Transition from hydrothermal vents to cold seeps records timing of carbon release in the Guaymas Basin, Gulf of California

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Abstract

The Guaymas Basin in the Gulf of California is an ideal site to test the hypothesis that magmatic intrusions into organic-rich sediments can cause the release of large amounts of thermogenic methane and CO₂ that may lead to climate warming. In this study pore fluids close (~500 m) to a hydrothermal vent field and at cold seeps up to 20 km away from the northern rift axis were studied to determine the influence of magmatic intrusions on pore fluid composition and gas migration. Pore fluids close to the hydrothermal vent area show predominantly seawater composition, indicating a shallow circulation system transporting seawater to the hydrothermal catchment area rather than being influenced by hydrothermal fluids themselves. Only in the deeper part of the sediment core, composed of hydrothermal vent debris, Sr isotopes indicate a mixture with hydrothermal fluids of ~3%. Also cold seep pore fluids show mainly seawater composition. Most of the methane is of microbial origin and consumed by anaerobic oxidation in shallow sediments, whereas ethane has a clear thermogenic signature. Fluid and gas flow might have been active during sill emplacement in the Guaymas Basin, but ceased 28 to 7 thousand years ago, based on sediment thickness above extinct conduits. Our results indicate that carbon release depends on the longevity of sill-induced, hydrothermal systems which is a currently unconstrained factor.
1 Introduction

Climate change events in Earth’s history have been partly related to the injection of large amounts of greenhouse gases into the atmosphere (e.g. Svensen et al., 2004; Gutjahr et al., 2017). One of the most prominent events was the Paleocene-Eocene Thermal Maximum (PETM) during which the Earth’s atmosphere warmed by about 8°C in less than 10,000 years (Zachos et al., 2003). The PETM was possibly triggered by the emission of about 2000 Gt of carbon (Dickens, 2003; Zachos et al., 2003). Processes discussed to release these large amounts of carbon in a relatively short time are gas hydrate dissociation and igneous intrusions into organic-rich sediments, triggering the release of carbon during contact metamorphism (Kennett et al., 2000; Svensen et al., 2004). The Guaymas Basin in the Gulf of California is considered one of the few key sites to study carbon release in a rift basin exposed to high sedimentation rates.

The Gulf of California is located between the Mexican mainland and the Baja California Peninsula, north of the East Pacific Rise (EPR; Fig. 1). The spreading regime at EPR continues into the Gulf of California and changes from a mature, open ocean-type to an early-opening continental rifting environment with spreading rates of about 6 cm yr⁻¹ (Curray & Moore, 1982). The Guaymas Basin, which is about 240 km long, 60 km wide, and reaching water depths of up to 2000 m, is known as a region of vigorous hydrothermal activity (e.g. Curray and Moore, 1982; Gieskes et al., 1982; Von Damm et al., 1985). Its spreading axis consists of two graben systems (northern and southern troughs) offset by a transform fault (Fig. 1). In contrast to open ocean spreading centres like the EPR, the rifting environment in the Guaymas Basin shows a high sediment accumulation rate of up to 0.8-2.5 m kyr⁻¹ resulting in organic-rich sedimentary deposits of several hundreds of meters in thickness (e.g. Calvert, 1966; DeMaster, 1981; Berndt et al., 2016). The high sedimentation rate is caused by high biological productivity in the water column and influx of terrigenous matter from the Mexican mainland (Calvert, 1966).

Hydrothermal activity in the Guaymas Basin was first reported in the southern trough (e.g. Lupton, 1979; Gieskes et al., 1982; Campbell and Gieskes, 1984; Von Damm et al., 1985). Here, fluids emanate, partly from Black Smoker type vents at temperatures of up to 315°C.
Sills and dikes intruding into the sediment cover significantly affect temperature distribution, and hence environmental conditions (Biddle et al., 2012; Einsele et al., 1980; Kastner, 1982; Kastner and Siever, 1983; Simoneit et al., 1992; Lizarralde et al., 2010; Teske et al., 2014). The magmatic intrusions accelerate early-diagenetic processes and strongly influence the chemistry of the interstitial waters (e.g. Gieskes et al., 1982; Brumsack and Gieskes, 1983; Kastner and Siever, 1983; Von Damm et al., 1985). Lizarralde et al. (2010) reported that sills intruded into the sediment cover and that cold seeps at the seafloor are visible up to 50 km away from the rift axis. They proposed a recently active magmatic process that released much higher amounts of carbon into the water column than previously thought. It was assumed that magmatic intrusions trigger the alteration of organic-rich sediments and release thermogenic methane and CO₂. Varying methane concentrations and temperature anomalies in the water column were interpreted as active thermogenic methane production generated by contact metamorphism (Lizarralde et al., 2010). This process might cause a maximum carbon flux of 240 kt C yr⁻¹ and might induce profound climatic changes.

During the SO241 expedition in June/July 2015 a new hydrothermal vent field was discovered at the flank of the northern trough (Fig. 1; Berndt et al., 2016). The discovered mound rises up to 100 m above the seafloor and predominantly Black Smoker type vents suggest similar endmember temperatures and geochemical composition as found at the southern trough (Berndt et al., 2016; von Damm et al. 1985). Berndt et al. (2016) discovered an active hydrothermal vent system comprised of black smoker-type chimneys that release methane-rich fluids with a helium isotope signature indicative of mid-ocean ridge basalt. The vigorous release of large amounts of methane and CO₂ several hundred of meters into the water column combined with magmatic intrusions into underlying sediments led Berndt et al. (2016) to support the hypothesis that this process might have triggered the PETM during opening of the North Atlantic as proposed by Svensen et al. (2004).

During RV SONNE cruise SO241, both, the recently discovered hydrothermal vent in the northern trough (Berndt et al., 2016) and some of the off-axis seeps (Lizarralde et al. 2010) which are located above potential sill intrusions were investigated by sediment, carbonate, and water column sampling. Here, we present fluid and gas geochemical data from both...
systems as well as carbonate data and discuss these data in the context of seismic data in order to constrain subsurface processes and fluid origin.

2 Materials and methods

2.1 Sampling devices and strategy

During the RV SONNE expedition SO241 seven sites across the central graben of the Guaymas basin were investigated (Fig. 1). Site-specific sampling and data recording was performed using a (1) video-guided multicorer (MUC), (2) gravity corer (GC), (3) temperature loggers attached to the GC or sediment probe, (5) CTD / Rosette water sampler, and (6) video-guided hydraulic grab (VgHG). Sites were selected according to published data on the location of seeps (Lizarralde et al., 2010) and seismic data acquired during the cruise (see below).

