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**Barium Cycling in Shallow Sediment Above Active
Mud Volcanoes in the Gulf of Mexico**

by

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ABSTRACT

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Two mud volcanoes in the Gulf of Mexico were examined to understand barium cycling in shallow seafloor sediment at regions of intense methane expulsion. Due to anaerobic oxidation of methane and sulfate reduction, barium interacts with methane and sulfate, producing barite fronts at the sulfate-methane transition and barium-rich pore fluids underneath. Formation waters likely feed volcanoes and deliver large amounts of Ba^{2+} to the system from below. Locally elevated Ba^{2+} concentrations amplified cycling, producing sigmodal pore water profiles in the shallowest sediment. The expulsion of Ba-rich fluids directly to the water column concentrates barite in surficial sediments, which can also enhance cycling. Further, two types of barium-rich, carbonate nodules were recovered. Rocky nodules resemble buried carbonate crusts, diagenetically altered by pore fluids. Smooth nodules are likely preserved barite fronts marking past sulfate-methane transitions. Both types of nodules can serve as a modern analogue for barite deposits in the geologic record.

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1. Introduction

Shallow sediments on continental slopes hold enormous quantities of low molecular weight hydrocarbons, particularly methane, in the form of gas hydrate, free gas and dissolved gas (e.g. Kvenvolden and Lorenson, 2001). Collectively, these gas phases in marine sediment form open systems, with uninhibited connections to the ocean (Dickens, 2003). Considerable methane leaves through anaerobic oxidation of methane (AOM) near the seafloor at the sulfate-methane transition (SMT) (Reeburgh, 1976; Borowski et al., 1996, 1999; Hoelher et al., 2000). In some places, methane also escapes into the water column via seafloor venting (e.g. Torres et al., 2002a; Lüdmann and Wong, 2003; Sassen et al., 2003) (**Figure 1**). These gas fluxes are important because they fuel various geochemical cycles near the sediment-water interface (e.g. Suess et al., 1999; Tsunogai et al., 2002), and perhaps on a global basis (e.g. Dickens, 2003). The abundance and distribution of gas phases in marine sediment, especially gas hydrate, depends on pressure and temperature (e.g. Sloan, 1990). Methane fluxes from continental slopes might, therefore, vary significantly over time in response to environmental changes (Dickens, 2003). The dynamic nature of seafloor methane systems presents an outstanding issue, and proxies for past methane outflow from marine sediment are clearly needed.

In bathyal environments, past methane fluxes might be assessed using authigenic barite (Dickens, 2001; Torres et al., 2003). As discussed below, methane-charged fluids in deep-marine settings generally contain elevated concentrations of dissolved barium (Ba^{2+}). These fluids precipitate barite (BaSO_4) when they contact sulfate (SO_4^{2-}) in bottom water (Fu et al., 1994; Torres et al., 1996b; Greinert et al., 2002), or in pore water

of shallow sediment (Dean et al., 1978; Brumsack, 1986; Torres et al., 1996a; Dickens, 2001; Kasten et al., 2004; Snyder et al., submitted). Authigenic barite in deep marine strata might, therefore, record past methane venting from the seafloor, or methane consumption by AOM within shallow sediment. Documentation of barite structures around modern seafloor gas vents (Fu et al., 1994; Torres et al., 1996b; Fu and Aharon, 1997; Greinert et al., 2002; Torres et al., 2002b) and barite fronts at the current SMT in deep-marine sediment sequences (Torres et al., 1996a; Dickens, 2001; Snyder et al., submitted) clearly support this idea. Additionally, some barite mounds and nodules that have been found in ancient deep-sea strata appear to reflect past methane expulsion (Torres et al., 2003; Clari et al., 2004). However, remarkably few studies have detailed the geochemical coupling of methane, sulfate, and barium in present-day seafloor sediment, especially around areas of gas venting.

The Gulf of Mexico (GOM) seems an ideal region to examine the postulated coupling between the methane and barium cycles. Gas hydrate and free gas have accumulated in shallow sediment at many locations (e.g. Brooks et al., 1990; MacDonald et al., 1994), and methane venting occurs at numerous mud volcanoes and seeps (e.g. Roberts et al., 1990; Sassen et al., 2003). Methane and other hydrocarbons expelled from mud volcanoes likely drive AOM through sulfate reduction (Suess et al., 1999), although the overall process remain unclear in the GOM (Aharon and Fu, 2003; Joye et al., 2004). Elevated barium concentrations occur in deep formation waters (Macpherson, 1989), and especially in interstitial waters at seeps (Fu and Aharon, 1998).

In this study, I investigate barium cycling in shallow sediment from piston cores across two mud volcanoes in the northern GOM. Unlike most previous work conducted

at other locations (e.g. Torres et al., 1996a; Dickens, 2001; Aloisi et al., 2004), both solid and dissolved constituents are examined within the context of the modern SMT. The work also deviates significantly from previous studies of barium at vent sites in the GOM, which only focus on the upper 40 cm of sediment precisely at the location of venting (Fu et al., 1994; Fu and Aharon, 1997, 1998). The results clearly show a strong geochemical coupling between methane, sulfate, and barium. Hydrocarbon fluxes unquestionably affect barium cycling at these locations, although the link is more complicated than discussed in current literature (Torres et al., 1996a; Dickens, 2001; Aloisi et al., 2004; Snyder et al., submitted).

2. Theoretical Background

2.1 Seafloor Methane Cycling

Significant amounts of organic matter reach the seafloor along many continental margins. Burial of this carbon over time induces microbially mediated reduction-oxidation (redox) reactions, which generally proceed according to free energy yield and affect the chemistry of sediment and pore water (e.g. Oppenheimer, 1960; Froelich et al., 1979; Wakeham, 2002).

In areas of high organic carbon accumulation, available electron acceptors in seawater (O_2 , NO_3 , SO_4^{2-}) or sediment (MnO_2 , Fe_2OOH) are readily consumed. Acetate fermentation and carbon dioxide reduction then begin converting organic matter and its intermediates to biogenic methane (e.g. Wakeham, 2002). At depth, where temperatures exceed $50^\circ C$, thermal cracking of hydrocarbons (kerogen, coal, and oil) also generates thermogenic methane (e.g. Tissot and Welte, 1984; Hunt, 1996; Seewald, 2003). Collectively, biogenic and thermogenic sources produce high concentrations of methane in sediment along many continental margins. These elevated methane concentrations result in an upward migration of gas towards the seafloor, either by advection or diffusion (Tissot and Welte, 1984; Hunt, 1996; Egeberg and Dickens, 1999; Hoelher et al., 2000).

For systems dominated by diffusion, upward methane fluxing fuels AOM and consumption of SO_4^{2-} in shallow sediment (Reeburgh, 1976; Borowski et al., 1996, 1999; Hoelher et al., 2000; Boetius et al., 2000). Typically, complete removal of downward diffusing sulfate and upward migrating methane occurs across a thin depth interval. This horizon, termed the SMT, often lies between 10 and 40 m below seafloor (mbsf) in areas of slow methane flux (Borowski et al., 1996, 1999; D'Hondt et al., 2002). In advection-

dominated regimes, however, methane and other hydrocarbons can migrate rapidly along conduits to drive both AOM at or near the seafloor and gas venting (Suess et al, 1999; Aharon and Fu, 2003; Joye et al., 2004) (**Figure 1**). This type of regime characterizes mud volcanoes and seeps in the GOM.

In theory, the upward flux of methane should dictate the rate of AOM and the depth of the SMT (Reeburgh, 1976; Borowski et al., 1996, 1999; Hoelher et al., 2000; D'Hondt et al., 2002). Consequently, complete sulfate consumption should occur close to the sediment-water interface at active mud volcanoes. Away from locations of methane fluxing, the SMT should deepen (**Figure 1**). This expectation is suggested by limited studies in the GOM (Aharon and Fu, 2000, 2003; Joye et al., 2004).

2.2 Methane-Sulfate-Barium Coupling in Shallow Sediments

Upward fluxing methane impacts the geochemical cycling of barium in marine sediments, particularly in deep waters. Micro-crystalline barite forms in the water column when sinking organic carbon decays (Ganeshram et al., 2003), and reaches the seafloor in most bathyal settings (e.g. Chow and Goldberg, 1960; Dehairs et al., 1980). Although some of this barite dissolves near the seafloor, much is buried along with other sediment (Dehairs et al., 1980). When this barite passes through a SMT and into sulfate-depleted, methane-rich fluids, it dissolves, producing high interstitial Ba^{2+} concentrations (**Figure 2**). In diffusive systems, dissolved Ba^{2+} then moves upwards to re-precipitate barite just above the SMT (Torres et al, 1996a; Dickens, 2001; Kasten et al., 2004; Snyder et al., submitted). These barite fronts can record the depth of the SMT and, ultimately, constrain the flux of methane over time (Dickens, 2001). In areas of high

3. Regional Geology and Geochemistry

The GOM is an area dominated by active salt tectonism, where structural features, bathymetry and deep formational water chemistry reflect the movement of Middle to Late Jurassic evaporite deposits (e.g. Worrall and Snelson, 1989). Down-slope migration of salt beginning in the late Jurassic and early Cretaceous has caused extensional faulting in the north and contractional faulting in the south (e.g. Worrall and Snelson, 1989; Peel et al., 1995; McBride, 1998). A series of structural highs and mini-basins have therefore developed between the shelf/slope break and the Sigsbee Escarpment (e.g. Diegel et al., 1995; Peel et al., 1995; McBride, 1998) (**Figure 3**). The seafloor bathymetry in this region is hummocky, reflecting these underlying structural elements (e.g. Worrall and Snelson, 1989; McBride, 1995).

As salt bodies move, they create differential stress on surrounding sedimentary packages, which induces fracturing and faulting of strata (e.g. Jackson et al., 1994; Rowan et al. 1999), as well as the upward migration of fluids (Roberts and Nunn, 1995; Revil and Cathles, 2002). The phenomenon may be related because changes in fluid pressure can cause faults to expand and contract (Roberts and Nunn, 1995; Revil and Cathles, 2002). In the GOM, basinal fluids are often hydrocarbon-rich brines. The brines form when salt dissolves at depth, and they contain greatly elevated concentrations of chloride, calcium, sodium, potassium, bromide and trace metals, including lead, zinc, manganese and barium (e.g. Manheim and Bischoff, 1969; Kharaka et al., 1987; Macpherson, 1989).

Seeps and mud volcanoes form where fluids rise from depth and breach the seafloor (e.g. O'Brien, 1968; Brown, 1990; Milkov, 2000; Dimitrov, 2002). Common

features of these mud volcanoes include: 1) a central caldera or crater; 2) mud flows; 3) side or periphery vents; and 4) the visible expulsion of fluid into the overlying water column (e.g. Neurauter and Roberts, 1994; Milkov et al., 2004).

Fluids emanating from mud volcanoes in the GOM have a distinct chemistry. Light hydrocarbons (C_1 - C_6), predominately methane (C_1), are a ubiquitous component (Reitsema et al., 1978; Roberts et al., 1990; MacDonald et al., 2000; Sassen et al., 2003). Because they originate at depth, the fluids typically have high concentrations of dissolved species found in brines (Kharaka et al., 1987; Macpherson, 1989). Notably, elevated barium concentrations have been reported in pore waters from the upper 40 cm of sediment at a few seep sites on the upper slope (Fu and Aharon, 1998).

4. Site Description and Sampling

4.1 Site Description

Two sites of active methane expulsion in the GOM were examined in this study: one in Garden Banks lease block 425 (GB 425), and one at the border between Mississippi Canyon lease blocks 852 and 853 (MC 852/853) (**Figure 3**). Seafloor morphology exhibits conical features with significant relief at both sites. Sediment cores at both locations also contain rip-up clasts and evidence of sediment flow. Based on these criteria, both features can be classified as mud volcanoes. The mud volcanoes in this study lie approximately 10.9 km (Garden Banks) and 58.6 km (Mississippi Canyon) from those examined by Aharon and colleagues (**Figure 3**).

The GB 425 mud volcano is located at 27.555°N, 92.540°W on the upper slope between 550 and 600 m water depth (**Figure 3a**). The major vent at this site is conical with ~ 40 m relief. A small, side vent with 20 m of gently dipping relief lies about 1.5 km to the south. A second main volcano, with ~ 40 m relief, is located approximately 2.7 km north but was not examined in this study.

The MC 852/853 mud volcano is located at 28.123°N, 89.140°W in a submarine canyon at water depths between 1010 and 1100 m (**Figure 3c**). Unlike at Garden Banks, the mud volcano at Mississippi Canyon is a single, distinct vent with bathymetric relief of 40 m.

Although we classify both vent structures as mud volcanoes, they have different characteristics that may affect chemistry near the seafloor. First, the mud volcano at MC 852/853 (~1000 m) is in water twice as deep as the mud volcano at GB 425 (~550 m). Other factors (i.e. temperature, salinity, gas composition) being equal, the gas hydrate

stability zone is thinner at GB 425. Second, recent heat flow measurements (Ruppel et al., in press) suggest a much higher flux of heat and fluids at MC 852/853.

4.2 Sample Collection

Cruise 08/02 of the *R/V Seward Johnson I* (October 17 through November 1, 2002) was dedicated to understanding physical and chemical fluxes around vent structures on the northern slope of the GOM. The main tool for obtaining sediment was a piston corer (PC) deployed as a gravity corer for mechanical reasons. At GB 425, 15 cores were collected in a “T” pattern across the mud volcano (**Figure 3b**). A similar coring strategy was employed at MC 852/853, although only six cores were collected (**Figure 3c**). The location, water depth, length and proximity to the center of the mud volcano have been compiled for each core (**Table 1**). Core lengths at both sites ranged from 1.5 m to 3.5 m (**Table 1**).

Upon retrieval, cores were immediately inspected for gas hydrates both visually and using a handheld infrared camera (ThermaCAM 2000 by FLIR systems; Ford et al., 2003). Intervals of gas hydrate were detected in two cores from MC 852/853, MC-PC-25 and MC-PC-30 (Weinberger, unpublished data) (**Figure 4**). This observation is important because gas hydrate dissociation during core recovery releases fresh water, which can dilute dissolved constituents in pore water (Hesse and Harrison, 1981; Egeberg and Dickens, 1999). The presence of gas hydrate within 3 m of the seafloor also implies a steep hydrocarbon concentration gradient.

Whole-round sediment intervals were cut from cores on deck for pore water sampling. To minimize oxidation, these were transported immediately to a shipboard

chemistry laboratory for pore water extraction. Samples were trimmed to remove sediment contamination and placed into a modified Reeburgh squeezing vessel (Reeburgh, 1967) pressurized with N₂ at 40 psi. The Reeburgh system uses gas pressure against rubber diaphragms to squeeze interstitial fluids from sediment through a series of filtering membranes and into a syringe. Once collected, pore waters were filtered again with a Low Protein Binding Durapore (PVDF) membrane (0.22 µm). The first 1 mL aliquot was taken for shipboard salinity measurements. A second 2 mL aliquot was treated with 0.01 mL of concentrated, ultrapure HNO₃ to inhibit metal precipitation, and stored in a sealed glass vial for shorebased metal analyses. A third 2 mL aliquot was purged with N₂ gas for one minute to degas dissolved sulfide, and sealed in a glass vial for shorebased anion measurements.

Unsampled core intervals were temporarily stored in a refrigerated van on ship and subsequently transferred to a cold room (~ 4.5°C) at Georgia Tech University for shore-based description and sampling. Cores were described visually for their sediment color, grain size and texture (**Appendix I**). The most striking observation in general core descriptions are cm-scale nodules (**Appendix IV**), which were found in six of the cores, all proximal to the center of the mud volcanoes (**Figures 3, 4**).

Bulk sediment samples of ~3 cm³ were taken down 15 of the cores for chemical analyses. Typically, these samples were spaced every 10 cm. However, using the pore water barium and sulfate profiles (discussed in the following sections), the SMT was identified in 10 of these cores (and 18 of 21 cores in total). Samples were taken every 2 cm through these zones. All nodules were also removed for chemical and mineralogical analyses.

5. Laboratory Analyses

5.1 Pore Fluid Analysis

Salinity was measured on the ship using a handheld refractometer. The aliquots taken for anion analyses were also re-examined on shore with a refractometer to verify shipboard measurements, and to determine whether evaporation had occurred. Salinity measurements were reproducible within 5%, so minimal water loss occurred during transport and storage.

Pore water Cl^- and SO_4^{2-} were analyzed using a Dionex Ion Chromatograph (IC) system with an IonPac AS11-HC column using 26.5 mM NaOH eluent at the Environmental Engineering Laboratory, Rice University. Concentrations were determined by comparing sample peak intensities to standard peaks having known concentrations. All Cl^- concentrations were reproducible within 10% of one another, even at high concentrations ($\text{Cl}^- > 2700 \text{ mM}$). The precision of SO_4^{2-} concentrations was highly variable. The basic problem was determining low SO_4^{2-} concentrations in waters of extremely high salinity ($S > 100 \text{ ‰}$), which compromises sulfate detection on the IC. It was hoped that different operating conditions on a different instrument could improve SO_4^{2-} measurements. Consequently, all fluid samples were re-measured on a Dionex IC in the Laboratory for Oceanographic and Environmental Research (LOER), Texas A&M University, Galveston. These SO_4^{2-} measurements also had low precision at low concentrations. As a result, sulfate profiles presented in this paper are only valid in the general sense.

