., 2006; Sassen et al., 2006). The field is located on the upper continental slope of the northern Gulf of Mexico, centered at 28.8523°N and 88.4920°W, at approximately 890 m depth along an overall gently sloping seafloor. Locally, the seafloor within the vicinity of the hydrate and cold seep field is influenced by numerous factors including gas hydrate formation, hydrocarbon (gas and petroleum) seepage and apparent seafloor warping from shallow salt deposits. Visible outcroppings of gas hydrates, faulted carbonate "hard-grounds" and pockmark features consistent with gas and petroleum seepage cover approximately 1 km^2 of the seafloor (Sassen et al., 2006; Sleeper et al., 2006; Macelloni et al., 2010, 2012). While the seaward slope across the study area typically ranges from 3° to 4°, slopes of 10° to 12° are present locally across the area of gas-hydrate formation and cold seepage where pockmarks exists (Sleeper et al., 2006).

Regionally, the bathymetry of the Gulf of Mexico continental slope is heavily influenced by the extensive Louann (Jurassic in age) salt formation (Diegel et al., 1995; Galloway et al., 2000; Jackson, 1995). Deformation of salt within the basin has contributed to the present-day hummocky bathymetry of the northern Gulf of Mexico slope (Jackson, 1995). At MC118, a salt diapir lies approximately 300 m below the ocean floor and is a probable migration pathway for light hydrocarbons sourced by "leaky" reservoirs at depth (Macelloni et al., 2012), such diapirs are prolific along the northern Gulf-of-Mexico slope (McBride, 1998).

Ingram et al. (2010) document the lithostratigraphy, biostratigraphy, and chronostratigraphy for MC118 using the same core material as in the present study. Previous analysis identified four stratigraphic intervals: Unit IA, Unit IB, Unit II, and Unit III (Fig. 2), which also follow distinct changes in chemostratigraphy (Fig. 3). Stratigraphic "Unit IA" is a massive, calcareous nannofossil clay and is Late Holocene (2.3 Ka to present) in age (Fig. 2). Unit IA is defined at its top by the shallowest recovered sediment (core tops), and at its base by the onset of a more $CaCO_3$-rich interval (defining the sub-adjacent "Unit IB"). The higher clay content of Unit IA, while not obvious from visual description, is apparent from published Ca/Ti XRF scans (Ingram et al., 2010). Sediments of Unit IA are relatively thin and extend to 38 cmbsf at its greatest (HAT-02) to less than 5 cm at its shallowest (HAT-03, PEL-04, -15 and -08). At the most