2.1.1 Seismic data recording

Seismic data were collected using a Geometrics GeoEel Streamer of 150 to 183.5 m length and 96 and 112 channels, respectively. Two GI guns in harmonic mode (105/105 cubic inch) served as the seismic source. Processing included navigation processing (1.5625 m crooked line binning), 20, 45, 250, 400 Hz frequency filtering, and poststack Stolt migration with water velocity yielding approximately 2 m horizontal and 5 m vertical resolution close to the seafloor.

2.1.2 Sediment and pore fluid sampling

At seepage and vent sites, the video-guided multicorer was used to discover recent fluid release, which is indicated by typical chemosynthetic biological communities at the seafloor (bacterial mats, bivalves, etc.). However, small-scale, patchy distributions of active seepage spots and visibility of authigenic concretions made it difficult to select the “best possible” sampling locations for getting fine-grained sediment samples. Hence, comparing results from different seeps might be biased in this regard. GC deployments were typically performed at
pre-inspected MUC sites or at the center of suspected seeps (based on bathymetry and seismic data).

In total, we present pore fluid data collected at three seepage sites, North (GC01, MUC11), Central (GC03, GC13, GC15, MUC04), and Ring Seeps (MUC05), one Reference Site (no active seep site, see definition above; GC04, MUC02), and one active hydrothermal site, Smoker (GC09, GC10, MUC15, MUC16). A Reference Site, that did not show active seepage or faults indicated by seismic data, was chosen to obtain geochemical background values. In addition, the slope towards the Mexican mainland was sampled as well (GC07) (Fig. 1, Table 1). After core retrieval, gravity cores were cut and split on deck and immediately sampled. Samples were transferred into a cooling lab at 4°C and processed within 1 or 2 hours. Pore fluids were obtained by pressure filtration. Sediment samples for hydrocarbon gases were taken on deck with syringes and transferred to vials containing concentrated NaCl solution (after Sommer et al., 2009). After multicorer retrieval, bottom water was sampled and immediately filtered for further analyses. The sediment was transferred into a cooling lab and sampling was executed in an argon-flushed glove bag. Pore fluids were retrieved by centrifugation and subsequent filtration using 0.2 µm cellulose acetate membrane filters.
Figure 1: Sample locations in the Guaymas Basin, Gulf of California, during RV SONNE expedition SO241. Black lines refer to seismic profiles, displayed in Fig. 2. Graben Site refers to water column sampling only.

2.1.3 Subseafloor temperature measurements

Temperature gradients and thermal conductivity were measured at North Seep, Central Seep, Reference Site, and Smoker Site as well as along a transect across the newly discovered hydrothermal vent field and the rift valley. Miniaturized temperature loggers (MTL) were attached to gravity cores or to a 5 m long sediment lance at a sampling rate of 1 s. The absolute accuracy of these temperature measurements is about 0.1 K and the temperature resolution is 0.001 K (Pfender and Villinger, 2002).

Thermal conductivity was measured on recovered core material in close vicinity to the MTLs using the KD2 Pro Needle Probe instrument. For temperature measurements obtained by a lance, a constant thermal conductivity of 0.7 W/m K was assumed. Data processing was done according to Hartmann and Villinger (2002).

2.1.4 Water column sampling

Water samples were taken by using a video-guided Niskin Water sampler Rosette System (Schmidt et al., 2015) in order to study water column chemistry (i.e. dissolved CH4) and oceanographic parameters (i.e. temperature, salinity, turbidity). Eight water sampling locations were chosen in the vicinity of MUC and GC stations and are termed North (VCTD03), Central (VCTD02), Ring (VCTD01), Graben (CTD01; no video-guided sampling), Smoker (VCTD06 and 10), and Slope (VCTD07). Additionally, hydrocarbon data published in Berndt et al. (2016) from the Smoker Site (VCTD09) are shown. The (V)CTDs were either used in a towed mode (VCTD03, 06, 09, 10) or in station (CTD01; VCTD01, 02, 07) keeping hydrocast mode. The water depth was controlled based on pressure readings, altitude sensors (<50 m distance to bottom), and online video observation (1 - 2 m above the seafloor).

2.1.5 Authigenic carbonate sampling
At Central Seep a block (approx. 1 x 0.5 x 0.3 m) mainly consisting of solidified carbonate matrix covered by a whitish carbonate rim and characterized by coarse open pore space in mm to cm scale (see supplementary Fig. 1S) was recovered in 1843 m water depth from the surface of a typical cold seep environment (close to high abundance of tube worms) by the deployment of a video-guided hydraulic grab (VgHG, GEOMAR).

2.2 Sample treatment and analytical procedures

Pore fluids were analyzed onboard by photometry (hydrogen sulfide and NH₄) and titration (total alkalinity = TA). Subsamples were analyzed in shore-based laboratories for major anions and cations using ion chromatography (IC, METROHM 761 Compact, conductivity mode) and inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN 720-ES), respectively. Detailed descriptions can be found elsewhere (e.g. Scholz et al., 2013). All chemical analyses were tested for accuracy and reproducibility using the IAPSO salinity standard (Gieskes et al., 1991).

Strontium isotope ratios were analyzed by Thermal Ionization Mass Spectrometry (TIMS, Triton, ThermoFisher Scientific). The samples were chemically separated via cation exchange chromatography using the SrSpec resin (Eichrom). The isotope ratios were normalized to NIST SRM 987 value of 0.710248 (Howarth and McArthur, 2004) which reached a precision of ± 0.000015 (2 sd, n = 12).

Water samples taken from Niskin bottles were transferred into 100 ml glass vials with helium headspace of 5 ml and poisoned with 50 µl of saturated mercury chloride solution.

Hydrocarbon composition of headspace gases was determined using a CE 8000 TOP gas chromatograph equipped with a 30 m capillary column (Restek Q-PLOT, 0.32 mm) and a flame ionization detector (FID). Replicate measurements yielded a precision of <3% (2 sd).

Stable carbon isotopes of methane were measured using a continuous flow isotope ratio mass spectrometer (cf-IRMS). A Thermo TRACE gas chromatograph was used to separate the light hydrocarbon gases by injecting up to 1 ml headspace gas on a ShinCarbon ST100/120 packed gas chromatography column. The separated gases were combusted and...
corresponding $\delta^{13}C$ values were determined using a Thermo MAT53 mass spectrometer. The reproducibility of $\delta^{13}C$ measurements was ±0.3‰ VPDB (2 sd).