Pore water metal concentrations were analyzed using a Varian Vista Pro ICP-AES in the Geochemistry Laboratory at Rice University. Elements measured (and their

corresponding lines) included Ca (396.847 nm), K (769.897 nm), Mg (280.270 nm and 383.829 nm), Sr (407.771 nm), and Ba (455.403 nm). Concentrations were determined by comparing peak areas to those determined by analyzing standard solutions with a similar NaCl matrix and known metal concentrations. A calibration run measuring standards and blanks was made prior to every 15 samples. An internal standard of Yttrium (1ppm) was also added to all standards and samples to monitor any instrumental drift. The precision of reported metal concentrations was determined by analyzing true replicates. Multiple analyses of samples consistently gave concentrations within 4% for each element.

5.2 Sediment Analysis

Sediment samples were washed three times with deionized water (18 M Ω) to remove dissolved ions, freeze-dried to remove water, and ground with a mortar and pestle. Approximately 0.1 g subsamples were weighed and digested in a solution containing 9.0 mL concentrated HCl and 3.0 mL concentrated HNO₃ for approximately 18 hours in a 70°C water bath. The digested solution was decanted and diluted with deionized water. This solution is assumed to comprise the “extractable”, non-terrigenous fraction of sediment; the remaining terrigenous (aluminosilicate) fraction (Rutten and de Lange, 2002) was not analyzed in this study. Digested solutions were then analyzed for Ca, K, Mg, Sr and Ba on the ICP-AES according to the procedure above. The precision of these measurements was determined by digesting and analyzing true replicate samples, and is within 5% for each element.

After measuring the extractable Ba content, five sediment samples from cores at MC 852/853 and containing variable amounts of Ba were subjected to a sequential extraction (Paytan et al., 1993; Eagle et al. 2003). The purpose of these extractions was to assess whether barite is the dominant carrier of Ba in certain sediment samples. Briefly, the extraction involved a series of 24-hour treatments using acetic acid, sodium hypochlorite solution, hydroxylamine hydrochloride solution, nitric acid and hydrofluoric acid. A barite standard was also subjected to this extraction procedure to determine how the process affected barite crystals. After extractions, residual material was weighed and examined using a JEOL JXA 840 Scanning Electron Microscope (SEM) equipped with a Energy Dispersive Spectrometer (EDS) at Rice University (**Appendix II**).

5.3 Nodules

Nodules were rinsed with deionized water to remove surrounding mud, photographed, and split in half with a trim saw. One half of each nodule was dried overnight in an oven at 80°C and then ground, powdered, digested and analyzed for elemental chemistry by ICP-AES as described above. Bulk mineralogy was also determined on a portion of the washed powder using a D/Max 2000/PC Rigaku X-Ray Diffraction (XRD) system equipped with a fixed monochromator in the Geochemistry Laboratory at Rice University. Samples were measured using a continuous scan from 20 to 50 2 θ at 40 kV and 40mA. The other halves of the concretions were used to make thin sections to assess their general fabric and texture. Thin sections were examined using a petrographic microscope and the aforementioned SEM-EDS system.

6. Results

6.1 Pore Fluid Chemistry

Pore water salinity (S) ranges from 35 ‰ to 130 ‰ at both GB 425 and MC 852/853 (**Table 2**). Chloride (Cl^-) covaries with S at both sites ($r^2 = 0.9083$), ranging from 500 to 2700 mM (**Table 2; Figure 4**). The extreme highs in S and Cl^- come from the base of cores taken within 300 m of the mud volcano centers; the lower values, approaching those of seawater, come from near-surface sediment and from outlying cores. Depth profiles of S and Cl^- that terminate at extremely high concentrations (e.g. in MC-PC-25 and MC-PC-30) are concave-down, suggesting strong upward fluid advection. This is consistent with heat flow measurements across the mud volcanoes (Ruppel et al., in press). By contrast, S and Cl^- depth profiles characterized by generally low concentrations (e.g. in GB-PC-15, GB-PC-21, and GB-PC-22) are either concave-up, suggesting downward hydrologic flow, or straight, indicating a more diffusive regime (**Figure 4**). Overall, the shapes of S and Cl^- profiles and their distribution with respect to proximal mud volcanoes are similar at GB 425 and MC 852/853.

Sulfate (SO_4^{2-}) concentrations range from 28 mM to below detection (<0.10 mM) at both GB 425 and MC 852/853 (**Table 2**). Unlike S and Cl^- , however, SO_4^{2-} concentrations are generally lowest near the center of the mud volcanoes. Cores closest to venting sites have SO_4^{2-} concentrations <5 mM within 10 cm below the seafloor (cmbsf), suggesting that SO_4^{2-} consumption occurs at or very close to the sediment-water interface (Aharon and Fu, 2003; Joye et al., 2004). In cores taken from flanks of the mud volcanoes, however, a decreasing SO_4^{2-} gradient can be observed from seawater concentrations (~ 28 mM) at the sediment-water interface. In some cores, this gradient is

sufficiently high so that SO_4^{2-} drops below 0.10 mM within the core. This depth, presumably the SMT, depends on proximity to the mud volcano. In general, the SMT deepens away from the mud volcanoes (**Figure 4**). Overall, an inverse relationship exists between SO_4^{2-} and Cl^- . Concentrations of SO_4^{2-} are measurable where Cl^- values are near those of seawater; SO_4^{2-} is < 0.10 mM where Cl^- concentrations exceed twice that of seawater (1120 mM).

Dissolved barium (Ba^{2+}) concentrations are extremely high in pore waters at the mud volcanoes, reaching 7,800 μM at 171 cmbsf in Core GB-PC-24 and 12,000 μM at 72.5 cmbsf in Core MC-PC-30 (**Table 3**). By contrast, Ba^{2+} concentrations are < 2.0 μM in pore waters collected from the upper 200 cm of cores away from the mud volcanoes. However, in some cores from the flanks of the mud volcanoes, Ba^{2+} concentrations do increase significantly with depth, reaching 1,700 μM at 347.5 cmbsf in Core GB-PC-22, and 330 μM at 272 cmbsf in Core MC-PC-26. Generally, dissolved Ba^{2+} concentrations are uniformly low (< 3 μM) above the SMT, but increase rapidly below this horizon (**Figure 4**). A notable exception occurs in the two cores from the center of the mud volcano at MC 852/853. In MC-PC-25 and MC-PC-30, pore water Ba^{2+} concentrations are very high in shallow sediment, but decrease down-core.

Like dissolved Ba^{2+} , concentrations of dissolved calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and strontium (Sr^{2+}) are greatly elevated near the center of mud volcanoes (**Figure 5**). At GB 425, maximum values are 38 mM for Ca^{2+} , 49 mM for Mg^{2+} , 38 mM for K^+ , and 2.7 mM for Sr^{2+} . At MC 852/853, maximum values are 65 mM for Ca^{2+} , 117 mM for Mg^{2+} , 40 mM for K^+ , and 1.5 mM for Sr^{2+} (**Table 3**). Concentrations of these cations are generally lower and much closer to those of seawater

on the flanks of the mud volcanoes. The shape of Ca^{2+} , Mg^{2+} , K^+ and Sr^{2+} profiles generally mimic those of Ba^{2+} and Cl^- in cores collected close to the center of the mud volcanoes. Only three Mg^{2+} profiles deviate from this general rule (GB-PC-15; GB-PC-22; GB-PC-24), where Ba^{2+} is increasing while Mg^{2+} is decreasing. Conversely, cores taken from the flanks typically yield straight pore water profiles for major elements.

6.2 Sediment Chemistry

The extractable Ba content of most sediment examined, especially from cores away from the mud volcanoes, ranges from 70 to 2,000 mg/kg (**Table 4**). Superimposed on these modest “background” Ba contents, however, are discrete horizons of significantly elevated Ba in eight of the cores (**Figure 4**). Three cores (GB-PC-24, MC-PC-25 and MC-PC-30) have two to four maxima where solid phase Ba content reaches between 14,600 and 23,000 mg/kg. Another five cores (GB-PC-15, GB-PC-21, GB-PC-22, MC-PC-26 and MC-PC-29) have a single peak where Ba content exceeds 20,000 mg/kg. The depths of these sedimentary Ba peaks closely correspond with (1) the depth of SO_4^{2-} depletion (and the inferred SMT), (2) horizons containing nodules, or (3) both (**Figure 4**). Like pore waters, the solid phase “background” Ba content as well as the number and magnitude of Ba maxima are greatest at the center of the mud volcanoes and diminish outward. As a result, a concentric pattern of Ba content exists in sediment around the mud volcanoes, even in samples within 2 cm of the seafloor (**Figure 6**).

Sequential extractions show that barite dominates the Ba-rich sediment intervals. After the procedure to isolate barite, samples from Ba maxima (MC-PC-30, 0-2 cm and 170-172 cm) had the greatest proportion of material remaining (>13%). Moreover, barite

crystals, up to 15 μm in width, are very common in these high yield extractions (**Figure 7**). By contrast, samples of sediment with low total Ba contents (MC-PC-27, 0-2 cm; MC-PC-30, 50-52 and 140-142 cm) render relatively low amounts of material after extraction (<3%). These residues also have little to no barite. Instead, SEM examinations show these residues are primarily titanium oxides and alumino-silicate minerals, such as clays (**Figure 7**).

Extractable major element contents vary little from core to core (**Figure 5**). Within a given core, contents can range from 7 to 190 g/kg for Ca; 8 to 25 g/kg for Mg; 1 to 21 g/kg for K; and 68 to 966 mg/kg for Sr (**Table 4**). Of the elements measured, only Sr profiles show discreet horizons of elevated content, as high as 3,100 mg/kg. Although Sr horizons do correspond to nodule or sulfate depletion horizons, they do not consistently correlate to a specific type of horizon and are not found in every core.

6.3 Nodules

Nodules found in the cores can be described as either rocky or smooth, depending on morphology and texture (**Figure 8**). Rocky nodules are rough conglomerates with sand, fossil fragments and other debris welded together in a grey matrix with large macroscopic voids. These nodules are friable and crumble easily. Smooth nodules have a homogeneous surface, generally elongate shape, and consist of well-sorted sand in a mud matrix. Smooth nodules are also more consolidated than rocky nodules. In the 15 cores examined, four rocky nodules and seven smooth nodules were recovered from a total of six cores (**Table 5**).

Both rocky and smooth nodules comprise variable amounts of six minerals, at least as detected by XRD (**Table 5**). Calcite dominates all of the nodules with the exception of nodule G-13N1, which is predominately composed of barite. Assuming that peak areas on diffraction profiles are related to mineral abundances, barite is the second most abundant mineral in five nodules. In the other five nodules, barite was not detected by XRD. Other accessory minerals in the nodules include high-magnesium calcite, aragonite and quartz. It is interesting to note, though, that quartz was only found in nodules from cores close to the mud volcanoes (**Appendix III**). Some of the barite reported for six of the nodules are lead-rich according to the d-spacing determined through XRD; however, this was not confirmed with chemical data.

Rocky nodules in thin section (**Figures 8, 9**) are amalgamations of well-rounded carbonate clasts and abundant quartz grains of variable size (20 - 200 μm) and roundness. Microfossils are common, and include foraminifera and bi-valve fragments. Brown organic material (presumably kerogen; Fu and Aharon, 1997) also exists near the outer edges of nodules. Importantly, copious void spaces in these nodules are filled with small, blocky barite crystals. This barite in-filling is most complete in the deepest rocky nodules (**Appendix IV**).

In contrast, smooth nodules in thin section have a relatively uniform carbonate matrix containing barite crystals, quartz grains and quartz veins (**Figure 8 and 9; Appendix IV**). Barite occurs in two crystal habits, which appear to correspond to the concentration of dissolved Ba^{2+} in surrounding pore waters. In Ba-rich waters at the center of mud volcanoes, acicular barite crystals (150-200 μm) form radial patterns. Conversely, in Ba-poor waters on the volcano flanks, small blocky barite crystals (<10

μm) are scattered throughout the matrix. Quartz grains vary in size, but are typically <10 μm and finer than those in rocky nodules. Many of these grains are secondary, showing undulating extinction and forming veins that cross-cut acicular barite crystals (**Figure 9**).

Given the above mineralogy and thin section descriptions, it is not surprising that nodules contain high contents of Ca and Mg, from 140 to 290 g/kg and 80 to 360 g/kg, respectively. Similarly, Ba and Sr are also elevated, ranging from 460 to 24,000 mg/kg for Ba, and from 1,100 to 2,600 mg/kg for Sr. It is noteworthy that nodules with the smallest barite peaks on XRD traces also have the lowest Ba contents (**Table 6**). Less concentrated is K, from 8 to 26 g/kg (**Table 6**). Although not measured, the remaining mass probably consists of mostly O, C and, to a lesser extent, S. Interestingly, the Ba content of rocky nodules in core MC-PC-30 increases with depth. The shallow rocky nodule has 17,000 mg/kg Ba, whereas the deep rocky nodule has 24,000 mg/kg Ba.

7. Discussion

7.1 Sulfate-Methane Transition Across Mud Volcanoes

The relationship between pore water methane and sulfate concentrations is well documented for gas-charged sediment along continental margins, at least at regional scale (Borowski et al., 1999; D'Hondt et al., 2002). In general, sulfate drops from ~ 28 mM at the seafloor to ~ 0 mM at some relatively shallow depth. Below this depth - the SMT - dissolved methane increases rapidly. In systems dominated by diffusion, such as Blake Ridge, the SMT typically occurs between 5 and 50 mbsf (Borowski et al., 1996, 1999; D'Hondt et al., 2002). Multiple lines of evidence suggest that the SMT depends on the upward methane flux at these locations (Borowski et al., 1996, 1999; Dickens, 2003). The SMT is much shallower in systems dominated by fluid advection, sometimes occurring within the upper 30 cmbsf (Tsunogai et al., 2002; Aharon and Fu, 2003; Haese et al., 2003). Consumption of SO_4^{2-} in these environments might also involve higher hydrocarbons (Joye et al., 2004), so that the SMT may reflect total hydrocarbon flux instead of just methane. Nevertheless, the SMT should shoal significantly across a mud volcano (**Figure 1**).

Methane and other hydrocarbons concentrations were not measured in this study. Given the ubiquitous relationship between CH_4 and SO_4^{2-} found elsewhere, however, the SO_4^{2-} profiles can be used to infer the SMT (**Figure 4**). Specifically, the SMT is placed at the depth where pore water SO_4^{2-} drops to below detection. With this assumption, the SMT varies predictably across both mud volcanoes: it lies at or near the sediment-water interface at the center, and deepens on the flanks. Intense hydrocarbon expulsion at the center of mud volcanoes effectively pushes the SMT to the seafloor. With lower

hydrocarbon fluxes on the flanks, SO_4^{2-} diffuses from overlying seawater into the sediment. Thus, mud volcanism in the GOM leads to considerable variation in the depth of the SMT at the local (< 1 km) scale.

Several recent studies have tried to quantify the rates of AOM and SO_4^{2-} removal in sediment at seeps and mud volcanoes in the GOM (Aharon and Fu, 2000, 2003; Joye et al., 2004). These investigations, generally using limited cores and samples collected adjacent to venting and various other tracers, have proposed that SO_4^{2-} reduction is coupled to CH_4 and hydrocarbon fluxing in the GOM (Aharon and Fu, 2000, 2003; Joye et al., 2004). This interpretation is inconsistent with the clear correlation between the location of venting and the SMT (**Figure 4**).

7.2 Barite Fronts at the Sulfate-Methane Transition

Investigations of deep-sea sediment cores away from the GOM (Brumsack, 1986; Torres et al., 1996a; Dickens, 2001; Snyder et al., submitted) have suggested that characteristic barium profiles develop across the SMT because of barite dissolution and re-precipitation (**Figure 2**). Above the SMT, dissolved Ba^{2+} concentrations are very low and some barite occurs in sediment through pelagic accumulation. Below the SMT, dissolved Ba^{2+} rapidly increases as the barite dissolves. A front of labile barium forms just above the SMT when dissolved Ba^{2+} released at depth migrates up and precipitates as barite upon contact with seawater SO_4^{2-} .

The expected barium profiles are observed in sediment around mud volcanoes in the GOM. Of the 15 cores examined, eight contain a discrete horizon of elevated sedimentary barium that lies within 0 to 30 cm above the SMT (**Figure 4**). Pore water

Ba^{2+} concentrations in these cores are less than $3.0\ \mu\text{M}$ above barium fronts, but increase by three to four orders of magnitude immediately below. Sulfate does not drop below $2.5\ \text{mM}$ within the other seven cores, so neither a solid barium front nor a rise in dissolved Ba^{2+} is observed (although both likely occur deeper beyond the length of the cores).

In theory, the solid phase barium front immediately above the SMT should comprise barite (**Figure 2**), although this has been demonstrated rarely (Snyder et al., submitted). Sequential extractions of sediment from cores in this study confirm that barite dominates the solid barium fronts (**Figure 7**). All data in this paper indicate that barium cycles across the SMT because of barite dissolution and precipitation. Moreover, because the SMT varies systematically across the mud volcano, and because the upward flux of hydrocarbons controls the interstitial SO_4^{2-} concentrations, hydrocarbons also dictate dissolved Ba^{2+} concentrations and the presence of barite.

