

Links between spatially heterogeneous pore water geochemistry, fluid migration, and methane hydrate near a seafloor mound venting structure on the south Chilean Margin (41°S)

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Abstract

Pore water freshening (i.e., decreases in dissolved Cl) has been documented in marine sediments along most active margins, with the migration of deep fluids or methane hydrate dissociation often invoked as sources of freshening in the sediment column. During D/V JOIDES Resolution Expedition 379T in 2019, two new sites (J1005 and J1006) were cored near ODP Site 1233 (41°S), adjacent to a seafloor mound venting structure. The three sites are less than 10 km apart but show marked differences in pore water chemistry and methane hydrate occurrence. The extent of Cl decrease is a function of distance from the mound, with the strongest freshening occurring at the closest site (J1006), which is the only site where methane hydrate was observed. Methane fluxes follow the same pattern, suggesting a common control. Increasing oxygen and decreasing hydrogen isotopes point to deep mineral bound water as the primary source of freshening near the mound, with fluids originating ~2.5 km below seafloor near the décollement. Secondary influences from methane hydrate dissociation and ash diagenesis also appear to influence regional pore water chemistry. The variability in pore water freshening suggests that fluid migration and eventual expulsion at the venting structure follows narrow pathways, likely along faults within the forearc complex. The migration of deep, gas-charged fluids may also support methane hydrate saturations greater than in situ organic carbon diagenesis would allow, but nonetheless consistent with geophysical estimates. Together, the data highlight an important link between fluid migration and methane hydrate formation on the Chilean Margin.

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Key Points:

1) Sediment cores taken <10 km apart near a seafloor mound venting structure have different pore water chemistry

2) Pore water freshening is attributable to clay dehydration at depth, manifesting in fluid discharge at the venting structure

3) Active fluid and gas migration may support the formation of methane hydrate near the mound

Abstract

Pore water freshening (i.e., decreases in dissolved Cl⁻) has been documented in marine sediments along most active margins, with the migration of deep fluids or methane hydrate dissociation often invoked as sources of freshening in the sediment column. During D/V *JOIDES Resolution* Expedition 379T in 2019, two new sites (J1005 and J1006) were cored near ODP Site 1233 (41°S), adjacent to a seafloor mound venting structure. The three sites are less than 10 km apart but show marked differences in pore water chemistry and methane hydrate occurrence. The extent of Cl⁻ decrease is a function of distance from the mound, with the strongest freshening occurring at the closest site (J1006), which is the only site where methane hydrate was observed. Methane fluxes follow the same pattern, suggesting a common control. Increasing oxygen and decreasing hydrogen isotopes point to deep mineral bound water as the primary source of freshening near the mound, with fluids originating ~2.5 km below seafloor near the décollement. Secondary contributions from methane hydrate dissociation and ash diagenesis also appear to influence regional pore water chemistry. The variability in pore water freshening suggests that fluid migration and eventual expulsion at the venting structure follows narrow pathways, likely along faults within the forearc complex. The migration of deep, gas-charged fluids may also support methane hydrate saturations greater than *in situ* organic carbon diagenesis would allow, but nonetheless consistent with geophysical estimates. Together, the data highlight an important link between fluid migration and methane hydrate formation on the Chilean Margin.

Plain Language Summary

The Chilean Margin is one of the world's largest subduction zones and has a substantial methane hydrate reservoir at shallow depths in the sediment column. However, it is still poorly understood how methane hydrate forms here since organic carbon content is low. We use the chemical

43 composition of marine sedimentary pore water to show that fresh, gas-rich fluid migrates from
44 much deeper in the sediment column to shallow depths where methane hydrate has been observed.
45 Our results suggest that this might be one such way that methane hydrate forms in higher
46 saturations than anticipated.

1. Introduction

Compressional tectonics, sediment loading, and the subsequent reductions in porosity are the principal processes controlling the vertical migration of fluids and gas through accreted sediments at convergent margins [Moore and Vrolijk, 1992]. Within these forearc complexes, the circulation and alteration of fluids can influence subduction mechanics and the cycling of elements between the ocean, lithosphere, and mantle [Chan and Kastner, 2000; Peacock, 1990; Saffer and Tobin, 2011]. At the sediment-seawater interface, fluids and gas can be expelled to the ocean through various seafloor venting structures like cold seeps and submarine mud volcanoes, which have been documented globally [Brown, 1990; Kopf, 2002; Milkov, 2000]. Provided sufficient volumetric fluxes, the transfer of fluid from sedimentary to oceanic regimes through these structures could exert influence on marine elemental and isotopic budgets [Elderfield et al., 1990; Gieskes et al., 1989; Kastner et al., 1991].