Stable hydrogen isotope compositions of methane were analyzed by separating methane from other gases by online gas chromatography (Thermo Trace GC; isotherm at 30°C; 30 m RT-Q-Bond column, 0.25 mm ID, film thickness 8 µm). Prior to stable isotope analysis using a coupled MAT 253 mass spectrometer (Thermo) methane-H was reduced to dihydrogen at 1420°C. Data are reported in per mil relative to Standard Mean Ocean Water (SMOW). The precision of $\delta D$-CH$_4$ measurements was ±3‰ (2 sd).

$^{210}$Pb (46.52 keV) and $^{214}$Pb (351.99 keV) were simultaneously measured by two HPGe gamma spectrometry systems (ORTEC GMX-120265 and GWL-100230), each interfaced to a digital gamma-ray spectrometer (DSpecPlus™). Efficiency calibration of the gamma detectors were calibrated using IAEA reference materials, coupled with an in-house secondary standard for various masses (Huh et al., 2006; Lee et al., 2004). $^{214}$Pb was used as an index of $^{226}$Ra (supported $^{210}$Pb) whose activity concentration was subtracted from the total $^{210}$Pb to obtain excess $^{210}$Pb ($^{210}$Pb$_{ex}$). The activities of radionuclides were decay-corrected to the date of sample collection. All radionuclide data are calculated on salt-free dry weight basis.

A representative sample of the authigenic carbonate (cm-scale) was broken from the upper surface of the block, gently cleaned from loosely bound sediment and organic remains and dried at 20°C for 12 hrs. Two different subsamples were prepared by drilling material with a handheld mm-sized mini-drill from the outer rim (whitish coating, lab code: 470-15) and the related inner core (dark matrix, lab code: 472-15).

Prior to aliquot procedures both subsamples were finely ground in an agate mortar providing homogeneous aliquots of suitable grain size for the combined approach of mineral identification by X-ray diffractometry (XRD) (Philips X-ray diffractometer PW 1710 in monochromatic CuKα mode between 2 and 70 2θ (incident angle), for details see supplement), $\delta^{18}$O and $\delta^{13}C$ analyses by stable isotope ratio mass spectrometry (SIRMS) and U-Th geochronology by multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) on a parallel leachate / sequential dissolution approach for single and isochron ages (method see supplement) as well as $^{87}$Sr/$^{86}$Sr isotope signatures for aliquots of the individual U-Th solutions by thermal ionization mass spectrometry (TIMS, for method details please...
refer to pore water Sr isotope analyses). Lipids extracts for biomarker determination were analyzed as well (see below).

From each homogenized carbonate powder sample (see above), an aliquot of 10 mg was separated for carbon $\delta^{13}$C and oxygen $\delta^{18}$O stable isotope analysis. A fraction from this (approximately 1 mg) was dissolved by water-free phosphoric acid at 73°C in a “Carbo-Kiel” (Thermo Fischer Scientific Inc.) online carbonate preparation line and measured for carbon and oxygen stable isotope ratios with a MAT 253 mass spectrometer (Thermo-Fischer Inc.). The $\delta^{13}$C and $\delta^{18}$O values are calculated as deviations from laboratory standard referred to the PDB scale and reported in ‰ relative to V-PDB. The external reproducibility was checked by replicate analyses of laboratory standards as being better than ±0.04‰ for $\delta^{13}$C and ±0.1‰ for $\delta^{18}$O (1SD, n=7) for this sample set. However, the single measurement uncertainties were significantly better and the resulting 2SD (n=3) for both main samples are given in the supplement table S5.

Biomarkers were determined by grounding 4g of the sample and were then sequentially extracted with dichloromethane (DCM)/methanol (3/1, v/v), DCM, and n-hexane (ultrasonication, 20 min). The combined extracts were dried, derivatized using a BSTFA/trimethylchlorosilane mixture (95/5, v/v; 1h; 40°C) and analysed by coupled gas chromatography-mass spectrometry (GC-MS). GC-MS analyses were carried out with a Thermo Fisher Trace 1310 GC coupled to a Quantum XLS Ultra MS. The GC was equipped with a Phenomenex Zebron ZB 5MS capillary column (30 m, 0.1 μm film thickness, inner diameter 0.25 mm). Fractions were injected splitless at 270°C. The carrier gas was He (1.5 mL/min). The GC oven temperature was ramped from 80°C (1 min) to 310°C at 5°C min-1 and held for 20 min. Electron ionization mass spectra were recorded at 70 eV.

3 Results

3.1 Subsurface structure and evidence for sill-related fluid mobilization

Seismic profiles show a wide range of sediment deformation (Fig. 2). Seismic amplitude blanking along vertical zones below the seafloor indicates apparent fluid flow at North, Central, and Ring Seep (Fig. 2). Underneath these locations, sediments are deformed.
Blankening of the seismic signal is attributed to sediment mobilization due to the hydrothermal activity in response to sill intrusion. In contrast, at the Reference Site sediments show a more or less continuous succession without vertical disturbance. At North Seep, a shallow high-amplitude reversed polarity reflector occurs at 50-60 mbsf. Sill depths are inferred from the seismic profiles at ~500 to 600 m for North Seep and with ~350 to 400 mbsf at the other sites, assuming seismic interval velocities of 1600 to 2000 m s\(^{-1}\). Seismic images suggest that massive disturbance of sediments and vertical pipe structures are related to channeled fluid and/or gas advection caused by sill intrusions (Fig. 2). Faults are indicated which may serve as fluid pathways above potential sill intrusions. Closer inspection of the seismic reflectors at the Central Seep (Fig 2c) shows onlap onto a doming structure. On the NW flank of the dome the deepest onlap occurs at 60 ms or 48 m below the sea floor (assuming 1600 m s\(^{-1}\) sediment interval velocity) whereas on the SE flank the shallowest onlap occurs at 15 ms or 12 m below the sea floor.

Fig.2: Seismic profiles of North Seep (a), Smoker Site (b) as well as of Central Seep and Reference Site (c). Seismic section showing doming above the Central Seep. There are
different phases of onlap starting about 60 mbsf (maximum deposition) until about 15 mbsf (minimum deposition) or 48 and 12 mbsf respectively assuming a sediment interval velocity of 1600 m s\(^{-1}\).