Barium cycling in sediments around mud volcanoes in the GOM is generally analogous to that found or predicted at other deep-sea locations (Brumsack, 1986; Torres et al., 1996a; Dickens, 2001; Aloisi et al., 2004; Snyder et al., submitted). However, this cycling is more complicated than implied in current literature (e.g. Dickens, 2001). First, basinal fluids driving mud volcanism contain significant dissolved ions, including Ba^{2+} . Thus, not all barium comes from the surface. Second, barite-rich carbonate nodules are found below the SMT. These could provide a local source for dissolved Ba^{2+} . Third, expulsion of Ba-rich fluids into bottom water might occur during mud volcano eruptions. Potentially, this process amplifies overall barium cycling. These complexities are discussed below.

7.3 Effect of Deep Brines and Formation Waters

Compared to seawater, formation waters collected from deep boreholes in the northern GOM are greatly enriched in Cl^- and a suite of major cations (e.g. Kharaka et al., 1987; Macpherson, 1989). These basinal brines also contain high dissolved Ba^{2+} , with concentrations between 45 and 30,000 μM (Macpherson, 1989). The elevated Cl^- concentrations result from dissolution of salt (Land and Macpherson, 1992). The high Ba^{2+} concentrations may come from diagenesis of potassium-rich feldspars in arkosic sandstone horizons (Macpherson, 1989).

Pore waters from the center of the mud volcanoes have much higher dissolved Ba^{2+} concentrations in than those reported from most marine environments, including other regions with CH_4 -charged sediment. For example, at Blake Ridge, dissolved Ba^{2+} concentrations do not exceed 60 μM , even below the SMT (Snyder et al., submitted). Here, it is important to highlight three observations (**Figure 10**). First, both mud volcano pore waters and deep formation waters have high Cl^- and Ba^{2+} concentrations. Second, dissolved Cl^- and Ba^{2+} concentrations generally covary in both fluids. Third, pore water Cl^- concentrations at the mud volcanoes increase with depth from seawater values near the seafloor. Collectively, these observations suggest that upward fluid migration supplies large amounts of both Cl^- and Ba^{2+} . At nearby mud volcanoes (**Figure 3**), some pore fluid samples from the upper 40 cm of a few cores have been examined for Ba^{2+} and Cl^- concentrations as well as oxygen, strontium, and sulfur isotopes compositions (Fu and Aharon, 1998; Aharon et al., 2001). Correlations between the elemental and isotopic properties also suggest that significant amounts of Ba^{2+} come from depth (Fu and Aharon, 1998; Aharon et al., 2001).

In current views for barium cycling across the SMT (Torres et al., 1996a; Dickens, 2001; Snyder et al., submitted), remobilized pelagic barite is the main source for elevated dissolved Ba^{2+} and shallow barite fronts. Although pelagic barite may contribute barium to sediment around GOM mud volcanoes, it is likely that fluids from below supply much of the barium to the system.

The barium contribution from deep formation waters to shallow sediment around mud volcanoes over time might be assessed using the accumulation and chemical composition of sediment, and the flux and dissolved concentrations of vent fluids. Significant curvature in the salinity (and heat) profiles above the mud volcanoes suggests strong upward advection of water, on the order of 0.05 to 0.15 m/yr across MC 853/854 (Ruppel et al., in press). Given the bathymetric expression of this mud volcano ($\sim 1 \text{ km}^2$), and the dissolved Ba^{2+} concentrations at the base of cores (300 to 1200 μM), formation waters may contribute around 0.03 to 0.12 $\text{mol/m}^2\text{-yr}$ of Ba to shallow sediment at MC 853/854. This is orders of magnitude faster than Ba is supplied to sediment from the pelagic rain of organic carbon (e.g., Pfeifer et al., 2001). The average extractable Ba content in the upper few m of sediment at MC 853/854 is difficult to assess because of the extreme heterogeneity (**Figure 6**), although 1000 mg/kg seems reasonable (**Table 4**). Formation fluids could supply this excess barium in about 1000 years.

Despite the high input of Ba from below, the dissolved Cl^- and Ba^{2+} concentrations of relevant fluids (**Figure 10**) reveal an additional constraint regarding barium cycling in the time domain: for a given Cl^- concentration, formation waters generally contain less Ba^{2+} than shallow pore waters at mud volcanoes. The simplest explanation is that shallow pore waters hold excess dissolved Ba^{2+} compared to formation

waters. Although upward advection of fluids supply much of the barium to shallow sediment at the GOM mud volcanoes, processes within the upper few meters of sediment cycle and retain this barium over time. This interpretation contrasts somewhat with previous work (Fu and Aharon, 1998), which assumed that high Ba^{2+} concentrations reflect similarly elevated concentrations at depth.

Depth profiles of dissolved Ba^{2+} from the center of the mud volcano at MC 852/853 hint at this shallow cycling and retention of barium. Both cores MC-PC-30 and MC-PC-25 have a marked rise in dissolved Ba^{2+} below a near seafloor SMT. However, dissolved Ba^{2+} concentrations then decrease toward those formation water values at the base of these cores (**Figures 4, 10**). Evidently, dissolved Ba^{2+} is being released and consumed in the upper few meters of sediment above the mud volcanoes.

7.4 Carbonate Nodules

The barite-rich nodules found at the center of the mud volcanoes (**Figure 8, 9**) complicate ideas regarding CH_4 fluxing and the shallow barium cycle. Authigenic barite accumulations, either as mounds on the seafloor or fronts in the sediment, are generally considered to have formed in SO_4^{2-} -rich waters above the SMT (e.g. Brumsack, 1986; Torres et al., 1996a, 2002b; Greinert et al., 2002; Snyder et al., submitted). However, many of the nodules at the mud volcanoes exist below the SMT (**Figure 4**), where barite should dissolve. Additionally, the distinct morphologies and barite crystal habits also suggest that rocky and smooth nodules formed by two different processes.

Rocky nodules have three distinguishing characteristics that hint at their genesis. First, the conglomeratic texture of large (~ 1 cm), poorly supported carbonate clasts

suggests fracturing by fluids. Second, the sizable (5 cm) bivalve fragments in some nodules (**Figure 9**) indicate they formed at or near the seafloor. Finally, the infilling of large and common void spaces by anhedral barite crystals (**Figure 8, 9; Appendix IV**) suggests that barite rapidly precipitated into pre-existing space.

A specific sequence of processes at mud volcanoes may produce rocky nodules (**Figure 11**). Carbonate crusts and bivalve communities often form around active hydrocarbon vents in the GOM (and elsewhere), because the microbial consumption of CH_4 and other hydrocarbons generates consumable biomass and HCO_3^- , which then reacts with seawater Ca^{2+} (Roberts and Aharon, 1994). Periodic yet violent eruptions (e.g. Neurauter and Roberts, 1994; Kopf, 2003) would break these crusts and communities, leaving Ba-rich vent fluids in the interstices of carbonate fragments. Rapid mixing of these fluids with SO_4^{2-} would precipitate anhedral barite crystals in open pore spaces. After the eruption, mudflows and sedimentation would bury the barite-rich carbonate conglomerates. Once below the SMT, they may begin to dissolve, releasing Ba^{2+} to surrounding pore fluids. Crusts dominated by barite and calcite with minor amounts of kerogen has been documented within 40 cm of the seafloor at nearby mud volcanoes (**Figure 3**). With available information (Fu and Aharon, 1997), these crusts have some similarities to the rocky nodules although shells and void spaces were not reported for crusts. On the basis of sulfur isotopes, barite in these crusts appears to have formed near the seafloor but from microbially modified seawater, where significant SO_4^{2-} had been consumed (Fu and Aharon, 1997). This could also be the case for rocky nodules.

Smooth nodules probably have a different origin, especially considering two additional observations. First, they consist of interlocking barite and carbonate (**Figure 8, 9**), suggesting that the two minerals precipitated contemporaneously. Second, several of the smooth nodules occur within 10 cm of the modern SMT (**Figure 4; Table 2, 3**).

Smooth nodules may represent lithified horizons where the SMT has remained fixed for extended time (**Figures 2, 11**). Like aerobic oxidation of CH_4 , AOM removes SO_4^{2-} and produces HCO_3^- (e.g. Borowski et al., 1996; Wakeham, 2002). Authigenic barite and carbonate might, therefore, precipitate together at or near the SMT. Under conditions of steady sedimentation, however, the two minerals should have different fates upon passage through the SMT - barite would dissolve while carbonate would remain - so that they will not accumulate together in significant concentrations. The co-existence and intermingling of the two minerals within large nodules thus suggests a non steady state history, where barite and carbonate precipitated at the same depth over a prolonged time interval, presumably because the SMT did not migrate upwards with sedimentation or because sedimentation effectively ceased. Potentially, these nodules could signify decreasing hydrocarbon flux after an eruption.

In cores with multiple smooth nodules (**Figure 4**), the SMT has been preserved while new horizons develop. During periods of rapid sedimentation (i.e. mud volcano eruptions), the current SMT is buried and a new SMT is re-established in shallower sediment. Several fronts are observed at once because deeper fronts have not had sufficient time to dissolve completely.

As noted previously, barite crystals found in smooth nodules are either acicular or blocky. Nodules with acicular crystals are typically found near vents whereas blocky

crystals typify barite in nodules on the flanks. Because Ba^{2+} is greatest proximal to venting, the crystal habit may reflect the amount of dissolved Ba^{2+} during nucleation. Cross-cutting quartz veins are also found in nodules closest to venting. These features may reflect thermal alteration as warm fluids migrate through surrounding sediment.

7.5 Barium Expulsion

At both the GB 425 and MC 852/853 study areas, the barium content of surface sediment appears to form a concentric pattern around the mud volcano (**Figure 6**). In the upper 2 cm of sediment, barium contents exceed 19,000 mg/kg at the center of the mud volcanoes but systematically decrease to less than 40 mg/kg within 683 m down the flanks. Clearly, some process supplies excess barium to sediment around vents.

A straightforward mechanism involving periodic fluid eruptions can explain these elevated barium contents (**Figure 11**). As observed in several places, including the GOM (Torres et al., 1996b, 2002b; Fu and Aharon, 1997), fluids charged with methane and barium can vent into the overlying water column. The dissolved Ba^{2+} reacts with SO_4^{2-} in seawater to form small, anhedral barite crystals within the water column (Torres et al., 1996b, 2002b; Fu and Aharon, 1997). Presumably, these crystals rain down onto the seafloor. Because the fluid is focused at the mud volcano, the barite content of shallow sediment should gradually decrease away from this source.

Excess barium in surface sediment further distinguishes the barium cycle at GOM mud volcanoes compared to most previously studied regions. In bathyal settings away from hydrothermal systems, barite accumulating on the seafloor is often assumed to have arrived by sinking through the water column in association with organic carbon (e.g.

Chow and Goldberg, 1960; Dehairs et al., 1980). Indeed, this is the presumed source of barite supplying barium to barite fronts above SMTs elsewhere (**Figure 2**). Although some fraction of the overall barium budget at GOM mud volcanoes may come from “biogenic barite”, even the barite in surface sediment may ultimately come from vent fluids. Most papers regarding the global marine barium cycle (e.g., Wolgemuth and Broecker, 1970; Paytan and Kastner, 1996) have not considered barium inputs from hydrocarbon vents. The extreme dissolved Ba^{2+} concentrations at mud volcanoes in the GOM and certain other methane charged systems (e.g., the Sea of Okhotsk), along with compelling evidence for periodic discharge of barium to bottom waters, instigate an obvious question (Dickens et al., 2003; Aloisi et al., 2004): do hydrocarbon vents impact regional and global Ba cycling? This study cannot rigorously address the issue because the release of dissolved Ba^{2+} from individual mud volcanoes and other seafloor seep features is undoubtedly variable and episodic, and because the fluid composition of GOM mud volcanoes may not represent hydrocarbon vents in general. Some fraction of dissolved Ba^{2+} also clearly precipitates around the vents (**Figure 6**), rather than continuing in aqueous solution. Nonetheless, the upper 3 m of sediment at the MC 852/853 mud volcano holds nominally 10×10^6 moles of dissolved Ba^{2+} , assuming aforementioned parameters, an average dissolved Ba^{2+} concentration of 5000 μM , and a porosity of 70%. Even if all this Ba suddenly escaped, it would be a fairly small input compared to the $18,000 \times 10^6$ or so mol of Ba annually added to the ocean by rivers and hydrothermal activity (Dickens et al., 2003). Seemingly, thousands of mud volcanoes with elevated dissolved Ba^{2+} would have to discharge simultaneously to impact the global marine Ba cycle.

7.6 Understanding the Barium Cycle in the Rock Record

With advances in deep-sea research, mud volcanism and hydrocarbon seepage are increasingly considered common phenomena along continental margins (e.g. Torres et al., 1996b, 2002b; Milkov, 2000; Dimitrov, 2002; Greinert et al., 2002; Kopf, 2003). A growing number of studies have taken this knowledge to link certain features in the rock record to methane expulsion. To date, most of this work has focused on cold seep fauna (Gómez-Pérez, 2003; Barbieri and Panieri, 2004) or authogenic carbonates (Clari et al., 2004). However, barite-rich deposits are also associated with deep methane venting (Torres et al., 2003).

Stratiform bedded barite formations are described as conformable, meter-scale layers or lenses within sedimentary deposits (Maynard and Okita, 1991). Torres et al. (2003) describe the similarities between Paleozoic stratiform barite deposits in Nevada, Arkansas, Mexico and south China to barite mounds found at the Peru margin, the California margin (including those along the San Clemente fault), the Sea of Okhotsk and the Gulf of Mexico. Evidence for this comparison entails geologic/structural setting, sedimentary host lithologies, well-defined barite crystal habits/forms, biology/paleontology consisting of tubeworms and bivalves, and similar Sr isotope composition of barites.

Chaotic sequences within diapiric structures found in the geologic records are also compared to modern mud volcanism (Clari et al., 2004). The best example is found in northwest Italy, where a chaotic complex in the Monferrato Formation (Cenozoic) is re-interpreted as a mud volcano (Clari, et al., 2004). Here, the local lithology consists of

8. Conclusions

Recent studies have suggested a link between upward fluxing methane and barium cycling in shallow marine sediments (Torres et al., 1996a; Dickens, 2001; Aloisi et al., 2004). In this view, methane from below fuels AOM and sulfate consumption at a SMT, while barium dissolves and precipitates below and above the SMT (**Figure 1**). Previous work at mud volcanoes in the GOM has identified barite structures on the seafloor and high dissolved Ba^{2+} concentrations in pore water samples from a few shallow (40 cm) sediment cores (Fu and Aharon, 1998; Aharon et al., 2001), supporting some link between hydrocarbon fluxing and barium cycling in this region.

In this study, I collected 16 cores across two mud volcanoes in the GOM. Pore waters were extracted and analyzed for salinity, Cl^- , SO_4^{2-} , Ba^{2+} , and major cations. Digested sediments were also analyzed for Ba^{2+} and major elements. Carbonate nodules were extracted from cores and examined for their chemistry, mineralogy and petrography.

In the GOM, the SMT shoals across mud volcanoes, presumably in response to the expulsion of methane and other hydrocarbons. This finding is consistent with limited work in the GOM by previous investigators (Aharon and Fu, 2000, 2003; Joye et al., 2004), and the general observation that methane fluxing drives AOM and the depth of the SMT (Borowski et al., 1996, 1999; Hoelher et al., 2000). Further, both dissolved and solid phase barium data clearly show that the proposed methane-sulfate-barium link (**Figure 1**) occurs across the SMT. Sequential extractions also show that this barium cycle involves barite precipitation at fronts.

Barium cycling at GOM mud volcanoes is, however, more complicated than that suggested for other regions. Deep formation waters supply Ba from below so that most of the barium does not come from pelagic rain. Even the barite in surface sediment surrounding the mud volcanoes probably comes from below, when periodic fluid venting induces barite precipitation in the water column.

Barium-rich, carbonate nodules are found at both sites and appear to play an important role in barium cycling. Smooth nodules probably represent lithified barite fronts formed when the SMT remains stationary for extended time, perhaps between episodic pulses in venting. Rocky nodules may form when Ba-rich fluids erupt through carbonate crusts that cap mud volcanoes. Upon burial, both types of nodules can release dissolved Ba^{2+} below the SMT, further complicating the shallow Ba cycle.

Recent studies have attempted to link certain barite deposits in the geologic record to barite structures found at and around modern seafloor methane vents (Torres et al., 2003). As shown in this study, hydrocarbon expulsion unquestionably impacts the barium cycle in shallow sediment and leads to barite features, some with clear similarities to those found in ancient rocks. For example, the crystal habit and morphology of nodules at the GOM mud volcanoes are strikingly close to those documented in Miocene structures inferred to represent mud volcanoes (Clari et al., 2004).

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Figure Captions

Figure 1: The sulfate-methane transition (SMT) across two hypothetical end-member flux regimes in marine sediment. In low flux environments, anaerobic oxidation of methane (AOM) and complete removal of pore water sulfate occurs deep below the seafloor. In high flux environments, AOM and loss of sulfate occur at or near the sediment-water interface. Active mud volcanoes should represent high flux systems.