Prior examination of pore water chemistry near seafloor venting structures have offered a better understanding of the hydrogeological and geochemical processes taking place well beyond the limits of modern ocean drilling [Dahmann and de Lange, 2003]. The elemental and isotopic composition of these fluids often reflect subduction mechanics, diagenetic reactions, and mineral dehydration processes taking place deep within the accretionary prism. Indeed, pore water studies on the Barbados, Mediterranean, Nankai, Gulf of Cadiz, and Taiwan accretionary prisms (among others) have provided critical insight on the roles of dewatering in megathrust tectonism, fluid expulsion in oceanic geochemical budgets, and deep gas migration in supporting methane hydrate formation [Chen et al., 2020; Deyhle and Kopf, 2001; Dia et al., 1999; Godon et al., 2004; Haese et al., 2006; Hensen et al., 2007; Kopf and Deyhle, 2002; Martin et al., 1996; Menapace et al., 2017; Nishio et al., 2015; Scholz et al., 2009; Vanneste et al., 2011].

Despite these advances, the south Chilean Margin—a 1500 km convergent plate boundary and one of the most tectonically-active regions on Earth [Melnick et al., 2006; Völker et al., 2013]—remains one such setting where cold seeps and mud volcanoes have only been documented within a limited sector of the margin near the Concepción Methane Seep Area (36°S) [Sellanes et al., 2004; Vargas-Cordero et al., 2020]. Recently, cold seeps have also been observed near the Chile Triple Junction in the south (46°S) [Villar-Muñoz et al., 2021]. The scarcity of documented venting systems is in stark contrast with fluid budget estimates in the forearc complex, which remain unbalanced and require transfer of fluid and volatiles from subducted sediments back to the ocean [Volker et al., 2014]. Moreover, pore water studies near sites of active fluid and gas discharge on the Chilean Margin are limited [Coffin et al., 2007; Scholz et al., 2013; Zheng et al., 1995]; thus, a comprehensive geochemical characterization of deep fluids remains incomplete. Addressing this deficiency can provide critical insight on a number of fronts, including the interaction between deep-seated fluids and tectonism on the Chilean Margin [Contreras-Reyes et al., 2013; Saffer and Tobin, 2011; Völker and Stipp, 2015] and how fluid and gas migration within this accretionary prism supports a robust methane hydrate reservoir in shallow margin sediments despite relatively

low organic carbon content [Brown *et al.*, 1996; Vargas-Cordero *et al.*, 2017; Vargas-Cordero *et al.*, 2021; Villar-Muñoz *et al.*, 2019].

Recent implementation of D/V *JOIDES Resolution* Expedition 379T (JR100) in July-August 2019 recovered 120 m sediment cores at Sites J1005 and J1006 (41°S) near the previously cored ODP Site 1233 [Bova *et al.*, 2019]. The three sites are less than 10 km apart and underway seismic data from this expedition, as well as ODP Leg 202 [Mix *et al.*, 2003], reveal that J1005, J1006, and ODP 1233 are proximal to a ~4 km wide, ~25 m tall seafloor mound (Figure 1). The anticlinal geometry of this sediment structure and observance of a gas flare just off axis of the meridional seismic line suggest that this mound could be a mud volcano with active fluid and gas expulsion occurring near the sites (Figure 1). However, the lack of documented mud breccia at any of the three sites is in contrast with this interpretation, suggesting it could be a cold seep instead. In the absence of higher resolution seismic data to better characterize this structure, we broadly define the observed mound as a “seafloor venting structure”.

Despite the proximity of these three sites to both the mound structure and each other (Table 1), Sites J1005, J1006, and ODP 1233 have distinct pore water chemical compositions, most notably in the downcore chloride concentration (Figure 1), which may indicate spatial heterogeneities in fluid migration within this sector of the forearc complex. In this paper, we report on high-resolution pore water elemental and isotope data from Sites J1005 and J1006, with the objectives to: (1) characterize the source(s) of pore fluids in the vicinity of this mound using the elemental and isotopic (oxygen, hydrogen, and strontium) composition of pore waters; (2) constrain fluid migration pathways and reasons for spatially variable pore water chemistry; and (3) assess how fluid and gas transport near venting structures on the Chilean Margin might support regional methane hydrate formation.