3.2 Temperature measurements

Heat flow and temperature gradients were measured at North and Central Seep, Reference Site, and Smoker Site (attached to GCs) as well as in transects along the hydrothermal ridge and rift axis (attached to a temperature lance; Fig. 3, Table 1). Highest heat flow values occurred close to the Smoker Site and range between 599 and 10835 mW m\(^{-2}\). Temperature gradients were also highest at the Smoker Site (~15 K m\(^{-1}\)). In contrast, heat flow values and temperature gradients in the rift valley close to the rift axis ranged between 262 and 338 mW m\(^{-2}\) and 0.4 to 0.5 K m\(^{-1}\), respectively. Generally heat flow values decreased with increasing distance to the rift axis with 140 mW m\(^{-2}\) at the Reference Site, 113 mW m\(^{-2}\) at Central Seep, and 28 mW m\(^{-2}\) at North Seep. Temperature gradients are 0.22 K m\(^{-1}\) at the Reference Site, 0.16 K m\(^{-1}\) at Central Site and 0.14 K m\(^{-1}\) at North Site.

Figure 3: Heat flow in the Guaymas Basin in relative distance to the rift axis.

3.3 Sediment characteristics and sedimentation rates

The sediments are mainly composed of organic-rich diatomaceous clay, consistent with earlier analyses (e.g. Kastner, 1982). At North Seep, the sediments are composed of homogeneous diatomaceous clay. Rare shell fragments and carbonate concretions are
present. Gas hydrates were discovered at 2.5 meters below seafloor (mbsf). Authigenic carbonates were present at the seafloor. At Ring Seep, SW of North Seep, sediments are predominantly composed of diatomaceous clay. At Central Seep, located between North Seep and Smoker Site, sediments are composed of homogeneous diatomaceous clay intercalated with shell fragments and banding of whitish layers in the lower meter of the GC. At the seafloor, authigenic carbonates were present as well. At Smoker Site, ca. 500 m SE of the hydrothermal vent field, surface sediments are likewise composed of diatomaceous clay with light and dark greyish banding. Traces of bioturbation are visible in the upper 4 m. Below about 4 m depth, a sharp contact defines the transition to hydrothermal deposits, which are composed of mm-to-cm sized black to grey Fe-rich sulfides (for a detailed description see Berndt et al. (2016)). Within the hydrothermal deposits brownish to grey clay lenses appear. At the Slope Site, sediments are laminated in the mm- to cm-range. The sediment is dominated by diatomaceous clay and only a few ash lenses exist.

The sedimentation rates ranged between 0.4 m kyr$^{-1}$ at Smoker Site and 3.5 m kyr$^{-1}$ at North seep based on radionuclides measurements (Table 1). Sedimentation rates at all other sites are about 2 m kyr$^{-1}$.

3.4 Pore water geochemistry

All pore water data and isotope measurements of $^{87}$Sr/$^{86}$Sr are listed in supplementary table S2. Pore water profiles of alkalinity, H$_2$S, SO$_4^{2-}$, CH$_4$, NH$_4^+$, Cl$^-$, Mg, and Li are shown in Fig. 4a (GCs) and 4b (MUCs).
Figure 4: Pore water profiles of GCs (a) and MUCs (b). Endmember composition of hydrothermal solutions from Von Damm et al. (1985) and hydrothermal plume geochemical composition from Berndt et al. (2016) are shown as well in (a).
Pore water constituents plotted in Figure 4 were selected to characterize variations in organic matter diagenesis, anaerobic oxidation of methane (AOM), as well as potential water-rock interactions related to subsurface hydrothermal activity. In general, methane concentrations are elevated at the seep locations and at the slope, thus enhancing AOM. Alkalinity and H$_2$S increase with depth for North Seep, Central Seep, and Slope Site, while SO$_4^{2-}$ is decreasing. AOM depths can only be inferred for North Seep with ~160cm and Slope Site with ~300cm. NH$_4$ is only slightly increasing with depth; higher NH$_4$-levels are only found at the Slope Site (Fig. 4). Concentrations of Cl$, Mg$, and Li do not show significant variations from seawater.

Sr concentrations and isotopes are plotted in Fig. 5. Sr concentrations show predominantly modern seawater values, except at North Seep where they strongly decrease. The $^{87}$Sr/$^{86}$Sr isotope ratios also show predominantly seawater values (0.709176; Howarth and McArthur, 2004). North and Ring Seeps show slight decreases in $^{87}$Sr/$^{86}$Sr, whereas values at the Smoker Site decrease strongly below the transition between hemipelagic sediments and hydrothermal deposits (Fig. 5). The ratios show a similar depletion as those from the hydrothermal plume (Berndt et al., 2016).
Fig. 5. Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for GCs (upper panels) and MUCs (lower panels).

For comparison, data from the hydrothermal smoker plume (Berndt et al., 2016), the hydrothermal endmember (Von Damm et al., 1985), and modern seawater (Howarth and McArthur, 2004) are shown in the upper panel. Note the different scale for MUC $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

3.5 Pore water hydrocarbon gases, carbon and hydrogen isotope data

Concentrations of dissolved hydrocarbons and $\delta^{13}\text{C}_{\text{CH}_4}$, $\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$, and $\delta\text{D}_{\text{CH}_4}$ data are reported in supplementary table S3. Overall, our data show a large variability in CH$_4$/(C$_2$H$_6$+C$_3$H$_8$) with ratios between 100 and 10,000 and $\delta^{13}\text{C}_{\text{CH}_4}$ between -25 and -90 ‰. The $\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$ values range between -26.1 and -38.3 ‰ for North Seep and -29.6 and -37.7 ‰ for Central Seep. The $\delta\text{D}_{\text{CH}_4}$ values at both seeps range between -97 and -196 ‰, for Slope Site between -192 and -196 ‰, and for the Smoker hydrothermal plume between -98 and -113 ‰.