Figure 2: Schematic profiles of pore water methane, sulfate, alkalinity and barium concentrations in shallow marine sediments above gas-rich strata (adopted from Dickens, 2001). (A) Seawater sulfate diffuses down to react with upward migrating methane across the sulfate-methane transition (SMT). (B) Anaerobic oxidation of methane (AOM) increases alkalinity, which can lead to precipitation of authigenic carbonates that coincides with the depth of the SMT. (C) Solid barite accumulation at the surface is buried during sedimentation. As it passes through the SMT, dissolved Ba^{2+} is released. This dissolved Ba^{2+} can then migrate upwards to precipitate barite in a barium front at the SMT.

Figure 3: Location maps for study areas in the Gulf of Mexico. (A) Regional map showing significant structural and topographic features. Sites included in this study are circles; other known barium-rich seeps are triangles (Fu and Aharon, 1998). (B) Bathymetric map and seismic line of the mud volcano in Garden Banks lease block

425 (GB 425) and (C) the mud volcano in Mississippi Canyon lease blocks 852 and 853 (MC 852/853). The locations of the cores are also shown.

Figure 4: Pore water profiles of dissolved barium, chloride and sulfate, and solid phase profiles of barium for cores in this study. (A) MC 852/853, and (B) through (D) GB 425. Profiles at each location have been plotted according to the distance from the center of mud volcanoes. Also shown on these plots are the inferred SMT horizons, nodule horizons and zones where hydrate was detected. Please note that some cores only have data for dissolved species.

Figure 5: Select pore water profiles of dissolved barium, calcium and magnesium from MC 852/853 and GB 425.

Figure 6: Barium content of the upper 2 cm of sediment around the mud volcanoes. (A) GB 425, and (B) MC 852/853. At both sites, solid barium content is greatest at the center of the mud volcano and decreases away from the venting.

Figure 7: Residual sediment after sequential extraction for barite. (A) Showing abundant barite in high yield samples ($> 13\%$) and some other minerals, including titanium oxides and alumino-silicates. Note the pitted and rounded nature of the barite crystals, which may result from the extraction procedure. (B) Low yield samples ($< 3\%$) with negligible barite, but common alumino-silicates and titanium oxides.

Figure 8: Images of (A) whole smooth nodule and representative thin section of nodules from core GB-PC-21, (B) smooth nodules from core MC-PC-30, and (C) a rocky nodules from MC-PC-30. In hand sample, smooth nodules look similar in texture and have an oblong morphology. However, SEM-EDS images (magnified 140x when taken) reveal a distinct difference in crystal structure. Nodules from areas with higher venting rates (B) yield higher barium content and distinct barite crystals that are acicular and organized in a radial pattern. Barite crystals are small and blocky (A) in nodules from areas with lower venting rates and lower barium content. The rocky nodule (C) has a distinctly different morphology to smooth nodules. SEM images (magnified 70x when taken) show in-filling textures where barite is a secondary mineral phase within large void spaces.

Figure 9: Photomicrographs of smooth and rocky nodules. Smooth nodules from low flux environments (G-21N2) are fine grained with organics and quartz. Smooth nodules from high flux environment show well-developed barite crystals (G-24N2, M-30N2) that are often cross cut by quartz veins (M-30N2, G-24N3). Quartz veins exhibit undulating extinction, suggesting some thermal alteration.

Figure 10: Plot of dissolved barium and chloride for pore water from (A) GB 425, and (B) MC 852/853, formation waters (Macpherson, 1989) and seawater (Quinby-Hunt and Turekian, 1983). These plots show zones of distinct mixing between formation water and seawater, producing composite pore water values. However, in some

cases, proximal pore waters are enriched with Ba^{2+} as a result of amplified barium cycling.

Figure 11: A revised model for Ba cycling in high flux environments. (A) Methane- and Ba^{2+} -rich fluids are expelled from the mud volcano into the overlying water column. The SMT is at or near the sediment-water interface and deepens on the flanks of the mud volcano. (B) Dissolved Ba^{2+} rapidly reacts with seawater sulfate, producing small barite crystals that rain-down on the seafloor. A carbonate crust forms above the mud volcano during periods of less violent eruptions. This crust may become Ba-rich as fluids pass through void spaces and crystallize barite. The barite front is established and mimics the modern SMT; smooth nodules form at the barite front. (C) A period of more violent eruptions occurs, producing mud flows on top of fractured carbonate crusts. The SMT migrates upward to accommodate sedimentation. As a result, the old barite front is abandoned, leaving smooth nodules. A barite front begins to form above the new SMT. (D) Fractured carbonate crust is buried as discrete rocky nodules. These nodules and other smooth nodules begin to dissolve because they are below the modern SMT, creating locally elevated dissolved Ba^{2+} concentrations. A new horizon of smooth nodules develops at the barite front.

Figure 1.

Figure 2.

Figure 3. (B) GB 425

Figure 3. (C) MC 852/853

Figure 4. Legend

Figure 4. (A)

Figure 4. (B)

Figure 4. (C)

Figure 4. (D)

Figure 5.

Figure 6.

Figure 7.

(A) High Yield Samples

(B) Low Yield Samples

Figure 8.

(A) Smooth Nodule - Low Barium Concentrations

(B) Smooth Nodule - High Barium Concentrations

(C) Rocky Nodule

Figure 9.

Figure 10.

Figure 11.

Table 1. Geographical information for cores taken from GB 425 and MC 852/853.

Core	Latitude (N)	Longitude (W)	Water Depth (m)	Core Length (m)	Distance from Center (m)
<i>GB 425</i>					
GB-GC-7	27° 33.214'	92° 32.318'	568	1.1	520
GB-PC-11	27° 33.349'	92° 32.327'	564	1.2	270
GB-PC-12	27° 33.310'	92° 32.945'	625	2.0	1071
GB-PC-13	27° 33.309'	92° 33.088'	627	2.9	1296
GB-PC-14	27° 33.299'	92° 32.399'	564	2.4	382
GB-PC-15	27° 33.347'	92° 32.087'	569	2.2	480
GB-PC-17	27° 33.640'	92° 32.221'	566	2.4	320
GB-PC-18	27° 32.643'	92° 32.227'	639	2.7	1586
GB-PC-19R	27° 32.743'	92° 32.227'	639	3.0	1402
GB-PC-19	27° 32.727'	92° 32.956'	647	3.5	1758
GB-PC-20	27° 32.579'	92° 32.447'	652	2.0	1708
GB-PC-21	27° 32.274'	92° 32.482'	642	3.7	2276
GB-PC-22	27° 32.269'	92° 32.956'	650	3.7	2494
GB-PC-23	27° 32.270'	92° 34.302'	587	1.8	3958
GB-PC-24	27° 33.291'	92° 32.598'	574	2.8	584
<i>MC 852/853</i>					
MC-PC-25	28° 7.380'	89° 8.381'	1067	1.7	47
MC-PC-26	28° 7.065'	89° 8.386'	1013	2.7	594
MC-PC-27	28° 6.393'	89° 8.350'	1098	4.0	1840
MC-PC-28	28° 7.388'	89° 8.827'	1093	1.6	683
MC-PC-29	28° 7.389'	89° 8.104'	1068	2.7	498
MC-PC-30	28° 7.385'	89° 8.409'	1070	3.5	0

Table 2. Pore water data for anions.

Sample	Avg Depth (cm)	Shipboard S	Shorebased S	Sulfate (mM)	Chloride (mM)
<i>GB 425</i>					
GB-GC-7-1	7.5	37	40	28.40	853.6
GB-GC-7-2	17.5	40	47	1.97	1080.2
GB-GC-7-3	27.5	47	52	0.41	1197.5
GB-GC-7-4	62.5	61	64	0.00	1464.2
GB-GC-7-5	92.5	68	74	0.00	1657.3
GB-PC-11-1	12.5	41	45	0.47	783.7
GB-PC-11-2	22.5	52	55	1.36	901.1
GB-PC-11-3	32.5	70	75	0.00	1215.4
GB-PC-11-4	52.5	81	84	0.00	1483.2
GB-PC-11-5	62.5	84	86	0.00	1508.2
GB-PC-11-6	72.5	85	86	0.00	1474.0
GB-PC-11-7	82.5	85	89	0.00	1543.1
GB-PC-11-8	92.5	85	87	0.00	1162.9
GB-PC-11-9	132.5	85	86	0.00	1450.7
GB-PC-12-1	12.5	34	37	7.21	490.6
GB-PC-12-2	17.5	34	36	7.03	544.2
GB-PC-12-3	22.5	34	36	6.92	534.3
GB-PC-12-4	52.5	34	36	5.95	554.4
GB-PC-12-5	82.5	35	36	4.93	532.0
GB-PC-12-6	112.5	35	37	3.75	572.1
GB-PC-12-7	142.5	35	37	2.30	555.9
GB-PC-12-8	172.5	35	36	2.02	537.4
GB-PC-12-9	197.5	37	40	0.08	592.0
GB-PC-13-1	12.5	35	36	9.42	537.0
GB-PC-13-2	42.5	35	36	9.21	540.9
GB-PC-13-3	72.5	35	36	7.95	512.8
GB-PC-13-4	107.5	35	36	7.20	550.1
GB-PC-13-5	147.5	35	36	5.30	523.3
GB-PC-13-6	187.5	33	35	4.65	567.0
GB-PC-13-7	227.5	33	36	11.29	620.0
GB-PC-13-8	267.5	33	36	1.84	646.9
GB-PC-13-9	293	35	35	0.02	620.2
GB-PC-14-1	12.5	87	90	0.00	2138.5
GB-PC-14-2	42.5	94	97	0.00	2468.4
GB-PC-14-3	72.5	108	114	0.00	2632.1
GB-PC-14-4	102.5	108	116	0.00	2732.6
GB-PC-14-5	142.5	108	118	0.00	2656.6
GB-PC-14-6	172.5	110	116	0.00	2032.0
GB-PC-14-7	202.5	110	116	0.00	2723.5

GB-PC-14-8	225	108	116	0.00	2710.7
GB-PC-15-1	12.5	35	36	4.89	596.6
GB-PC-15-2	42.5	38	40	2.47	874.3
GB-PC-15-3	72.5	44	44	0.43	964.9
GB-PC-15-4	102.5	47	46	0.00	1074.5
GB-PC-15-5	132.5	55	50	0.00	1156.9
GB-PC-15-6	162.5	64	57	0.00	1318.8
GB-PC-15-7	192.5	65	66	0.00	1620.5
GB-PC-15-8	217.5	73	75	0.07	1793.8
GB-PC-17-1	8.5	57	60	0.00	1378.4
GB-PC-17-2	17.5	60	62	0.00	1423.8
GB-PC-17-3	47.5	71	74	0.00	1748.4
GB-PC-17-4	72.5	77	80	0.00	1848.8
GB-PC-17-5	102.5	79	84	0.09	2011.9
GB-PC-17-6	132.5	81	85	0.00	2044.2
GB-PC-17-7	162.5	82	85	0.00	2056.1
GB-PC-17-8	192.5	84	85	0.18	2005.2
GB-PC-18-1	7.5	34	36	5.70	539.0
GB-PC-18-2	17.5	34	36	5.27	553.8
GB-PC-18-3	52.5	35	36	4.51	542.9
GB-PC-18-4	82.5	35	36	4.06	575.3
GB-PC-18-5	117.5	34	36	3.52	533.2
GB-PC-18-6	142.5	34	35	3.24	555.4
GB-PC-18-7	177.5	34	35	0.80	764.3
GB-PC-18-8	222.5	35	37	0.00	812.2
GB-PC-19-1	12.5	35	36	5.90	533.3
GB-PC-19-2	22.5	35	36	5.64	560.2
GB-PC-19-3	52.5	34	35	5.03	525.2
GB-PC-19-4	92.5	34	35	5.11	570.1
GB-PC-19-5	132.5	35	35	5.15	535.4
GB-PC-19-6	172.5	35	36	5.47	531.9
GB-PC-19-7	212.5	35	35	4.33	546.2
GB-PC-19-8	252.5	35	35	4.57	564.5
GB-PC-19-9	292.5	35	36	3.47	540.1
GB-PC-19-10	322.5	35	35	2.39	566.0
GB-PC-20-1	12.5	35	36	6.07	670.3
GB-PC-20-2	22.5	35	37	4.66	573.3
GB-PC-20-3	52.5	35	37	4.20	573.7
GB-PC-20-4	92.5	39	41	2.53	662.1
GB-PC-21-1	12.5	35	37	4.13	533.5
GB-PC-21-2	22.5	35	37	5.67	569.5

GB-PC-21-3	57.5	36	38	4.16	551.8
GB-PC-21-4	87.5	37	39	4.30	579.2
GB-PC-21-5	127.5	39	40	2.55	572.4
GB-PC-21-6	167.5	44	46	1.48	774.6
GB-PC-21-7	217.5	57	61	0.41	1457.0
GB-PC-21-8	267.5	66	69	0.56	1667.8
GB-PC-21-9	317.5	83	85	0.00	2004.0
GB-PC-21-10	357.5	94	98	0.00	2346.5
GB-PC-22-1	12.5	36	39	4.56	540.5
GB-PC-22-2	22.5	36	37	3.70	578.1
GB-PC-22-3	67.5	39	40	3.68	562.2
GB-PC-22-4	107.5	40	42	3.59	649.7
GB-PC-22-5	147.5	44	45	3.22	706.5
GB-PC-22-6	187.5	48	50	2.41	802.7
GB-PC-22-7	227.5	62	64	0.00	1281.7
GB-PC-22-8	267.5	69	70	0.00	1395.0
GB-PC-22-9	307.5	75	74	0.00	1542.7
GB-PC-22-10	347.5	93	96	0.00	2056.6
GB-PC-23-1	12.5	36	36	4.36	530.5
GB-PC-23-2	22.5	36	36	4.73	551.5
GB-PC-23-3	52.5	35	37	3.51	511.5
GB-PC-23-4	92.5	36	36	3.15	540.4
GB-PC-23-5	127.5	37	37	7.64	428.8
GB-PC-23-6	162.5	37	37	5.84	664.4
GB-PC-24-1	12.5	37	40	10.47	598.3
GB-PC-24-2	22.5	37	40	18.03	596.3
GB-PC-24-3	52.5	37	49	6.57	760.3
GB-PC-24-4	92.5	61	65	6.26	1167.8
GB-PC-24-5	132.5	87	90	0.00	1748.5
GB-PC-24-6	192.5	110	116	0.00	2269.5
GB-PC-24-7	232.5	120	128	0.27	2326.8
GB-PC-24-8	282.5	130	134	0.00	2617.1
<i>MC 852/853</i>					
MC-PC-25-1	12.5	71	74	0.00	1324.9
MC-PC-25-2	22.5	81	85	0.00	1716.3
MC-PC-25-3	42.5	104	112	0.00	2138.6
MC-PC-25-4	72.5	130	138	0.00	2566.3
MC-PC-25-5	102.5	136	140	0.00	2387.3
MC-PC-25-6	132.5	130	134	0.00	2606.4
MC-PC-25-7	172.5	120	128	0.00	2357.6
MC-PC-26-1	12.5	35	40	8.24	579.2
MC-PC-26-2	22.5	36	39	6.50	501.9

MC-PC-26-3	62.5	54	56	0.00	1022.3
MC-PC-26-4	102.5	66	73	0.00	1375.4
MC-PC-26-5	142.5	75	79	0.00	1474.8
MC-PC-26-6	182.5	80	83	0.00	1558.6
MC-PC-26-7	222.5	86	89	0.00	1666.9
MC-PC-26-8	272	88	91	0.00	1747.3
MC-PC-26-9	0	34	36	8.27	488.6
MC-PC-27-1	12.5	35	36	26.14	618.9
MC-PC-27-2	22.5	30	39	26.18	641.2
MC-PC-27-3	72.5	31	39	28.82	664.0
MC-PC-27-4	122.5	31	37	22.68	516.9
MC-PC-27-5	172.5	30	36	25.65	597.8
MC-PC-27-6	222.5	32	38	26.91	601.0
MC-PC-27-7	272.5	32	36	27.71	613.1
MC-PC-27-8	322.5	30	36	26.40	611.9
MC-PC-27-9	372.5	35	37	28.23	607.7
MC-PC-27-10	0	34	39	28.71	650.9
MC-PC-28-1	12.5	33	36	8.78	539.6
MC-PC-28-2	22.5	27	36	7.69	549.8
MC-PC-28-3	52.5	33	38	5.35	425.5
MC-PC-28-4	82.5	32	36	6.04	525.0
MC-PC-28-5	112.5	34	38	6.41	549.8
MC-PC-28-6	157.5	32	36	2.79	398.6
MC-PC-29-1	12.5	35	36	8.75	534.7
MC-PC-29-2	22.5	35	36	8.27	528.7
MC-PC-29-3	62.5	35	38	7.43	585.5
MC-PC-29-4	102.5	36	38	5.52	529.0
MC-PC-29-5	152.5	39	40	4.56	574.2
MC-PC-29-6	192.5	38	39	8.94	666.8
MC-PC-29-7	232.5	38	40	4.30	758.1
MC-PC-29-8	272.5	54	40	0.81	714.0
MC-PC-30-1	12.5	35	96	0.00	1744.7
MC-PC-30-2	22.5	35	128	0.00	2334.8
MC-PC-30-3	72.5	35	140	0.00	2562.9
MC-PC-30-4	112.5	36	140	0.00	2531.3
MC-PC-30-5	192.5	39	142	0.00	2518.2
MC-PC-30-6	257.5	38	102	0.00	1898.8
MC-PC-30-7	267.5	38	104	0.00	1813.1
MC-PC-30-8	277.5	54	134	0.00	2392.6
MC-PC-30-9	302.5	35	160	0.00	2168.7

Notes: Sulfate values listed as zero are below the detection limit.