2. Study Area

2.1 Geologic and tectonic setting

The south Chilean Margin (32–46°S) is one of the longest convergent continental margins on Earth. Here, subduction of the Nazca plate beneath the South American plate is rapid (66 mm yr⁻¹) and the region has produced some of the most destructive earthquakes in recent history (e.g., M_w 9.5, Valdivia, 1960; M_w 8.8, Maule, 2010) [Melnick *et al.*, 2006; Völker *et al.*, 2013]. Hemipelagic sedimentation along the Chilean Margin reflects influences from the regional hydroclimate and steep catchment basins along the coastline. Prevailing westerlies yield annual rainfall in excess of 7,500–10,000 mm yr⁻¹ [Garreaud *et al.*, 2013], resulting in extensive erosion and deposition of 21 km³ yr⁻¹ terrigenous material rich in detrital clays (e.g., smectite) [Lamy *et al.*, 1998]. Frontal accretion and high sedimentation rates have manifested in the complete burial of the structural trench and the development of a prominent forearc complex perpendicular to the trench [Maksymowicz, 2015; Völker *et al.*, 2013]. This consists of an active accretionary prism that is ~25 km wide and 2.5–3 km thick; the broader forearc complex is ~60 km wide and ~20 km thick

at its thickest, extending from the upper continental slope and shelf to the décollement [Geersen *et al.*, 2011; Völker *et al.*, 2011].

Active subduction and frequent megathrust earthquakes have manifested in normal and splay faulting throughout the forearc complex [Völker *et al.*, 2014]. Gas seepage on the south Chilean Margin was first reported by Sellanes *et al.* [2004] in what is now called the Concepción Methane Seepage Area (CMSA), with more recent evidence for active and paleo seepage [Klaucke *et al.*, 2012]. Seepage of methane-rich fluids typically cluster near these faults and support robust chemosynthetic communities near the seafloor [Munoz *et al.*, 2016; Sellanes *et al.*, 2008]. It has been suggested that onset of seepage in this region may be linked to the tectonic history of the margin, potentially as recent as the 2010 Maule earthquake in some sectors of the margin [Geersen *et al.*, 2016; Villar-Muñoz *et al.*, 2021]. Low pore water chloride concentrations in a small set of multicores near the CMSA were interpreted to reflect freshening from deep fluids released during clay dehydration processes at depth, potentially providing a mechanism for vertical migration of gas saturated fluids at these seeps [Scholz *et al.*, 2013]. However, pore water freshening is not a necessarily widespread feature at venting sites [Coffin *et al.*, 2007]. In contrast, high $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios ($\delta^{18}\text{O}$ and δD , respectively) in pore waters near a newly discovered chain of small (meter-scale) mud volcanoes upslope and just south of the CMSA indicate that regional fluid migration and discharge may be linked to methane hydrate dissociation [Vargas-Cordero *et al.*, 2020].

Methane hydrates are ubiquitous on the south Chilean Margin and have often, but not only, been observed near sites of active venting [Bangs *et al.*, 1993; Behrmann *et al.*, 1992; Coffin *et al.*, 2007; Vargas-Cordero *et al.*, 2010; Vargas-Cordero *et al.*, 2017; Villar-Muñoz *et al.*, 2018; Villar-Muñoz *et al.*, 2019]. Steep redox gradients indicate that marine sediments in the region are highly reducing owing to sediment loading and microbial degradation of organic carbon (~0.5-2 wt%) [Bova *et al.*, 2019; Mix *et al.*, 2003; Scholz *et al.*, 2013]. Anaerobic oxidation of methane (AOM) from sulfate reduction typically occurs in the upper few meters of the sediment column, with methanogenic conditions below [Bova *et al.*, 2019; Coffin *et al.*, 2007; Mix *et al.*, 2003; Scholz *et al.*, 2013]. A widespread bottom simulating reflector marks the transition between methane hydrate-rich sediments and free gas below [Rodrigo *et al.*, 2009]. On the Chilean Margin, this horizon is relatively shallow, typically less than 150 meters below sea floor (mbsf), with methane hydrate occupying 5-15% of the pore space [Alessandrini *et al.*, 2019; Vargas-Cordero *et al.*, 2017]. Sites of active venting often have the shallowest sulfate-methane transition zone, which can be <1 mbsf or even at the sediment-seawater interface itself owing to high vertical fluxes of gas-saturated fluids [Coffin *et al.*, 2007]. Elevated pore water alkalinity concentrations have been observed throughout much of the margin, which likely reflect AOM via sulfate reduction but could also be attributed to marine silicate weathering in the anoxic sedimentary system [Torres *et al.*, 2020; Wallmann *et al.*, 2008]. The alkalinity generated by these processes promote authigenic carbonate precipitation below the SMTZ or even on the seafloor [Bohrmann *et al.*, 1998; Klaucke

et al., 2012]. Similarly, methane hydrate near the CMSA can be found at or within a few meters of the seafloor [Vargas-Cordero *et al.*, 2020].