3.6 Water column data

Water column characteristics like temperature, salinity, turbidity as well as methane concentrations are shown in figure 6 and supplementary table S4. Surface waters in the Guaymas Basin show warm temperatures up to 29.5°C (salinity: 34.5‰) close to the Mexican mainland (Slope, VCTD07) and up to 24.6°C (34.6‰) in the central basin (Central, VCTD02). With depth, temperatures decrease continuously to 2.8 to 3.0°C (salinity: 34.6‰) close to the sea floor (1600 - 1800m). Turbidity values are high in the deep water layer (~1400-1800m) and indicate a well-mixed deep basin, also shown by relatively homogeneous temperature and salinity data. Only the water column directly above the hydrothermal smoker field (VCTD09) shows strongly elevated temperature (28.4°C) and salinity (35.1‰) (Berndt et al., 2016). Methane concentrations are highest close to the smoker vent field (up to 400 µM, (VCTD09; Berndt et al., 2016)), but still vary in the deep water column of the basin between 2 and 28.1 nM (Central (VCTD02) and Ring (VCTD01), respectively).
Fig. 6: Water column temperature, salinity, turbidity, and methane concentrations. Note that the upper ~300 m bsl in the turbidity data are not shown for scale matters. VCDT10 temperature data are from Berndt et al. (2016).

3.7 Authigenic carbonate data

The authigenic carbonate sample (Fig. S1) consists of 88 to 90% aragonite and 6 to 12% calcite (supplementary Table S5). The bulk outer rim carbonate has an average carbon isotope signature ($\delta^{13}C_{VPDB}$) of -46.6±0.2‰ and an oxygen isotope signature ($\delta^{18}O_{VPDB}$) of 3.7±0.2‰. Inner core carbonate isotope signatures yield similar values with $\delta^{13}C_{VPDB}$ of -44.7±0.2‰ and $\delta^{18}O_{VPDB}$ of 3.6±0.1‰ (Table S5). The average outer rim $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.709184 and the inner core ratio is 0.709176. External reproducibility of NIST-SRM987 is 0.000015 (2 SEM). The U-Th carbonate dating approach on these authigenic carbonates implies formation ages younger than 240 yrs BP.

Lipid extracts obtained from seep carbonate 56-VgHG-4 (Central Site) revealed a strong signal of specific prokaryote-derived biomarkers (Fig. S1). These compounds encompassed archaeal isoprenoid lipids, namely crocetane, 2,6,10,15,19-pentamethyllicosane(-icosenes (PMI, PMIΔ) archaeol, and $\text{sn}2$-hydroxyarchaeol (see Fig. S1 for structures). In addition, the sample contained a suite of non-isoprenoid 1,2-dialkylglycerolethers (DAGE) of bacterial origin. Typical compounds of planktonic origin, such as sterols, were also present, but low in abundance.
4 Discussion

4.2 Origin of seeping fluids

4.2.1 Black Smoker Site

The water column above the newly discovered vent exhibits elevated CH$_4$ concentrations (up to 400 µM) and pCO$_2$ data (>6000 µatm), and the range of measured stable isotope signature of methane ($^{13}$C$_{CH_4}$ between -39‰ and -14.9‰) and a Helium ($^3$He) isotope anomaly clearly indicates gas exhalations from thermogenic organic matter degradation with contributions from a mantle source (Berndt et al., 2016). These northern trough hydrothermal fluids are comparable in their gas geochemistry to the southern trough (Lupton, 1979; Von Damm et al., 1985) as was demonstrated by endmember calculations in Berndt et al., 2016. However, the highest heat flow values up to 10835 mW/m$^2$ are found close to the Smoker Site and are much higher than observed in earlier studies in which maximal 2000 mW/m$^2$ were measured in the center of the trough (Fisher and Becker, 1991).

The high heat flow at Smoker Site even exceeds the hydrothermally more active southern trough where heat flow values of 2000 to 9000 mW/m$^2$ were measured (Fisher and Becker, 1991; Lonsdale and Becker, 1985). This might indicate that hydrothermal activity at the northern trough is younger and a more recent process compared to the southern trough.

Despite the proximity of the gravity cores (GC09, GC10) and multicorer-cores (MUC15, MUC16) to the hydrothermal vent field (~500m distance; temperatures measured immediately after retrieval are up to 60°C) pore fluid geochemical signatures within nearby sediments are not much different from those in seawater (Fig. 4). Specifically Mg, Li, Cl, and $^{87}$Sr/$^{86}$Sr which are considered as good indicators for hydrothermal alterations and/or deep-seated diagenetic processes do not show any prominent excursions from seawater values.

Hydrothermal fluids are typically depleted in Mg and highly enriched in fluid-mobile elements like Li caused by high-temperature reactions with mafic rocks (here sills) and/or sediments through which they percolate (e.g. Einsele et al., 1980; Gieskes et al., 1982; Kastner, 1982; Von Damm et al., 1985; Lizarralde et al., 2010; Teske et al., 2016). Such compositions are reported from DSDP site 477 (Gieskes et al., 1982) and fluids obtained by Alvin dives (Von Damm et al., 1985). Although strongly diluted, CTD samples from the Black Smoker plume in the Northern trough show this trend (Berndt et al., 2016). Our data
therefore suggest that the sediments surrounding the Black Smoker area are not percolated by hydrothermal fluids. We hypothesize that hydrothermal venting causes a shallow convection cell (e.g. Henry et al., 1996) drawing seawater through the sediments towards the smoker, while the sediments become heated by lateral heat conduction.

Geochemical indicators for a diagenetic or catagenetic breakdown of organic matter like NH₄ are only poorly enriched in sediments surrounding the black smoker vents. Expected endmember values should be similar to those reported from the southern trough (20mM; Von Damm et al. (1985)), but they remain well below (≤0.3mM). For comparison, intense organic matter breakdown occurs in areas with high sediment accumulation rates like the continental slope (Simoneit et al., 1986). Here, maximum NH₄-levels of 1-10 mM (accompanied by high levels of alkalinity and AOM; Fig. 3) are reached in the pore water already at subsurface depths of only a few meters, confirming that a fluid mobilized from greater subsurface depth must be enriched in NH₄ and other products of organic matter degradation. Overall, this confirms that early-diagenetic processes are not intense around the Smoker Mound and further indicates a shallow convection mixing seawater into the sediments in ≤4m depth.