Table 3. Major elements and dissolved metal concentrations for pore water.

Sample	Ba (uM)	Ca (mM)	K (mM)	Mg (mM)	Sr (mM)
<i>GB 425</i>					
GB-GC-7-1	0.796	11.8	13.0	47.6	0.159
GB-GC-7-2	8.48	14.8	12.6	38.6	0.353
GB-GC-7-3	331	18.2	12.7	35.8	0.446
GB-GC-7-4	2290	29.0	13.1	31.8	0.733
GB-GC-7-5	3100	33.9	13.4	30.8	0.876
GB-PC-11-1	14.2	10.3	11.6	39.6	0.280
GB-PC-11-2	5.43	19.0	10.3	34.4	0.456
GB-PC-11-3	1140	29.2	11.6	32.0	0.889
GB-PC-11-4	1170	33.4	11.2	32.5	1.01
GB-PC-11-5	1170	33.8	11.6	32.9	1.04
GB-PC-11-6	1180	33.7	11.9	32.9	1.05
GB-PC-11-7	1200	34.0	11.6	32.8	1.07
GB-PC-11-8	1290	34.3	11.4	32.6	1.09
GB-PC-11-9	1190	33.7	11.6	32.9	1.06
GB-PC-12-1	0.975	9.08	10.9	44.7	0.078
GB-PC-12-2	0.871	9.04	10.9	44.7	0.078
GB-PC-12-3	1.02	9.10	10.9	45.0	0.079
GB-PC-12-4	1.20	8.75	10.8	44.3	0.081
GB-PC-12-5	0.847	8.20	10.7	43.3	0.086
GB-PC-12-6	1.14	7.44	10.4	42.4	0.093
GB-PC-12-7	1.32	6.29	10.2	40.7	0.104
GB-PC-12-8	3.67	4.80	9.45	38.4	0.120
GB-PC-12-9	209	3.52	9.46	40.1	0.164
GB-PC-13-1	0.708	9.01	10.8	44.0	0.079
GB-PC-13-2	0.719	8.74	10.9	43.6	0.078
GB-PC-13-3	0.961	8.49	10.8	43.2	0.078
GB-PC-13-4	0.678	7.77	10.7	43.0	0.078
GB-PC-13-5	0.608	6.80	10.1	42.7	0.078
GB-PC-13-6	0.763	6.23	10.3	42.6	0.079
GB-PC-13-7	0.947	5.25	9.89	41.9	0.078
GB-PC-13-8	20.6	3.19	9.68	40.9	0.080
GB-PC-13-9	57.3	3.51	8.96	41.5	0.085
GB-PC-14-1	7690	36.9	24.7	34.7	1.48
GB-PC-14-2	7540	38.9	27.6	35.8	1.53
GB-PC-14-3	4750	43.8	30.7	39.1	1.57
GB-PC-14-4	4240	43.8	31.0	39.2	1.53
GB-PC-14-5	3810	44.6	31.5	39.5	1.54
GB-PC-14-6	3450	44.8	32.1	39.7	1.53
GB-PC-14-7	2780	44.6	32.5	39.6	1.49

GB-PC-14-8	2060	43.4	31.5	38.2	1.41
GB-PC-15-1	1.33	8.68	10.7	43.6	0.113
GB-PC-15-2	8.91	8.61	10.6	42.9	0.217
GB-PC-15-3	544	9.96	10.8	43.1	0.299
GB-PC-15-4	952	11.3	11.2	43.9	0.359
GB-PC-15-5	1420	12.2	12.4	45.8	0.413
GB-PC-15-6	178-	13.1	14.2	48.2	0.484
GB-PC-15-7	4130	15.3	18.5	44.7	0.698
GB-PC-15-8	6850	17.5	21.0	35.4	0.846
GB-PC-17-1	2680	21.0	12.6	32.5	0.667
GB-PC-17-2	3050	23.1	12.8	32.6	0.735
GB-PC-17-3	4250	28.6	14.6	33.5	0.929
GB-PC-17-4	4680	30.1	15.9	35.3	1.01
GB-PC-17-5	4900	30.8	16.5	35.3	1.03
GB-PC-17-6	5120	31.3	17.7	36.1	1.06
GB-PC-17-7	5180	29.8	18.8	35.7	1.05
GB-PC-17-8	5490	31.1	19.9	36.1	1.09
GB-PC-18-1	0.925	8.58	10.8	44.7	0.079
GB-PC-18-2	1.20	8.54	10.8	44.5	0.079
GB-PC-18-3	1.40	8.31	10.9	44.2	0.078
GB-PC-18-4	2.16	8.06	10.9	43.9	0.078
GB-PC-18-5	1.60	7.32	10.9	43.6	0.078
GB-PC-18-6	2.410	6.83	10.8	43.7	0.079
GB-PC18-7	27.2	3.19	10.9	42.4	0.073
GB-PC-18-8	644	4.01	11.0	42.1	0.134
GB-PC-19-1	0.849	9.40	11.0	45.4	0.081
GB-PC-19-2	0.515	12.0	10.3	50.7	0.090
GB-PC-19-3	0.664	12.1	10.2	50.4	0.089
GB-PC-19-4	2.14	12.0	10.2	50.1	0.089
GB-PC-19-5	0.703	12.2	10.0	49.9	0.088
GB-PC-19-6	0.526	12.0	10.1	49.6	0.089
GB-PC-19-7	0.539	12.2	9.96	49.9	0.089
GB-PC-19-8	0.597	11.7	9.81	49.9	0.090
GB-PC-19-9	0.623	11.7	9.42	49.7	0.093
GB-PC-19-10	1.20	12.1	6.81	47.9	0.101
GB-PC-20-1	0.947	12.4	10.1	49.8	0.094
GB-PC-20-2	1.24	12.5	9.91	49.7	0.093
GB-PC-20-3	1.16	12.8	9.82	51.0	0.105
GB-PC-20-4	0.973	13.3	9.63	56.4	0.156
GB-PC-21-1	0.556	12.0	10.3	49.6	0.098
GB-PC-21-2	0.590	12.1	10.3	49.9	0.099

GB-PC-21-3	0.567	12.0	10.5	49.7	0.113
GB-PC-21-4	0.675	12.1	10.8	49.0	0.153
GB-PC-21-5	0.799	12.7	11.7	46.8	0.268
GB-PC-21-6	1.37	14.0	14.8	44.5	0.461
GB-PC-21-7	174	14.2	20.7	44.1	0.609
GB-PC-21-8	395	14.4	29.1	46.1	0.826
GB-PC-21-9	677	15.2	33.4	48.0	0.939
GB-PC-21-10	641	12.2	10.6	50.2	0.104
GB-PC-22-1	0.665	12.2	10.6	49.9	0.107
GB-PC-22-2	0.747	12.1	11.5	50.4	0.122
GB-PC-22-3	0.637	12.7	12.9	50.2	0.159
GB-PC-22-4	0.699	12.5	14.6	50.5	0.199
GB-PC-22-5	1.99	12.7	15.5	53.0	0.212
GB-PC-22-6	0.958	15.1	32.7	38.9	0.712
GB-PC-22-7	1430	13.9	37.4	40.8	0.800
GB-PC-22-8	1470	43.9	14.4	41.0	0.804
GB-PC-22-9	1700	47.6	15.5	42.0	0.886
GB-PC-22-10	1670	57.2	15.6	45.2	1.07
GB-PC-23-1	0.695	11.8	12.1	50.2	0.089
GB-PC-23-2	0.788	11.8	12.0	50.6	0.090
GB-PC-23-3	0.641	11.4	12.0	50.3	0.093
GB-PC-23-4	0.762	11.2	12.2	50.4	0.100
GB-PC-23-5	2.53	10.5	12.1	50.0	0.113
GB-PC-23-6	1.15	8.15	12.1	49.6	0.137
GB-PC-24-1	0.863	12.3	13.2	49.3	0.123
GB-PC-24-2	0.781	12.8	14.3	48.6	0.160
GB-PC-24-3	2.37	14.8	16.3	45.9	0.361
GB-PC-24-4	3.99	18.5	20.4	42.4	0.725
GB-PC-24-5	6360	29.0	29.4	39.1	1.57
GB-PC-24-6	5920	37.8	38.1	39.1	2.32
GB-PC-24-7	6050	35.2	35.9	36.7	2.52
GB-PC-24-8	6090	37.3	37.9	36.5	2.68
<i>MC 852/853</i>					
MC-PC-25-1	1090	34.0	17.2	77.3	0.762
MC-PC-25-2	572	41.3	18.1	83.4	0.852
MC-PC-25-3	2150	53.1	23.5	97.8	1.23
MC-PC-25-4	3490	59.9	30.8	109	1.51
MC-PC-25-5	3630	61.6	33.8	112	1.56
MC-PC-25-6	1520	59.7	32.4	106	1.35
MC-PC-25-7	581	55.6	28.2	95.7	1.14
MC-PC-26-1	1.34	10.5	12.1	50.9	0.112
MC-PC-26-2	1.23	10.7	12.3	51.4	0.113

MC-PC-26-3	119	19.0	13.5	67.4	0.356
MC-PC-26-4	217	27.4	14.5	78.3	0.504
MC-PC-26-5	268	32.1	15.6	85.1	0.598
MC-PC-26-6	310	34.1	17.0	88.4	0.641
MC-PC-26-7	321	35.8	17.4	90.8	0.674
MC-PC-26-8	329	36.3	18.0	92.1	0.685
MC-PC-26-9	0.734	10.5	9.88	51.4	0.089
MC-PC-27-1	0.854	10.6	12.4	50.3	0.091
MC-PC-27-2	1.70	10.3	12.2	49.2	0.089
MC-PC-27-3	1.28	11.0	12.3	50.5	0.094
MC-PC-27-4	1.06	11.0	11.8	50.0	0.093
MC-PC-27-5	1.87	11.3	11.6	49.7	0.096
MC-PC-27-6	2.38	11.6	11.4	50.4	0.099
MC-PC-27-7	0.753	12.0	11.0	50.6	0.103
MC-PC-27-8	1.18	12.3	10.7	50.7	0.106
MC-PC-27-9	0.728	12.7	10.5	51.5	0.110
MC-PC-27-10	0.534	10.6	10.2	51.3	0.089
MC-PC-28-1	1.27	10.1	12.0	49.1	0.088
MC-PC-28-2	0.862	9.67	12.5	48.5	0.087
MC-PC-28-3	1.12	8.98	11.9	47.4	0.088
MC-PC-28-4	1.22	8.68	11.6	47.6	0.088
MC-PC-28-5	1.93	8.39	11.5	47.9	0.089
MC-PC-28-6	2.45	6.96	11.0	46.5	0.087
MC-PC-29-1	1.24	20.2	13.0	50.4	0.096
MC-PC-29-2	0.781	9.90	13.3	48.8	0.094
MC-PC-29-3	1.16	9.64	12.4	50.5	0.111
MC-PC-29-4	1.41	11.9	12.5	51.2	0.122
MC-PC-29-5	2.49	18.9	12.7	53.3	0.136
MC-PC-29-6	2.63	8.75	12.0	51.8	0.139
MC-PC-29-7	8.15	6.77	11.9	51.8	0.148
MC-PC-29-8	52.1	6.65	11.5	52.9	0.156
MC-PC-30-1	4020	47.1	21.7	92.4	1.24
MC-PC-30-2	12100	54.5	28.2	104	1.83
MC-PC-30-3	12100	57.6	32.9	108	1.87
MC-PC-30-4	10100	60.8	33.6	108	1.83
MC-PC-30-5	3640	62.1	33.6	108	1.45
MC-PC-30-6	1420	49.9	21.2	81.1	0.967
MC-PC-30-7	1040	52.4	22.4	82.4	0.953
MC-PC-30-8	944	59.2	31.4	103	1.26
MC-PC-30-9	1260	64.7	39.2	117	1.49

Table 4. Major elements and metal content of extracted sediment.

Core, Interval (cm)	Ca (g/kg)	Mg (g/kg)	K (g/kg)	Sr (mg/kg)	Ba (mg/kg)
<i>GB 425</i>					
GB-PC, 12 0-2	54.9	12.2	1.03	184	1200
GB-PC-12, 30-32	44.4	13.6	17.9	165	2000
GB-PC-12, 40-42	45.7	14.0	3.29	138	1130
GB-PC-12, 60-62	64.8	12.8	9.88	102	182.4
GB-PC-12, 90-92	44.3	12.2	1.12	97.3	78.6
GB-PC-12, 100-102	44.0	12.3	1.48	99.7	72.6
GB-PC-12, 120-122	46.6	12.9	8.54	101	71.6
GB-PC-12, 130-132	42.7	12.7	1.36	102	81.1
GB-PC-12, 150-152	43.8	13.5	16.6	98.1	70.9
GB-PC-12, 160-162	43.5	13.6	17.1	108	75.4
GB-PC-12, 168-170	43.8	13.2	3.45	101	77.8
GB-PC-12, 180-182	44.0	12.2	2.37	116	119
GB-PC-12, 184-186	42.8	12.4	9.03	114	129
GB-PC-12, 188-190	63.4	14.9	19.4	255	147
GB-PC-12, 192-194	65.1	16.8	2.70	246	231
GB-PC-13, 0-2	112	13.0	2.85	434	1680
GB-PC-13, 20-22	46.1	16.0	3.40	256	3950
GB-PC-13, 30-32	67.7	12.6	3.07	1210	8660
GB-PC-13, 32-34CW	56.4	10.5	1.55	747	14600
GB-PC-13, 50-52	47.6	14.1	3.62	120	585
GB-PC-13, 60-62	43.4	14.9	2.47	99.8	333
GB-PC-13, 80-82	45.8	13.2	3.63	119	553
GB-PC-13, 100-102	42.3	13.6	2.38	115	381
GB-PC-13, 115-117	46.3	15.0	3.02	115	224
GB-PC-13, 125-127	109	12.7	2.87	386	423
GB-PC-13, 135-137	62.9	13.4	2.12	244	393
GB-PC-13, 155-157	39.1	15.1	3.71	191	259
GB-PC-13, 165-167	43.3	14.1	1.78	188	337
GB-PC-13, 175-177	43.7	16.0	19.4	203	354
GB-PC-13, 195-197	51.9	15.8	3.29	217	313
GB-PC-13, 205-207	71.5	14.2	1.32	311	406
GB-PC-13, 215-217	61.3	15.9	3.30	257	354
GB-PC-13, 235-237	64.8	19.6	3.09	218	184
GB-PC-13, 245-247	63.4	16.6	3.29	257	224
GB-PC-13, 255-257	55.9	17.2	2.18	229	225
GB-PC-15, 0-2	33.6	11.4	2.59	158	2360
GB-PC-15, 20-22	41.3	12.8	3.11	177	3440
GB-PC-15, 30-32	44.3	12.5	3.05	139	1380
GB-PC-15, 40-42	44.3	13.5	3.35	125	476
GB-PC-15, 44-46	45.3	12.6	1.85	114	161
GB-PC-15, 48-50	44.6	13.0	3.07	116	464
GB-PC-15, 52-54	43.7	13.9	3.89	125	246
GB-PC-15, 56-58	44.6	13.1	3.29	123	270
GB-PC-15, 60	38.3	13.5	11.0	134	624
GB-PC-15, 80-82	45.5	13.0	2.32	129	638

GB-PC-15, 90-92	44.3	12.6	3.11	137	619
GB-PC-15, 110-112	43.9	13.7	3.58	115	388
GB-PC-15, 120-122	44.5	12.9	3.01	117	345
GB-PC-15, 140-142	43.4	12.3	3.03	134	491
GB-PC-15, 150-152	40.7	11.1	1.40	167	1450
GB-PC-15, 170-172	41.9	13.3	3.25	146	566
GB-PC-15, 180-182	43.4	13.6	3.85	No Data	No Data
GB-PC-15, 200-202	42.9	12.2	No Data	467	601
GB-PC-15, 210-212	47.2	13.2	No Data	408	521
GB-PC-19, 0-2	121	12.0	3.83	368	473
GB-PC-19, 30-32	101	12.0	No Data	149	201
GB-PC-19, 40-42	113	13.9	11.3	273	302
GB-PC-19, 60-62	88.1	14.8	11.4	231	275
GB-PC-19, 70-72	34.2	16.2	10.6	234	299
GB-PC-19, 80-82	62.9	15.2	19.5	206	283
GB-PC-19, 100-102	53.6	15.0	4.41	166	330
GB-PC-19, 110-112	49.9	16.0	12.7	149	310
GB-PC-19, 120-122	43.7	15.9	4.78	206	380
GB-PC-19, 140-142	36.2	19.8	14.0	288	385
GB-PC-19, 150-152	30.3	15.9	No Data	278	371
GB-PC-19, 160-162	45.7	17.5	13.1	242	356
GB-PC-19, 180-182	66.0	16.1	No Data	267	292
GB-PC-19, 190-192	64.4	18.0	12.7	241	243
GB-PC-19, 200-202	60.6	16.3	No Data	162	178
GB-PC-19, 220-222	64.4	16.2	No Data	190	220
GB-PC-19, 230-232	54.5	16.9	11.1	199	194
GB-PC-19, 240-242	64.9	20.6	4.21	141	158
GB-PC-19, 260-262	58.3	17.7	No Data	114	284
GB-PC-19, 270-272	60.6	16.5	10.9	111	298
GB-PC-19, 280-282	49.6	17.3	2.99	106	221
GB-PC-19, 300-302	43.5	12.7	No Data	112	177
GB-PC-19, 310-312	42.3	14.1	11.9	140	1070
GB-PC-19, 330-332	46.5	13.7	3.70	143	204
GB-PC-19, 340-342	46.4	16.9	21.4	No Data	No Data
GB-PC-19, 344-346	42.5	12.8	2.98	487	790
GB-PC-19, 348-350	52.8	13.7	3.76	485	651
GB-PC-19R, 0-2	126	11.2	6.20	502	557
GB-PC-19R, 10-12	134	11.3	6.55	408	512
GB-PC-19R, 20-22	139	11.4	2.66	369	494
GB-PC-19R, 30-32	145	11.4	6.33	333	450
GB-PC-19R, 40-42	111	12.5	2.99	214	277
GB-PC-19R, 50-52	96.6	12.8	6.02	236	259
GB-PC-19R, 60-62	80.1	13.4	No Data	222	233
GB-PC-19R, 70-72	53.2	14.3	7.02	206	250
GB-PC-19R, 80-82	545.0	14.2	3.58	232	329
GB-PC-19R, 90-92	49.4	14.4	6.72	187	331
GB-PC-19R, 100-102	46.0	15.1	7.01	149	327
GB-PC-19R, 110-112	55.8	15.0	3.84	160	324
GB-PC-19R, 120-122	44.4	15.2	6.75	189	363
GB-PC-19R, 130-132	32.4	15.5	3.63	238	385

GB-PC-19R, 140-142	36.0	16.9	7.08	289	403
GB-PC-19R, 150-152	46.6	15.9	9.40	284	367
GB-PC-19R, 160-162	58.3	15.8	3.32	262	357
GB-PC-19R, 170-172	71.9	17.0	3.00	249	357
GB-PC-19R, 174-176	67.6	16.3	12.2	265	382
GB-PC-19R, 178-180	66.6	16.5	3.34	258	333
GB-PC-19R, 182-184	64.2	16.4	3.39	273	316
GB-PC-19R, 186-188	63.0	18.4	13.1	256	320
GB-PC-19R, 190-192	67.3	16.5	7.00	259	318
GB-PC-19R, 194-196	69.2	16.1	3.16	256	327
GB-PC-19R, 198-200	66.0	16.6	3.27	276	273
GB-PC-19R, 200-202	65.1	16.1	3.09	229	234
GB-PC-19R, 204-206	63.1	15.8	3.26	241	237
GB-PC-19R, 208-210	62.6	17.7	12.2	179	194
GB-PC-19R, 212-214	66.7	17.3	6.22	184	205
GB-PC-19R, 216-218	66.0	17.2	6.57	106	105
GB-PC-19R, 220-222	65.1	19.5	6.26	216	218
GB-PC-19R, 224-226	56.1	18.8	10.6	248	243
GB-PC-19R, 228-230	73.8	25.3	5.59	158	172
GB-PC-19R, 240-242	64.3	17.1	6.54	88.6	196
GB-PC-19R, 250-252	66.5	17.5	No Data	105	78.8
GB-PC-19R, 260-262	48.2	17.3	10.4	99.5	68.2
GB-PC-19R, 270-272	44.8	19.3	12.2	102	72.5
GB-PC-19R, 280-282	42.7	12.5	2.86	No Data	No Data
GB-PC-19R, 290-292	45.7	12.7	2.23	421.4	889
GB-PC-19R, 300-302	42.4	14.1	8.86	137	552
GB-PC-20, 0-2	107	12.3	2.06	110	273
GB-PC-20, 30-32	47.4	13.0	No Data	105	183
GB-PC-20, 40-42	41.0	13.5	2.91	113	369
GB-PC-20, 60-62	43.8	13.3	No Data	405	1840
GB-PC-20, 70-72	42.6	12.5	No Data	No Data	No Data
GB-PC-20, 80-82	44.9	13.8	1.91	419	1050
GB-PC-20, 88-89	95.1	11.9	No Data	382	463
GB-PC-21, 0-2	109	12.0	3.11	419	1050
GB-PC-21, 30-32	107	14.8	3.48	382	463
GB-PC-21, 40-42	112	22.2	5.96	298	383
GB-PC-21, 60-62	42.9	15.0	4.31	195	289
GB-PC-21, 70-72	42.4	15.3	3.91	192	374
GB-PC-21, 90-92	57.4	15.9	3.33	203	399
GB-PC-21, 100-102	62.5	14.1	3.44	266	463
GB-PC-21, 110-112	57.0	14.7	3.75	236	339
GB-PC-21, 130-132	58.7	15.1	3.91	253	393
GB-PC-21, 140-142	61.6	15.0	4.11	277	469
GB-PC-21, 190-192	129	17.5	1.67	1030	5770
GB-PC-21, 200CW	117	25.6	0.68	526	2300
GB-PC-21, 206-208	56.4	17.3	1.75	255	124
GB-PC-21, 230-232	59.3	16.8	3.15	229	188
GB-PC-21, 240-242	72.2	16.8	2.85	271	224
GB-PC-21, 250-252	59.7	18.5	4.11	197	287
GB-PC-21, 270-272	63.8	15.9	4.20	247	154

GB-PC-21, 280-282	58.8	16.3	3.02	237	202
GB-PC-21, 290-292	76.3	21.9	5.48	214	123
GB-PC-21, 300-302	57.9	17.8	4.06	213	288
GB-PC-21, 320-322	57.7	18.7	3.56	157	705
GB-PC-21, 330-332	58.1	17.7	3.72	194	208
GB-PC-21, 340-342	57.4	19.4	3.34	157	156
GB-PC-21, 360-362	56.4	19.4	3.73	160	315
GB-PC-22, 0-2	96.7	12.7	11.1	424	1060
GB-PC-22, 30-32	111	14.2	9.00	420	555
GB-PC-22, 40-42	125	14.7	1.91	440	440
GB-PC-22, 50-52	123	15.1	2.40	412	362
GB-PC-22, 70-72	162	16.5	15.8	495	420
GB-PC-22, 80-82	94.1	13.9	11.5	356	420
GB-PC-22, 90-92	73.8	13.8	2.70	110	358
GB-PC-22, 90-92	42.6	12.7	1.54	297	430
GB-PC-22, 110-112	47.5	13.2	2.39	217	271
GB-PC-22, 120-122	44.6	13.3	2.40	215	256
GB-PC-22, 130-132	40.5	14.4	3.61	192	266
GB-PC-22, 150-152	40.4	14.2	1.98	197	468
GB-PC-22, 160-162	37.7	14.9	9.85	200	479
GB-PC-22, 170-172	47.2	14.4	10.3	238	583
GB-PC-22, 178-180	49.9	14.4	2.34	295	1190
GB-PC-22, 190-192	62.0	12.8	1.73	770	12900
GB-PC-22, 196-198	69.3	13.5	2.63	349	2500
GB-PC-22, 198-200	118	13.2	1.30	605	7910
GB-PC-22, 198-200CW	174	10.3	0.75	1530	21100
GB-PC-22, 202-204	63.8	13.8	9.98	266	427
GB-PC-22, 206-208	63.7	14.8	17.6	299	505
GB-PC-22, 210-212	54.1	13.6	2.65	238	241
GB-PC-22, 214-216	61.0	14.1	1.41	289	907
GB-PC-22, 218-220	59.7	14.3	1.52	264	262
GB-PC-22, 230-232	76.2	14.2	2.19	313	773
GB-PC-22, 240-242	61.2	15.2	14.0	288	596
GB-PC-22, 250-252	67.9	20.0	1.88	163	397
GB-PC-22, 270-272	69.7	24.8	No Data	105	388
GB-PC-22, 280-282	63.6	15.4	2.30	223	344
GB-PC-22, 290-292	61.8	14.8	2.52	249	366
GB-PC-22, 310-312	55.5	15.4	2.44	202	537
GB-PC-22, 320-322	80.0	13.7	1.80	281	351
GB-PC-22, 330-332	43.8	15.6	1.29	149	130
GB-PC-22, 350-352	52.2	12.2	1.46	138	284
GB-PC-24, 0-2	87.8	9.13	0.57	653	6840
GB-PC-24, 30-32	63.2	10.8	0.57	No Data	No Data
GB-PC-24, 40-42	56.1	12.9	1.91	415	3360
GB-PC-24, 60-62	42.2	12.9	2.36	180	1060
GB-PC-24, 70-72	105	12.2	1.17	652	1910
GB-PC-24, 80-82	39.8	11.5	0.98	138	98.2
GB-PC-24, 85-88CW	137	12.3	No Data	689	726
GB-PC-24, 88-90	45.6	11.3	1.89	154	381
GB-PC-24, 100-102	40.5	11.3	2.26	382	2810

GB-PC-24, 104-106	37.7	10.9	2.68	476	7530
GB-PC-24, 108-110	38.9	12.7	1.61	213	2590
GB-PC-24, 112-114	37.7	12.6	1.65	159	2730
GB-PC-24, 116-118	36.2	10.8	No Data	227	2670
GB-PC-24, 120-122	37.3	12.5	No Data	215	2700
GB-PC-24, 124-126	37.4	12.5	1.42	255	3970
GB-PC-24, 128-130	42.0	13.3	1.30	299	4110
GB-PC-24, 140-142	50.2	12.2	2.36	269	5220
GB-PC-24, 150-152	51.0	11.8	2.89	426	7770
GB-PC-24, 160-162	39.1	11.7	1.00	294	4960
GB-PC-24, 170-172	46.5	11.2	0.89	403	7840
GB-PC-24, 180-182	38.5	13.5	2.03	310	7750
GB-PC-24, 198-180CW	134	11.8	1.37	816	13500
GB-PC-24, 200-202	36.5	9.81	1.47	605	10900
GB-PC-24, 209-212CW	115	9.10	No Data	966	10000
GB-PC-24, 210-212	46.6	13.3	0.48	439	7870
GB-PC-24, 220-222	124	9.96	0.37	900	7350
GB-PC-24, 240-242	179	11.2	2.12	925	7870
GB-PC-24, 250-252	136	9.51	0.57	878	5620
GB-PC-24, 260-262	133	7.55	0.26	1080	8530
GB-PC-24, 270-272	115	11.3	0.64	1040	10900

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MC-PC-25, 0-2	23.7	13.4	1.12	889	13800
MC-PC-25, 4-6	81.1	17.9	28.7	747	14700
MC-PC-25, 8-10	29.4	13.3	0.63	624	13300
MC-PC-25, 30-32	50.3	17.4	5.59	197	2370
MC-PC-25, 50-52	48.5	18.1	2.86	162	1460
MC-PC-25, 60-62	52.4	20.8	19.1	136	970
MC-PC-25, 80-82	44.0	18.0	No Data	141	1000
MC-PC-25, 90-92	49.3	18.8	2.88	127	766
MC-PC-25, 110-112	49.1	23.8	1.63	130	706
MC-PC-25, 120-122	45.8	14.9	No Data	350	4740
MC-PC-25, 125-128CW	150	12.4	1.15	1710	4660
MC-PC-25, 140-142	168	12.9	No Data	762	2960
MC-PC-25, 150-152	147	14.0	1.28	607	2140
MC-PC-25, 160-162	63.3	15.4	No Data	192	524

MC-PC-26, 0-2	33.4	19.1	5.34	463	6360
MC-PC-26, 30-32	90.0	14.3	No Data	385	1750
MC-PC-26, 34-36	93.3	14.9	2.46	3110	16700
MC-PC-26, 42-44	134	16.4	1.20	395	444
MC-PC-26, 46-48	80.2	13.5	1.52	205	142
MC-PC-26, 54-56	38.2	13.8	2.82	118	124
MC-PC-26, 58-60	29.9	16.4	0.86	101	141
MC-PC-26, 70-72	32.4	14.4	1.62	126	140
MC-PC-26, 80-82	27.0	16.4	1.61	97.5	134
MC-PC-26, 110-112	55.5	13.3	1.03	192	153
MC-PC-26, 130-132	33.4	11.9	No Data	167	167
MC-PC-26, 150-152	29.4	10.8	1.20	164	218
MC-PC-26, 160-162	58.0	19.3	1.86	226	290
MC-PC-26, 170-172	79.5	12.8	No Data	336	416

MC-PC-26, 190-192	48.4	12.9	0.55	187	268
MC-PC-26, 200-202	46.4	14.3	1.67	196	192
MC-PC-26, 210-212	53.6	13.6	1.10	202	182
MC-PC-26, 220-222	43.7	15.1	1.03	172	137
MC-PC-26, 240-242	59.7	11.9	2.48	208	191
MC-PC-27, 0-2	61.4	12.3	3.98	277	319
MC-PC-27, 30-32	105	12.0	3.87	423	335
MC-PC-27, 40-42	104	11.2	4.02	414	303
MC-PC-27, 50-52	109	12.3	3.79	446	343
MC-PC-27, 60-62	106	11.5	3.68	440	361
MC-PC-27, 80-82	109	11.7	3.58	452	437
MC-PC-27, 90-92	124	11.6	16.4	524	548
MC-PC-27, 100-102	100	11.5	3.33	436	538
MC-PC-27, 110-112	95.5	12.6	3.00	415	541
MC-PC-27, 130-132	51.7	14.5	18.7	243	444
MC-PC-27, 140-142	41.1	15.7	3.73	127	290
MC-PC-27, 150-152	43.6	16.4	3.59	100	183
MC-PC-27, 160-162	42.4	15.8	2.53	115	230
MC-PC-27, 180-182	38.6	14.1	21.0	194	565
MC-PC-27, 190-192	45.0	16.8	2.60	103	217
MC-PC-27, 200-202	46.0	16.6	2.43	87.1	180
MC-PC-27, 210-212	29.4	15.4	3.69	72.3	133
MC-PC-27, 230-232	28.9	15.1	2.77	71.7	148
MC-PC-27, 240-242	30.6	16.0	2.89	73.5	154
MC-PC-27, 250-252	30.3	15.5	3.97	75.3	167
MC-PC-27, 260-262	42.8	13.2	10.2	189	490
MC-PC-27, 280-282	34.1	15.5	2.81	78.9	142
MC-PC-27, 290-292	31.2	15.7	16.6	73.8	134
MC-PC-27, 300-302	27.6	13.4	3.39	73.5	143
MC-PC-27, 310-312	31.4	14.4	2.32	76.1	139
MC-PC-27, 330-332	22.5	13.3	15.6	72.1	148
MC-PC-27, 340-342	23.0	13.3	2.77	68.3	144
MC-PC-27, 350-352	24.6	13.4	2.67	73.4	151
MC-PC-27, 360-362	27.5	12.9	2.27	69.3	141
MC-PC-27, 380-382	29.5	14.4	3.48	73.6	154
MC-PC-27, 390-392	26.5	13.6	3.01	74.90	149
MC-PC-27, 400-402	51.2	14.8	3.23	132	215
MC-PC-28, 0-2	41.2	11.7	4.20	223	818
MC-PC-28, 30-32	72.1	14.0	4.37	308	279
MC-PC-28, 40-42	83.3	12.2	2.22	386	337
MC-PC-28, 60-62	108	13.2	3.92	436	396
MC-PC-28, 70-72	107	13.5	3.28	416	383
MC-PC-28, 90-92	58.3	21.9	3.42	96.6	418
MC-PC-28, 100-102	62.7	22.2	3.73	96.9	227
MC-PC-28, 120-122	61.2	19.1	3.30	179	558
MC-PC-28, 130-132	59.2	21.6	3.36	106	434
MC-PC-28, 140-142	59.9	21.9	3.71	112	590
MC-PC-28, 150-152	58.0	20.5	3.73	118	223
MC-PC-29, 0-2	64.8	10.9	No Data	394	1980