Interestingly, there is a slight positive Li excursion at about 4 m depth in core GC09. This might be related to the mineralogy of this sediment section where the main composition changes from diatomaceous clay to hydrothermal deposit (Fe-rich sulfides; see also Sect. 3.3). We suspect that the positive Li anomaly is caused by weak admixing of hydrothermal solutions, as none of the other elements shows drastic concentration changes indicative of early-diagenetic reactions (Gieskes et al., 1982; Chan et al., 1994; Środoń, 1999; Chan and Kastner, 2000; Aloisi et al., 2004; Hensen et al., 2007; Wallmann et al., 2008; Scholz et al., 2009; 2010; 2013). Along with increasing Li concentrations, ⁸⁷Sr/⁸⁶Sr isotope ratios decrease to a value of 0.70908 (Fig.5) and thus tend towards the ⁸⁷Sr/⁸⁶Sr ratio of the local hydrothermal endmember (⁸⁷Sr/⁸⁶Sr = 0.7059; Von Damm, 1990). Hydrothermal endmember Li concentrations in the Guaymas Basin range between 630 and 1076 µM (Von Damm et al., 1985) and are thus 20 to 30 times higher than the Li concentrations measured at the lower end of the core at the Smoker Site (~34 µM; Fig. 4, Table S2) indicating a mixing between seawater and hydrothermal fluids with a hydrothermal component of about ~3% (Fig. 7).
Fig. 7: NH$_4$ (µM) (a) and $^{87}$Sr/$^{86}$Sr ratios (b) versus Li concentrations (µM) of Guaymas Basin cold seeps (North, Central) and the hydrothermal Smoker vent field. Guaymas deep Smoker fluids (GC09) mix with hydrothermal fluids with a share of ~3%. For comparison, Guaymas hydrothermal endmember fluid composition (Von Damm, 1985, 1990), Smoker plume fluid composition (Berndt et al., 2016), slope sediments (in (a) and deep-sourced cold seeps from the Gulf of Cadiz (in (a); Hensen et al., 2007)) are shown.

The hydrothermal activity in the northern trough of the Guaymas Basin can be summarized to occur only in a relatively confined area affecting the surrounding sediments in a minor way by lateral heat transfer. The diatomaceous clay might act as a seal to upwards migrating
fluids, which are channeled to the catchment area of the rising hydrothermal fluids of the Black Smoker vent field (Fig. 4 in Berndt et al., 2016). The geochemical composition of the upwards migrating hydrothermal fluids is likely influenced by high temperature chemical alteration reactions between the sediment and the intruded sills (Fig. 2b). However, shallower pore fluids of surface sediments at the smoker site (i.e. 0-4 m) are not affected by contributions from these fluids and show predominantly seawater signatures. Despite the elevated heat flow in the vicinity of the hydrothermal vent field, early-diagenetic reactions are also not enhanced as seen e.g. by only slightly elevated NH$_4$ concentrations and sulfate concentrations that remain at seawater values throughout the cores (Fig. 4).

4.2.2 Cold seeps

The selection of sampling sites at presumed seep locations was based on existing published data (Lizarralde et al., 2010) and information from seismic records (see Fig. 2). Seismic amplitude blanking along vertical zones below the seafloor indicates (active?) fluid conduits at North and Central Seep. Following the hypothesis that sill intrusions and related high-temperature alteration of sediments are driving the seepage, the expectation was to find deeply-sourced (average sill depth ~400m) fluids, characterized by a typical geochemical signature analogous to findings at Black Smoker vents in the Guaymas Basin (Von Damm et al., 1985; Berndt et al., 2016). Such characteristics are e.g. a high concentration of thermogenic hydrocarbon gases formed by organic-matter degradation, which is accompanied by enrichments in other organic tracers such as ammonium as well as depletion in Mg and a strong enrichment in fluid-mobile tracers like Li and B (e.g. Aloisi et al., 2004; Scholz et al., 2009).

The results from samples obtained using a video-guided MUC show that the highest methane concentrations compared to all other sites were measured at North, Central, and Ring Seeps (Fig. 4b). This and the fact that methane concentrations are exceeding those at the high-accumulation slope station underlines the visual evidence (abundant chemosynthetic biological communities) of active methane seepage. At the two most active sites, North and Central, high methane levels are accompanied by a significant drop in sulfate and increase in alkalinity and H$_2$S, providing evidence for AOM. These pore water trends are even more pronounced in GC01 (North) where the AOM zone was completely
penetrated and gas hydrate was found at about 2.5 mbsf. Unfortunately, GCs from similarly
active sites could not be obtained from Central and Ring seeps, mainly because of patchiness
of seepage spots and widespread occurrence of authigenic mineralizations at the seafloor
preventing sufficient penetration. Nevertheless, the occurrence of active methane seepage
at all three investigated sites is evident. A closer look at the lower panel of Fig. 4 a,b (and
Table S2) illustrates that the methane flux is not accompanied by any significant excursion of
major pore water constituents (e.g. Mg, Cl, Li) that would be typical for deeply-sourced,
high-temperature sediment-water interactions. Also Sr concentrations show seawater values
throughout all seep sites (Fig. 5), with the exception of North Seep where Sr concentrations
in conjunction with Ca (not shown) decrease and point to co-precipitation with Ca during
carbonate formation. The $^{87}$Sr/$^{86}$Sr ratios show predominantly seawater signatures as well
(Fig. 5, Table S2). Similarly, NH$_4$ concentrations, as tracer for the intensity of organic matter
decomposition, in both MUCs and GCs, remain at levels <1mM. This is much lower than the
end-member reported from vent fluids in the Southern Trough (Von Damm, 1985) and also
lower compared to high-accumulation areas like the Slope and the Graben Site (Fig. 4a,b).
Essentially, all data presented in Figure 4 show that, with exception of methane and sulfate,
the pore water corresponds to ambient diagenetic conditions, typically met in this shallow
subsurface depth. An explanation for the decoupling between high methane levels, sulfate
depletion at shallow depths, and otherwise more or less unchanged pore water composition
is that only methane in form of free gas is rising to the seafloor. This assumption requires a
closer look at the composition of dissolved hydrocarbons in general, which is given below.

4.3 Origin of hydrocarbon gases
4.3.1 Alteration effects
The origin of hydrocarbon gases can be deciphered by plotting hydrocarbon CH$_4$/(C$_2$H$_6$+C$_3$H$_8$)
ratios versus $\delta^{13}$C$_{CH_4}$ data in a modified Bernard diagram (Schmidt et al., 2005 and literature
therein) (Fig. 8) and $\delta^{13}$C$_{CH_4}$ versus $\delta D_{CH_4}$ after Whiticar (1999) and Welhan (1988) (Fig. 9).
Most of the measured stable isotope data of pore water methane indicate a microbial origin
or a mixed microbial and thermogenic origin (Fig. 8, 9). By contrast, the isotopic and
geochemical signature of hydrocarbons venting at the Smoker Site reflects a mixture of
methane of thermogenic and abiogenic (methane derived from water-rock interactions) origin (Berndt et al., 2016).

Figure 8: Hydrocarbon CH₄/(C₂H₆+C₃H₈) ratios versus δ¹³CCH₄ data are shown after a modified Bernard diagram (Schmidt et al., 2005). Pale symbols indicate samples above the AOM. Rayleigh fractionation lines show the effect of (microbial) methane oxidation, labels indicate the residual methane in %.
Figure 9: Carbon ($\delta^{13}$C$_{CH_4}$) and hydrogen $\delta^D$ isotope data after Whiticar (1999) and Welhan (1988). Pale symbols (Central Seep (MUC04)) indicate samples above AOM. Interestingly, all but two samples from North Seep sediments are located above the AOM (see Fig. 4) and could therefore be affected by oxidation (Fig. 8). Anaerobic methane oxidation enriches CO$_2$ in $^{12}$C which results in a progressively $^{13}$C-enriched methane residue shifting the $\delta^{13}$C$_{CH_4}$ values towards heavier values (e.g. Borowski et al., 1997; Dowell et al., 2016). Considering Slope Site methane signatures as a microbial endmember composition for the Guaymas Basin (Fig. 8), most of the data fall on calculated fractionation lines for methane oxidation following a Rayleigh trend (Whiticar et al., 1999). Methane sampled close to the Smoker Site (MUC15) is obviously also affected by anaerobic methane oxidation (Fig. 8). This process has recently been described by Dowell et al. (2016), who detected bacterial and archaeal communities in hydrothermal sediments of the southern trough of the Guaymas Basin, which were found to catalyze the oxidation of methane and higher hydrocarbons and shift $\delta^{13}$C$_{CH_4}$ values to heavier signatures. Origin of methane and oxidation effects can further be identified in the $\delta^{13}$C$_{CH_4}$ versus $\delta$D$_{CH_4}$ plot after Whiticar (1999) and Welhan (1988) (Fig. 9). Slope Site samples plot in the field of...
microbial CO₂ reduction while Smoker hydrothermal plume samples plot in the thermogenic field, one sample of the Smoker Site even points to a mantle signature, and thus show clear potential endmember isotope signatures. North Seep samples (pore fluids and gas hydrates) plot in the mixing region while samples from Central Seep clearly shift away from the microbial field and are considered to be affected by bacterial oxidation (Whiticar, 1999).

Considering only methane below the AOM as being unaltered, two North Seep samples and the majority of the Slope Site samples show a clear microbial source of methane (Fig. 8). All other samples appear to be affected by high degrees of oxidation following a Rayleigh fractionation process and show that only a fraction between 2 % (MUC 04, Central Seep) and 0.05 % (GC15, Central Seep) remains as unoxidized methane (Fig. 8).

### 4.3.2 Origin of unaltered samples

Unaltered North Seep samples show a mixing origin in the δ¹³C₂H₄ versus δD₂H₄ plot (Fig. 9), possibly stemming from microbial and thermogenic sources. Similar mixing signals of thermogenic and microbial methane have also been observed at Hydrate Ridge (Milkov et al., 2005) and seem to be a common phenomenon in hydrothermal and cold seep affected sediments. In a few samples from North and Central Seep ethane concentrations have been high enough to measure stable carbon isotopes and the δ¹³C₂H₆ values point to a thermogenic origin of ethane (Table S3).

### 4.4 Timing of active (thermogenic) methane release

Based on the presented data set, even when considering some uncertainties with respect to the fraction of thermogenic methane, the lack of any other geochemical evidence underlines that probably no deep-sourced fluid is migrating upwards at present at the cold seepage sites (compare deep-sourced seepage sites from the Gulf of Cadiz in Fig. 7). Hence, in terms of the original hypothesis that fluid emanation is directly linked to recent sill intrusions, the investigated “cold seep” sites cannot be considered as being active as claimed by Lizarralde et al. (2010), who argue that thermogenic carbon is released up to 50 km away from the rift axis causing a maximum carbon flux of 240 kt C yr⁻¹. First results by Lizarralde et al. (2010) showed temperature anomalies, high methane concentrations, and helium isotopic...
anomalies indicative of a magmatic source above bright features identified as bacterial mats, tubeworms, and authigenic carbonate. These features are situated above areas of shallow gas above sill intrusions comparable to structures identified in this study by seismic data (Fig. 2). The more detailed results of this study regarding pore fluid, water column, and gas geochemistry show that only traces of thermogenic methane were found up to ~20 km off axis (North Seep) and most methane was of microbial origin (Fig. 8, 9). Even pore fluids taken close to the hydrothermal vent area are dominated by shallow microbial degradation processes, indicating that hydrothermal fluid flow in the Guaymas Basin is rather localized and bound to focused fluid pathways. The temperature and chemical anomalies detected by Lizarralde et al. (2010) could also stem from the deep water layer in the Guaymas Basin itself which is influenced by hydrothermal fluids (Campbell and Gieskes, 1984). Hydrothermal activity in the Guaymas Basin produces hydrothermal plumes which rise to 100-300 m above seafloor and then spread out along density gradients throughout the basin (Campbell and Gieskes, 1984). Results of this study show that the Guaymas Basin has a well-mixed bottom seawater layer consisting of patchy and elevated CH₄, as well as temperatures ranging between 2.8 and 4.5°C in >1000 m depth (Fig. 6 and 10, Table S4). Off-axis methane concentrations vary quite considerably and show e.g. a range from 6 to 28 nM for Ring Seep and a temperature range from 2.8 to 3.9 for Central Seep. These bottom seawater variabilities are bigger than the reported anomalies by Lizarralde et al. (2010) and indicate that their findings might have been overrated.
Fig. 10. Water column CH\textsubscript{4} (colored symbols) and temperature (black crosses) at cold seeps and Smoker/Graben sites relative to the rift axis.