MC-PC-29, 30-32	103	12.7	1.80	579	1370
MC-PC-29, 40-42	99.4	13.3	1.21	549	1560
MC-PC-29, 50-52	81.5	12.8	0.47	437	1730
MC-PC-29, 70-72	28.2	16.3	2.92	103	263
MC-PC-29, 70-72	44.0	13.4	14.0	89.6	177
MC-PC-29, 80-82	24.8	17.4	1.51	98.9	307
MC-PC-29, 90-92	27.1	17.4	2.39	102	229
MC-PC-29, 110-112	29.9	14.6	No Data	142	287
MC-PC-29, 120-122	29.0	16.3	1.35	84.5	167
MC-PC-29, 130-132	23.7	15.1	2.16	80.8	157
MC-PC-29, 140-142	28.2	14.6	0.40	84.5	180
MC-PC-29, 160-162	22.4	14.7	No Data	78.0	143
MC-PC-29, 170-172	20.0	12.1	No Data	90.2	201
MC-PC-29, 180-182	22.6	14.6	1.80	111	197
MC-PC-29, 200-202	34.6	16.0	11.2	109	200
MC-PC-29, 210-212	33.4	14.9	3.65	126	380
MC-PC-29, 220-222	32.5	13.9	1.96	105	488
MC-PC-29, 240-242	32.8	15.4	1.72	101	434
MC-PC-29, 244-246	31.8	15.8	3.61	423	10500
MC-PC-29, 248-250	33.6	16.7	1.07	130	1100
MC-PC-29, 252-254	43.6	16.2	3.82	124	633
MC-PC-29, 256-258	33.7	16.4	2.08	191	544
MC-PC-29, 260-262	32.3	15.9	0.97	83.6	306
MC-PC-29, 264-266	38.8	17.6	No Data	122	368
MC-PC-29, 268-270	35.2	15.9	No Data	No Data	No Data
MC-PC-30, 0-2	54.0	12.1	0.53	671	19600
MC-PC-30, 4-6	50.8	15.2	1.00	546	15200
MC-PC-30, 8-10	54.4	13.7	1.93	679	13300
MC-PC-30, 30-32	39.0	16.2	1.96	159	1730
MC-PC-30, 40-42	42.0	20.8	1.84	137	1220
MC-PC-30, 50-52	37.9	19.0	1.50	157	1930
MC-PC-30, 60-62	41.1	16.8	1.65	159	2220
MC-PC-30, 80-82	40.5	15.9	1.01	168	2110
MC-PC-30, 90-92	40.9	16.1	1.31	140	1450
MC-PC-30, 100-102	41.3	16.0	1.33	168	2690
MC-PC-30, 110-112	41.4	18.7	1.43	143	1540
MC-PC-30, 140-142	41.8	18.5	2.05	203	3540
MC-PC-30, 150-152	37.1	14.8	1.75	498	12600
MC-PC-30, 153-155	7.03	2.80	No Data	741	23300
MC-PC-30, 160-162	11.1	7.30	0.68	596	10200
MC-PC-30, 170-172	69.9	13.4	0.94	658	10700
MC-PC-30, 180-182	64.2	16.2	1.50	820	13200
MC-PC-30, 180-182CW	116	14.9	0.52	1430	15900
MC-PC-30, 200-202	52.0	17.3	1.70	356	7320
MC-PC-30, 210-212	56.3	15.7	1.45	554	16600
MC-PC-30, 220-222	43.9	19.3	1.42	128	1230
MC-PC-30, 230-232	42.3	18.5	2.00	141	1410
MC-PC-30, 240-242	41.0	16.2	1.41	235	4460
MC-PC-30, 258-260CW	114	16.7	0.64	648	13000
MC-PC-30, 280-282	56.7	17.2	1.72	138	793
MC-PC-30, 290-292	43.9	19.3	1.83	113	287

MC-PC-30, 310-312	46.6	19.9	1.72	125	758
MC-PC-30, 320-322	44.4	11.9	1.77	241.1	481.5
MC-PC-30, 330-332	96.9	9.88	1.70	465	355
MC-PC-30, 340-342	184	12.1	0.88	839	3430
MC-PC-30, 343-345CW	190	15.1	No Data	875	5530

Notes: CW denotes sediment that coated carbonate nodules when removed. The sediment was washed off with deionized water and analyzed according to the procedures for sediment samples described above.

Table 5. XRD data from nodules.

Nodule	Core	Depth (cmbsf)	Major Peak	Major Peak Intensity (CPS)	Secondary Peak	Secondary Peak Intensity (CPS)	Minor Peaks
<i>Rocky</i>							
G-13N1	GB-PC-13	32-34	Barite	900	Aragonite	518	(Pb-rich) barite
M-25N1	MC-PC-25	125-128	Calcite	3299	High-Mg calcite	576	
M-30N1	MC-PC-30	180-182	Calcite	2633	Barite	293	Quartz
M-30N3	MC-PC-30	343-345	Calcite	2691	Barite	581	High-Mg calcite
<i>Smooth</i>							
G-21N1	GB-PC-21	190-192	Calcite				
G-21N2	GB-PC-21	200	Calcite	3381	High-Mg calcite	726	
G-22N1	GB-PC-22	198-200	Calcite	1841	Barite	557	High-Mg calcite
G-24N1	GB-PC-24	85-88	Calcite	3434	High-Mg calcite	464	
G-24N2	GB-PC-24	179-180	Calcite	2943	Barite	452	(Pb-rich barite), Quartz, Aragonite
G-24N3	GB-PC-24	209-212	Calcite	3139	Hi-Mg calcite	570	
M-30N2	MC-PC-30	208-210	Calcite	1347	(Pb-rich) barite	869	High-Mg calcite, Quartz

Notes: Intensity is measured in counts per second (CPS). Minor mineral phases are listed in order of abundance. Pb-rich barite was detected, however, it is not confirmed with chemical data.

Table 6. Major and minor element data for nodule digestions.

Nodule	Ca (g/kg)	Mg (g/kg)	K (g/kg)	Ba (mg/kg)	Sr (mg/kg)
<i>GB 425</i>					
G-13N1	221	79.7	8.32	17300	1360
G-21N1	290	321	25.6	3400	1350
G-21N2	285	362	22.9	459	1100
G-22N1	200	168	18.2	14900	1070
G-24N1	227	199	25.3	13700	1820
G-24N2	269	194	22.0	23500	2580
G-24N3	241	223	28.2	12800	1510
<i>MC 852/853</i>					
M-25N1	284	214	15.7	11100	1360
M-30N1	230	290	27.3	17100	1770
M-30N2a	143	209	22.5	17300	1130
M-30N2b	144	205	22.4	20700	1360
M-30N3	284	248	19.9	24300	1870

Appendix I: Core Descriptions

All cores sampled for sediment analysis were visually described based on color, grain size, texture and the presence of carbonate nodules or gravels. Generally, all cores consist of fine grey mud with minor amounts of sand. In a few key cores, carbonate nodules and gravels are observed; these horizons are particularly important for understanding the formation barite fronts.

The textures of the sediments, including “moussey”, wet, or full of voids, are important observations for detecting hydrate. Hydrate dissociates during core recovery because it is no longer within specific pressure and temperature boundaries. During this process, methane gas and other light hydrocarbons are released and excess water is left in the sediments. In some cores, the physical void space formerly occupied by the hydrate is preserved. Therefore, these textures are proxies for *in situ* hydrate deposits.

Legend for Core Descriptions

Lithologies

Mud or Mudstone

Sandy/Silty Mud or Mudstone

Interstitial Water Sample

Lithologic Accessories

Coarse Carbonate Gravel

Sand Lamina

Silt Lamina

Black Lamina

Bivalve Fragment

Carbonate Nodule

Core Disturbances

Soupy Sediment

Moussey Texture

Disturbed

GB 425: Core GB-PC-12

GB 425: Core GB-PC-13

GB 425: Core GB-PC-15

GB 425: Core GB-PC-19

GB 425: Core GB-PC-19 (cont.)

GB 425: Core GB-PC-19R

GB 425: Core GB-PC-20

GB 425: Core GB-PC-21

GB 425: Core GB-PC-21 (cont.)

GB 425: Core GB-PC-22

GB 425: Core GB-PC-22 (cont.)

GB 425: Core GB-PC-24

MC 852/853: Core MC-PC-25

MC 852/853: Core MC-PC-26

MC 852/853: Core MC-PC-27

MC 852/853: Core MC-PC-27 (cont.)

MC 852/853: Core MC-PC-28

MC 852/853: Core MC-PC-29

MC 852/853: Core MC-PC-30

MC 852/853: Core MC-PC-30 (cont.)

Appendix II: Sequential Barite Extractions

Introduction

Although bulk chemical analyses strongly suggest that barite is the dominant mineralogic phase for barium in the Gulf of Mexico, the specific solid phase in sediment samples is unknown. Therefore, the aim of this step in the procedure is to confirm the presence of barite in sediment samples using a sequential barite extraction.

Six samples were selected for extractions and included five from Mississippi Canyon (**Figure 3**) and one barite standard. The suite of sediments from Mississippi Canyon consists of a background sample (MC-PC-27, 0-2 cm) and four samples of increasing depth from the same core (MC-PC-30, 0-2 cm; 50-52 cm; 140-142 cm; and 170-172 cm). The barite standard was used to establish the amount of barite lost during the procedure and the extent of weathering on the crystals.

Methods

The extraction sequence, adapted from Paytan et al. (1993) and Eagle et al. (2003), involves a series of treatments using reagents listed in **Table AII-1**. In each step, the reagent was added to the samples and allowed to react for approximately 24 hours. At the end of each treatment, the leachate solution was decanted and the remaining sediment was washed three times with dionized water (18M Ω). Samples were not washed in between steps involving HF (steps 4 through 7). When all HF treatments were completed, samples were washed with aluminum chloride once and dionized water three times. Before the nitric acid treatments (steps 8 and 9), residual sediments were ashed in

a muffle furnace for one hour at 700°C and underwent two heavy liquid separations using sodium metatungstate. Because the sequential extraction also preserves titanium oxides and alumino-silicates, the final residual sediments were freeze dried and examined using a JEOL JXA 840 Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS) at Rice University.

Table AII-1. List of reagents used in sequential barite extraction.

Step	Treatment	Purpose
1	20 mL 4-N Acetic Acid	Remove carbonates
2	20 mL 6% Sodium Hypochlorite + 0.1 mL concentrated Nitric Acid in a hot water bath (~50°C)	Remove organics
3	30 mL hydroxylamine hydrochloride solution in a hot water bath (~80°C)	Remove Mn, Fe, Ba oxides
4	15 mL concentrated Nitric Acid + 5 mL HF	Remove silicates
5	10 mL concentrated Nitric Acid + 10 mL HF	Remove silicates
6	5 mL concentrated Nitric Acid + 15 mL HF	Remove silicates
7	5 mL concentrated Nitric Acid + 15 mL HF	Remove silicates
8	4 mL 50% concentrated Nitric Acid	Remove oxides that form in furnace
9	4 mL 50% concentrated Nitric Acid	Remove oxides that form in furnace

In marine sediment, barium can potentially be found in one of five forms: barite (biogenic or authigenic); barium carbonate (witherite or barytocalcite); barium associated with Mn, Fe, Ba oxides; barium cations sorbed onto organics or clays; and barium incorporated into alumino-silicates. To assess if barium is found in phases other than barite, aliquots of the leachate were taken from each sample after step 1 (removes carbonates), step 2 (removes extractable organics) and step 3 (removes Mn, Fe, Ba oxides). Leachate aliquots were analyzed for Ca, Sr and Ba using a Varian Vista Pro ICP-AES in the Geochemistry Laboratory at Rice University (please see section 5.1 *Pore Fluid Analysis* for procedural details). Wavelengths used include 318.127 nm (Ca), 407.771 nm (Sr) and 455.403 nm (Ba).

Results and Discussion

Two categories of samples emerge based on the amount of residual sediment extracted relative to the amount of original sediment used: high yield samples (> 13 % of original sample) and low yield samples (< 3 % of original sample). Given the bulk barium content of these sediments, it is not surprising that the amount of residual sediment is related to the sample location and depth. Low yield samples are from the flank of the mud volcano (MC-PC-27, 0-2 cm, background) or from depths between barium fronts (MC-PC-30, 50-52 cm; and 140-142 cm), whereas high yield samples are from barium fronts (MC-PC-30 0-2 cm; and 170-172 cm). SEM/EDS images show that low yield samples have little to no barite and consist largely of titanium oxides and clay minerals (alumino-silicates) (**Figure AII-1**). In contrast, large barite crystals are present in high yield samples and can be as long as 10 to 15 μm (**Figure AII-1**). However,

titanium oxides and alumino-silicates must also comprise a large portion of high yield samples because the experimental mass yield is considerably greater than the mass yield calculated from the bulk sediment (**Table AII-2**).

Table AII-2. Sediment masses for sequential barite extraction. Bulk barium content was compiled from sediment digestion data (**Table 3**) and was used to compute the calculated mass yield.

Sample	Authigenic barium content (mg/kg)	Original sample mass (g)	Calculated mass yield (mg)	Experimental mass yield (g)
PC-27 0-2	318.7	2.8	0.892	< 0.1
PC-30 0-2	19600	5.1	99.9	0.9
PC-30 50-52	1931	3.8	7.34	< 0.1
PC-30 140-142	3540	3.8	13.5	< 0.1
PC-30 170-172	10700	3.9	41.8	0.5
Barite standard	N/A	0.5	N/A	0.4

Chemical analyses of the leachates confirm that barite is the dominant mineral phase in high yield (barium front) samples, while barium bound in oxides comprises a large part of lower yield samples (**Figure AII-2**). When compared to the authigenic barium content of bulk sediment, only very low barium concentrations are associated with the carbonate fraction for all samples, implying that little to no barium is sequestered as witherite or barytocalcite. Because the amount of barium found with extractable organics is greater in low yield or non-barium front samples, it is possible that labile barium cations adsorb onto polar organic molecules in these environments. In this case, organic molecules would serve as a barium carrier or holder until the molecule reaches the barite front or is microbially consumed.

Table AII-3. Carbonate, extractable organic and oxide fractions of sediment samples based on the ICP measurements of the leachates.

Sample	Ca ($\mu\text{mol/kg}$)	Sr ($\mu\text{mol/kg}$)	Ba ($\mu\text{mol/kg}$)
<i>Carbonate Fraction</i>			
PC-27 0-2	1.01	2.51	0.02
PC-30 0-2	0.89	0.97	0.02
PC-30 50-52	0.56	1.18	0.03
PC-30 140-142	0.56	1.02	0.02
PC-30 170-172	0.67	0.99	0.02
Barite standard	below detection	0.01	0.24
<i>Extractable Organic Fraction</i>			
PC-27 0-2	0.10	0.29	0.15
PC-30 0-2	0.05	0.21	0.05
PC-30 50-52	0.15	0.28	0.11
PC-30 140-142	0.13	0.27	0.09
PC-30 170-172	0.07	0.30	0.08
Barite standard	below detection	0.02	2.08
<i>Oxide Fraction</i>			
PC-27 0-2	0.02	0.11	0.67
PC-30 0-2	0.13	0.40	0.12
PC-30 50-52	0.10	0.22	0.46
PC-30 140-142	0.11	0.21	0.16
PC-30 170-172	0.11	0.48	0.07
Barite standard	below detection	0.28	8.64

It is important to note that the sequential extraction procedure has important effects on the residual barite. Crystals from the treated barite standard are highly weathered as compared to crystals with no treatment. Crystals without treatment have angular edges, smooth cleavage plans and are as large as 250 μm . After the extraction

procedure, barite crystals are very rounded with large pits, particularly on surfaces that are not cleavage planes. With the exception of a few large crystals, treated barite crystals are smaller than untreated crystals and range from 10 to 100 μm in length. Consequentially, it is impossible to make any conclusions about the *in situ* barite dissolution using this method. Regardless, results from this sequential extraction are important because it confirms that barite is the dominant solid phase for barium in marine sediment.

Conclusions

Using a sequential extraction technique, I have isolated and positively identified barite as the dominant solid phase for barium fronts. At non-front sites, other barium minerals may play a role in the barium cycle, particularly barium bound in oxide minerals and barium associated with extractable organics. Although the barium mineralogy for these sediments is not complete, these data give considerable insight into barium cycling, particularly at mud volcanoes, in the Gulf of Mexico.

(A) Barite Standards

Barite Standard - No Treatment
Magnified 120x

Barite Standard - Treated
Magnified 220x

(B) High Yield Samples (Extraction)

MC-PC-30 0-2
Magnified 1800x

MC-PC-30 170-172
Magnified 2300x

Figure AII-1. (A) SEM images of the barite standard before and after treatment. Crystals with no treatment are very angular with well-defined crystals planes; large barite crystals are common. After treatment, crystals are considerably smaller and more rounded with pits in the surface of the crystal plane. (B) SEM images of high yield samples. Barite is very common but the crystals are small and highly pitted. Other particles, probably alumino-silicates and titanium oxides, are present and clump together with barite crystals.

(C) Low Yield Samples

Figure AII-1. (C) SEM images of low yield samples. There is considerably less residual material associated with these samples. Most crystals are likely aluminosilicates and titanium oxides, although traces amounts of barite are present. Like high yield samples, small crystals tend to clump together making them difficult to identify.

Figure AII-2. Bulk sediment barium content versus barium extracted during the first three steps. Data from barium fronts (high yield samples) have high bulk contents with very little contribution from the extracted fractions, implying that barite is the dominant phase. Non-front (low yield) samples show a range in extracted barium with respect to the bulk barium, suggesting that minor barium phases may play a role at these sites.

Appendix III: X-Ray Diffraction (XRD) Analysis

XRD analysis was used to determine the bulk mineralogy of all nodules. In preparation for analysis, all samples were washed three times with dionized water ($18\text{M}\Omega$), freeze-dried and powdered. XRD determination was conducted on a D/Max 2000/PC Rigaku system in the Geochemistry Laboratory at Rice University. Samples were measured using a continuous scan from 20 to $50^\circ 2\theta$ at 40 kV ; a limited 2θ scan was used because any peaks associated with minerals likely to occur in marine sediment would fall within this range. A silicon standard was run before and after all samples to calibrate the instrument and to detect any drift. Minerals were identified using Rigaku's Jade 6 software.