Pore fluids taken in a transect from the rift axis up to ~20 km away show no evidence for seepage of fluids that are affected by high-T reactions (Fig. 4). Shallow microbial degradation processes determine pore fluid signatures and control the majority of the released methane (Fig. 4, 8). It is likely the case that high temperature thermogenic reactions acted during sill emplacement and released large amounts of carbon, but these processes appear to have ceased since then. However, pipe structures still may act as high-permeability pathways and facilitate the advection of gas. Small amounts of thermogenic carbon might still be released as seen in microbial and thermogenic mixing signatures of δ\textsuperscript{13}C\textsubscript{CH\textsubscript{4}} and thermogenic δ\textsuperscript{13}C\textsubscript{C\textsubscript{2}H\textsubscript{6}} isotope data at North and Central Site. However, present methane advection rates are slow (probably <1 cm yr\textsuperscript{-1}) as observed by low methane gradients in the pore fluid profiles (Fig. 4).

These conditions favor an effective turnover of CH\textsubscript{4} to bicarbonate and authigenic carbonates by AOM (Karaca et al., 2010; Wallmann et al., 2006). The porous authigenic carbonate block recovered from the seafloor at Central Seep can provide long-term information about seepage in this area. The predominant biomarkers found in the seep carbonate from the Central Site (56-VgHG-4) are consistent with an origin from dual species microbial consortia performing the anaerobic oxidation of methane (AOM). High relative abundances of crocetane and sn2-hydroxyarchaeol, along with DAGE, indicate major contributions from methanotrophic archaea of the ANME-2 cluster and syntrophic sulfate-reducing bacteria, probably of the Desulfosarcina–Desulfococcus group (Blumenberg et al., 2004; Niemann and Elvert, 2008). These consortia appear to gain energy from AOM, with sulfate as the final electron acceptor, according to the net reaction

\[ \text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + \text{HS}^- + \text{H}_2\text{O} \]

(e.g. Nauhaus et al., 2005; see Wegener et al., 2016 for a recent update).

The increase in alkalinity due to the AOM reaction plausibly explains the precipitation of isotopically depleted authigenic carbonates. Particularly, ANME-2 biomarkers have been reported in association with abundant fibrous, often botryoidal aragonite cements (Leefmann et al., 2008), which is fully in line with the observations made at the Central Site (see ch. 3.3). Moreover, the inferred major abundance of ANME-2 indicates that seep
carbonate formation once took place under high sulfate concentrations, strong advective methane flow, but no elevated water temperatures (c.f. Nauhaus et al., 2005; Peckmann et al., 2009; Timmers et al., 2015). The observation of minor amounts of typical water column sterols also shows that these seep carbonates do not only carry their inherent AOM signature, but also captured detritus from the surrounding sediment and background water column sources during their ongoing cementation.

The bulk carbonate carbon isotope signature ($\delta^{13}C_{\text{VPDB}} = -46.6$‰) overlaps with the shallow heavy $\delta^{13}C_{\text{CH}_4}$ values (-27.5 and -48.6 ‰) in the pore fluids at Central Seep. Biomarkers found in the bulk carbonate confirm a dominant AOM signature with a significant planktonic and potentially $\delta^{13}C$ diluting background signal (Fig. S2). The oxygen isotope signature of the bulk carbonate points to a low formation temperature of about 3°C. This is consistent with a formation at ambient seawater which has bottom water temperatures between 2.8 and 3.0°C (Fig. 6, 10; Table S4). The $^{87}$Sr/$^{86}$Sr analyses support this assumption by values within uncertainty identical to modern seawater. Also U-Th carbonate dating performed at these authigenic carbonates provide formation ages younger than 240 yrs BP. In conclusion, authigenic carbonate shows a recent to sub-recent formation age with methane from shallow sources at ambient seawater and thus confirms the results from pore fluid and gas geochemistry of cessation of deep fluid and gas mobilization.

Taking a closer look at the seismic lines across the seep locations, it becomes obvious that the disrupted sediment layers are not reaching to the sediment surface (Fig. 2a, c). This implies that fluid mobilization ceased at some time before the uppermost sediment layers were deposited. The doming above the Central Seep provides some clues on the timing of fluid migration (Fig. 2c). Assuming that the doming is the result of buoyancy-related uplift (Koch et al., 2015) it represents the time when intrusion-related gas reached the sea floor. Assuming further a sedimentation rate of 1.7 m per 1000 years (Central Seep; Table 1) and maxima and minima deposition depths of 48 and 12 m respectively below seafloor (see Fig. 2c) this would imply that most of the gas reached the seafloor between 28 and 7 kyrs ago. Even assuming minima and maxima sedimentation rates of 3.5 m (North Seep) and 0.5 m (Ring Seep) per 1000 years gas flow would have ceased at the earliest between 14 and 3 kyrs ago or at the latest 96 and 24 kyrs ago. This finding supports the results of the pore fluid and
gas geochemistry which show no sign of active fluid flow from depth at cold seep sites in the northern Guaymas Basin.

Large amounts of CH₄ (and CO₂) must have been emitted to bottom waters during the calculated periods (s.a.), rapidly after sills intruded into the organic-rich sediments in the Guaymas Basin. However, these carbon emissions must have ceased after sill-emplacement ended and the impact on climate appears to depend on the durability of the magmatic system.

5 Conclusions

Magmatic intrusions into organic-rich sediments can potentially release large amounts of carbon into the water column and atmosphere and are therefore discussed as potential trigger mechanisms for rapid climate change, e.g. during the PETM. In the Guaymas Basin, off-axis cold seeps do not show indications for present-day hydrothermal activity. Pore fluids sampled from cold seep structures and in the vicinity of hydrothermal vents in the northern Guaymas Basin, are dominated by seawater concentrations and show no sign of deep fluids or temperature-related diagenesis. Methane measured at the investigated sites stems from a mixed origin (microbial and thermogenic sources), though mainly from microbial processes. This may suggest that hydrothermal circulation has stopped at depth and, based on seismic data, ceased more than 7kyrs ago. Sill-induced hydrothermal systems appear to be an effective way to release carbon, but the period of time depends on the longevity of the magmatic system.

Acknowledgments

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References


Kennett, J. P., Cannariato, K. G., Hendy, I. L. and Behl, R. J.: Carbon Isotopic Evidence for Methane Hydrate Instability During Quaternary Interstadials, Science (80- )., 288(5463), 128–133,


Table 1: Station list and site names of GCs and MUCs taken in the Guaymas Basin with according water depth. Heat flow and temperature gradient data measured either attached to GCs or to a sediment probe.

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* Sedimentation and mass accumulation rates at Station 33 of the 0-13 cm, 13-18 cm layers, respectively
+ Sedimentation and mass accumulation rates at Station 65 of the 0 - 7 cm, 7 - 17 cm layers, respectively