GB 425: Nodule G-13N1

Peak	2θ	Intensity (CPS)	Phase ID
1	20.357	115	Barite
2	22.740	286	Barite
3	24.801	261	Barite
4	25.203	126	Barite (Pb-rich)
5	25.859	765	Barite
6	26.117	484	Aragonite
7	26.562	730	
8	26.841	900	Barite
9	28.700	577	Barite
10	29.442	158	
11	29.742	213	
12	31.441	350	Barite
13	32.700	373	Barite
14	36.039	346	Barite
15	37.148	80	Aragonite
16	37.719	188	Aragonite
17	38.280	286	Aragonite
18	40.721	161	Barite
19	42.640	819	Barite
20	44.001	116	Barite
21	45.700	518	Aragonite
22	47.075	53	Barite
23	48.219	338	Aragonite
24	48.942	110	Barite

GB 425: Nodule G-21N1

Peak	2θ	Intensity (CPS)	Phase ID
1	23.124	359	Calcite
2	26.521	469	
3	29.541	3381	Calcite
4	30.883	178	
5	34.905	36	
6	36.178	441	High-Mg Calcite
7	39.621	726	High-Mg Calcite
8	43.438	588	High-Mg Calcite
9	47.500	331	Calcite
10	47.939	572	High-Mg Calcite
11	48.841	582	High-Mg Calcite

GB 425: Nodule G-21N2

Peak	2θ	Intensity (CPS)	Phase ID
1	23.124	359	Calcite
2	26.521	469	
3	29.541	3381	Calcite
4	30.883	178	
5	34.905	36	
6	36.178	441	High-Mg Calcite
7	39.621	726	High-Mg Calcite
8	43.438	588	High-Mg Calcite
9	47.500	331	Calcite
10	47.939	572	High-Mg Calcite
11	48.841	582	High-Mg Calcite

GB 425: Nodule G-22N1

Peak	2θ	Intensity (CPS)	Phase ID
1	20.377	127	Barite
2	22.698	307	Barite
3	23.039	155	Calcite
4	24.717	228	Barite
5	25.799	493	Barite
6	26.680	416	Barite
7	28.680	518	Barite
8	29.461	1841	Calcite
9	30.769	34	
10	31.404	301	Calcite
11	32.661	264	Barite
12	36.117	291	Barite
13	38.542	87	Barite
14	39.518	337	Barite
15	40.681	152	Barite
16	42.500	500	Barite
17	42.800	557	Barite
18	43.262	335	Calcite
19	43.959	132	Barite
20	47.045	104	Barite
21	47.299	192	Calcite
22	47.719	340	High-Mg Calcite
23	48.719	344	Calcite

GB 425: Nodule G-24N1

Peak	2θ	Intensity (CPS)	Phase ID
1	20.760	160	
2	22.829	152	
3	23.043	282	Calcite
4	25.954	124	
5	26.543	1961	
6	27.720	135	
7	29.461	3434	Calcite
8	30.820	59	
9	31.535	129	Calcite
10	32.716	39	
11	34.885	61	
12	36.099	415	Calcite
13	39.541	522	Calcite
14	41.155	33	
15	42.420	105	
16	43.281	435	Calcite
17	47.103	146	Calcite
18	47.382	286	Calcite
19	47.779	464	High-Mg Calcite
20	48.343	326	Calcite
21	48.722	545	

GB 425: Nodule G-24N2

Peak	2θ	Intensity (CPS)	Phase ID
1	20.406	55	Barite
2	20.821	91	Quartz
3	22.705	158	Barite
4	23.078	324	Calcite
5	24.799	137	Barite
6	25.838	182	Barite
7	26.540	630	Quartz
8	27.831	143	
9	28.738	265	Barite
10	29.460	2943	Calcite
11	30.830	153	Aragonite
12	31.536	196	Barite
13	34.849	53	
14	36.080	452	Barite
15	36.462	70	Barite (Pb-rich)
16	38.848	42	Barite (Pb-rich)
17	39.463	616	Quartz
18	40.760	95	Barite
19	42.503	259	Quartz
20	43.260	510	Calcite
21	47.323	266	Calcite
22	47.739	496	High-Mg Calcite
23	48.700	596	Aragonite

GB 425: Nodule G-24N3

Peak	2θ	Intensity (CPS)	Phase ID
1	23.018	285	Calcite
2	24.725	58	
3	25.755	78	
4	26.481	428	Calcite
5	27.445	232	
6	27.664	116	
7	29.400	3139	Calcite
8	30.437	44	
9	30.887	52	
10	31.472	103	Calcite
11	32.839	56	
12	34.604	43	
13	34.949	46	Calcite
14	36.018	445	
15	39.459	637	
16	41.719	174	Calcite
17	42.361	62	
18	42.566	87	
19	43.258	532	Calcite
20	44.001	24	
21	47.221	207	
22	47.640	570	High-Mg Calcite
23	48.600	613	Calcite

MC 852/853: Nodule M-25N1

Peak	2θ	Intensity (CPS)	Phase ID
1	20.825	132	
2	23.080	308	Calcite
3	26.559	456	
4	29.440	3299	Calcite
5	30.854	88	
6	31.499	157	Calcite
7	32.844	95	
8	34.811	62	
9	36.020	476	Calcite
10	36.552	169	High-Mg Calcite
11	36.961	65	
12	39.479	709	Calcite
13	40.982	45	
14	42.189	44	
15	42.444	73	
16	42.620	77	
17	43.260	598	Calcite
18	47.283	297	Calcite
19	47.679	576	High-Mg Calcite
20	48.679	638	Calcite

MC 852/853: Nodule M-30N1

Peak	2θ	Intensity (CPS)	Phase ID
1	20.380	74	Barite
2	20.795	90	Quartz
3	22.780	193	Barite
4	23.080	289	Calcite
5	24.897	187	Barite
6	25.319	48	
7	25.780	205	Barite
8	26.580	502	Quartz
9	27.417	69	
10	27.795	111	
11	28.818	293	Barite
12	29.461	2633	Calcite
13	30.824	154	
14	31.503	164	Barite
15	32.759	120	Barite
16	34.877	51	
17	35.099	46	
18	36.040	394	Calcite
19	36.584	186	Quartz
20	39.500	541	Quartz
21	40.801	51	Barite
22	42.541	261	Barite
23	43.240	446	Calcite
24	44.112	68	Barite
25	45.732	52	Quartz
26	47.639	418	Calcite
27	48.701	449	Calcite

MC 852/853: Nodule M-30N2

Peak	2θ	Intensity (CPS)	Phase ID
1	20.484	112	Barite (Pb-rich)
2	22.780	293	Barite (Pb-rich)
3	23.140	160	Calcite
4	24.821	869	Barite (Pb-rich)
5	25.838	370	Barite (Pb-rich)
6	26.841	798	Barite (Pb-rich)
7	28.740	454	Barite (Pb-rich)
8	29.480	1347	Calcite
9	30.863	177	
10	31.520	340	Calcite
11	32.881	214	Barite (Pb-rich)
12	34.737	51	
13	36.120	337	Calcite
14	38.742	88	Barite (Pb-rich)
15	39.618	365	Quartz
16	40.820	159	Barite (Pb-rich)
17	42.639	630	Barite (Pb-rich)
18	42.980	537	Calcite
19	43.408	214	High-Mg Calcite
20	44.045	124	
21	47.084	103	Calcite
22	47.564	183	High-Mg Calcite
23	47.920	132	High-Mg Calcite
24	48.581	243	Calcite
25	48.823	260	
26	49.019	226	High-Mg Calcite

MC 852/853: Nodule M-30N3

Peak	2θ	Intensity (CPS)	Phase ID
1	20.437	54	Barite
2	22.801	202	Barite
3	23.100	319	Calcite
4	24.837	113	Barite
5	25.761	199	Barite
6	26.518	274	
7	28.742	322	Barite
8	29.520	2691	Calcite
9	31.517	212	Barite
10	32.777	166	Barite
11	36.101	434	Barite
12	39.541	581	Barite
13	40.762	71	Barite
14	42.582	293	Barite
15	43.320	447	Calcite
16	44.034	152	Barite
17	47.322	237	Calcite
18	47.721	443	High-Mg Calcite
19	48.798	505	Barite

Silicon Standard

Peak	2θ	Intensity (CPS)	Phase ID
1	28.321	8396	Silicon
2	47.220	6326	Silicon
3	56.020	3792	Silicon
4	69.022	970	Silicon
5	76.300	1718	Silicon
6	87.487	52	Silicon
7	87.981	2195	Silicon
8	88.431	122	Silicon
9	94.898	1355	Silicon

Appendix IV: Petrographic Description of Nodules

Thin sections were made from at Texas Petrographic Service, Inc. of Houston, Texas. Clear epoxy was injected into all nodules for support during thin section production. Nodules were mounted on standard glass slide (25 x 46 mm) and ground to standard thickness (0.03 mm). For section description and photography, a Zeiss petrographic microscope connected to an Evolution LC digital camera was used and processed with Image Pro software. Thin sections were described based on the matrix (presumably carbonate for all nodules), clasts or crystals within the matrix and other prominent features such as veins, secondary mineralization, microfossils and organic material. The percentage of any given component was estimated visually. Some sections were coated with gold and examined using a JEOL JXA 840 Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS) at Rice University. The SEM-EDS was utilized to confirm the chemical composition of key features such as barite crystals, vein-fillings and clasts.

GB 425: Nodule G-13N1

Core: GB-PC-13

Depth: 32-34 cm

Type: Rocky

Mass: 10.2 g

Dimensions: 3.3 cm x 2.7 cm x 1.7 cm

Thin Section Description: Nodule G-13N1 is a conglomerate of clasts with a fine-grained, brown matrix. Large voids are very common and are being filled with long, acicular crystals with at least second or third order birefringence, likely barite. Quartz grains are common (~25%) and are typically well rounded and highly spherical. Grains range from very fine silt to sand size. Microfossils found in this nodule are abundant in quantity and diverse in type. Such fossils might include: bivalve fragments, foraminifera, and types of large bacteria.

Nodule G-13N1

SEM image of G-13N1 taken at 30x.

Photomicrograph of G-13N1 taken at 60x in plane polarized light.

GB 425: Nodule G-21N1

Core: GB-PC-21

Depth: 190-192 cm

Type: Smooth

Mass: 24.0 g

Dimensions: 5.3 cm x 4.0 cm x 2.1 cm

Thin Section Description: Nodule G-21N1 has a very fine grained brown matrix with very small, white crystals. The white crystals are found throughout the section (~ 30%) and tend to concentrate in particular regions. These crystals show little to no birefringence and no undulating extinction but could potentially be quartz clasts or barite crystals. Microfossils represent ~3 - 5% of the sample and appear to be preserved via mineral replacement. Brown organic material is also present (~2 - 3%).

Nodule G-21N1

Photomicrograph of G-21N1 taken at 60x in plane polarized light

GB 425: Nodule G-21N2

Core: GB-PC-21

Depth: 200 cm

Type: Smooth

Mass: 76.0 g

Dimensions: 7.1 cm x 4.4 cm x 2.3 cm

Thin Section Description: Nodule G-21N2 had a very fine grained, brown matrix with small, white grains. The white grains show little to no birefringence or undulating extinction but are well rounded and highly spherical. These grains are found throughout the section (~30%) and could potentially be quartz clasts or barite crystals. In some areas, the white grains are concentrated and show a vague preferred orientation. This nodule has few void spaces that are filled with small, blocky minerals around the edges and quartz with undulating extinction in the center. This in-filling pattern implies that the small block mineral, likely barite, is the primary precipitation and quartz is the secondary. Microfossils represent ~2% of the sample and appear to be preserved via mineral replacement. Brown organic material is also present (~7%).

Nodule G-21N2

SEM image of G-21N2 taken at 60x

Photomicrograph of G-21N2 taken at 60x in plane polarized light

GB 425: Nodule G-22N1

Core: GB-PC-22

Depth: 198-200 cm

Type: Smooth

Mass: 8.7 g

Dimensions: 3.3 cm x 1.9 cm x 1.5 cm

Thin Section Description: Nodule G-22N1 has a very fine grain, brown matrix with small, white grains. Grains vary in size, are well-rounded and highly spherical. White grains show no undulating extinction and birefringence is not apparent. Give other nodules, it is possible that the white grains are either quartz clasts, barite crystals, or both.

Microfossils occurs in ~2 - 3% of the sample whereas brown organic material occurs ~3 - 5%.

Nodule G-22N1

SEM image of G-22N1 taken at 60x

Photomicrograph of G-22N1 taken at 60x in plane polarized light

GB 425: Nodule G-24N1

Core: GB-PC-24

Depth: 85-88 cm

Type: Smooth

Mass: 28.3 g

Dimensions: 4.5 cm x 2.4 cm x 2.2 cm

Thin Section Description: Nodule G-24N1 has a very fine grain, brown matrix with small, white grains. White grains occur throughout the section (~30%) and show a vague preferred orientation. Grains vary in size and the smaller grains are more rounded and spherical. Larger grains are certainly quartz clasts, given the birefringence and slight undulating extinction. Organic material is present (2%) but not common.

Nodule G-24N1

SEM image of G-24N1 taken at 190x

Photomicrograph of G-24N1 taken at 60x
in plane polarized light

GB 425: Nodule G-24N2

Core: GB-PC-24

Depth: 179-180 cm

Type: Smooth

Mass: 16.4 g

Dimensions: 4.8 cm x 2.1 cm x 1.0 cm

Thin Section Description: Nodule G-24N2 has a very fine grain, brown matrix. Barite crystals occur in patches (15%) as elongate crystals organized in a radial pattern.

Quartz clasts are common (25 - 30%) and well rounded and highly spherical. Larger clasts are less spherical. Quartz also exhibits undulating extinction in specific patches of the clasts. Organic material is present (5%) but microfossils are not.

Nodule G-24N2

Photomicrograph of G-24N2 taken at 60x in plane polarized light

GB 425: Nodule G-24N3

Core: GB-PC-24

Depth: 209-212 cm

Type: Smooth

Mass: 44.8 g

Dimensions: 3.7 cm x 5.0 cm x 2.4 cm

Thin Section Description: Nodule G-24N3 has a very fine grain, brown matrix with small, white grains. White grains are found throughout the section (20%) and are well rounded and highly spherical. Clearly, at least some of the grains are quartz clasts, showing undulating extinction. A large vien in the section has white blocky crystals (barite? dolomite?) lining the sides and quartz filling the remainder, implying that the blocky crystals are the primary mineral precipitation and the quartz is the secondary. Further, the quartz in the vien exhibits undulating extinction as well; thus, it is likely that nodule G-24N3 was thermally altered after the quartz mineralization. Organic material (~3 - 5%) and glauconite (<1%) is present.

Nodule G-24N3

Photomicrograph of G-24N3 taken at 60x
in cross polars

MC 852/853: Nodule M-25N1

Core: MC-PC-25

Depth: 125-128 cm

Type: Rocky

Mass: 16.4 g

Dimensions: 5.4 cm x 5.2 cm x 2.8 cm

Thin Section Description: Nodule M-25N1 has a very fine grain, brown matrix. Large void spaces are common and are partially filled with small, white crystals (~30%). These crystals have a blocky habit, high birefringence and are likely barite. Quartz is common (~15%) and is characterized by well-rounded, low sphericity clasts with undulating extinction. Microfossil are also present (~5%) and include foraminifera, bacteria and possible bivalve fragments. Organic material is very common (15%) particularly in void spaces.

Nodule M-25N1

SEM images of M-25N1 taken at 55x

MC 852/853: Nodule M-30N1

Core: MC-PC-30

Depth: 180-182 cm

Type: Rocky

Mass: 27.6 g

Dimensions: 5.0 cm x 4.0 cm x 2.5 cm

Thin Section Description: Nodule M-30N1 has a very fine grain brown matrix. Void spaces are common but are filled with small, white crystals (~35%). These crystals have a block habit, high birefringence and are likely barite. Quartz is present (10%) as small clast that are well rounded and are highly spherical. Microfossils are less common in this nodule (~2 - 3%) although brown organic material is common (15%).

Nodule M-30N1

SEM image of M-30N1 taken at 70x

MC 852/853: Nodule M-30N2

Core: MC-PC-30

Depth: 208-210 cm

Type: Smooth

Mass: (A) 36.4 g (B) 18.1 g*

Dimensions: (A) 6.3 cm x 4.6 cm x 0.9 cm (B) 5.5 cm x 2.5 cm x 0.9 cm*

Thin Section Description: Nodule M-30N2 has a very fine grain, brown matrix with very prominent interlocking barite crystals (40%). Barite crystals are acicular and arranged in a radial pattern. Nodule M-30N2 also contains quartz clasts that are well rounded and highly spherical. Barite crystals appear to have grown around quartz clasts. Veins are present and are filled with quartz with undulating extinction. Such veins cross-cut radial barite crystals, implying that secondary quartz in-filling has occurred. Organic material is present but not common (~2 - 3%).

Nodule M-30N2

SEM image of M-30N2 taken at 140x

Photomicrograph of M-30N2 taken at 60x in plane polarized light

*Two nodules were found at this horizon and appear to be two pieces of a larger nodule.

MC 852/853: Nodule M-30N3

Core: MC-PC-30

Depth: 343-345 cm

Type: Rocky

Mass: 21.6 g

Dimensions: 2.6 cm x 3.5 cm x 3.0 cm

Thin Section Description: Nodule M-30N3 has a very fine grain, brown matrix. Large void spaces are present but entirely filled with barite crystals (~40 - 45%). Barite also occurs in patches independent of former void spaces. Barite crystals have a blocky to acicular habit and high birefringence. Quartz clasts are present in this nodule but are not common (~5 - 10%). Clasts are very small, spherical and well rounded. Microfossils are also sparse (~2%) and small relative to those found higher in this core.

Nodule M-30N3

SEM image of M-30N3 taken at 70x