2.2 Study sites

D/V *JOIDES Resolution* Expedition 379T (JR100) cored two sites at 41°S on the Chilean Margin. Sites J1005 and J1006 are located on a bench in the upper continental slope ~38 km offshore at 807- and 824-meters water depth, respectively (Figure 1; Table 1). Three holes (A, B, and C) were cored at each site using the advanced piston coring system, yielding complete stratigraphic sections of 118 mbsf at J1005 and 120 mbsf at J1006. Sediment at both sites are assigned to single lithologic units comprising of Pleistocene silty clay, with varying contributions from biogenic, volcanogenic, and authigenic (sulfidic, silicate, carbonate) components. Despite the proximity of the sites, the respective sediment columns have different bottom ages as indicated by shipboard correlation of paleomagnetic and physical properties data [Bova *et al.*, 2019] (Table 1).

Site J1006 is located near the apex of a seafloor mound, with Site J1005 positioned just upslope from this feature. Authigenic carbonate nodules were recovered at both sites (Figure S1); at J1005, small (1-3 cm) concretions were recovered ~30-60 mbsf, with larger concretions (5-13 cm) and an order of magnitude greater abundance at Site J1006 between 75-115 mbsf. Shipboard x-ray diffraction (XRD) analysis indicates that these authigenic carbonates are primarily dolomitic in composition [Bova *et al.*, 2019]. Likewise, methane hydrate nodules were recovered at Site J1006 ~85 mbsf (Figure S1). Sediment in the core sections within ±10 m of the hydrate interval was heavily cracked and expanded owing to depressurization of gas (and potentially methane hydrate dissociation) upon recovery (Figure S1). As a result, a substantial void between 88-104 mbsf exists at J1006. Intact bivalve fossils were recovered at Sites J1005 and J1006 and were identified to belong to the *Lucinidae* family of seawater clams (Figure S1). These burrowing bivalves live in reducing, sulfur-rich sediments and can be indicative of active (or past) seepage of gas-saturated fluids from the seafloor [Holmes *et al.*, 2005]. Full site reports are provided in the Expedition 379T Preliminary Report [Bova *et al.*, 2019].

Sites J1005 and J1006 were cored 10 km and 5 km SSE of ODP Site 1233, respectively, which was previously cored during ODP Leg 202 [Mix *et al.*, 2003]. Collectively, the three sites comprise a lateral transect across the mound structure, with J1006 the most proximal, followed by ODP Site 1233 (<5 km), and J1005 being the most distal (~10 km) (Table 1). Like the JR100 sites, a shallow SMTZ, methanogenic sediments, and authigenic carbonates were reported at ODP Site 1233 but methane hydrate was not recovered despite strong reductions in pore water chloride concentration >60 mbsf [Mix *et al.*, 2003]. The proximity of the three sites to the mound, similar lithologic and depositional features, and similar redox conditions but distinct pore water chemistry makes these sites uniquely suited to address the targeted research objectives outlined above.

3. Materials and Methods

3.1 Pore water sample collection for Sites J1005 and J1006

Whole round samples (5-10 cm) were immediately collected from the bottom of each 1.5 m core section upon recovery to the catwalk. A mudline sample was collected from Holes A and B in J1005 and J1006. Whole rounds were sealed and transferred to the shipboard geochemistry laboratory for processing. In total, 65 samples were taken from J1005 and 66 from J1006, with 13 and 14 analyzed onboard for interstitial water chemistry, respectively. The remainder of the pore water samples were split (~4-10 mL each), sealed in airtight glass vacuoles, and archived for shore-based isotope analysis.

For samples that underwent shipboard analysis, the sediment surface was carefully scraped and removed to prevent contamination. The sample was then placed in a titanium hydraulic press and subjected to 35,000 lb force for pore water extraction. Extraction fluid was filtered through a Whatman No. 1 filter (11 μ m) and 0.5 mL was discarded to avoid contamination. The remaining fluid was filtered into a sterile syringe and filtered again through a 0.45 μ m polysulfone filter prior to shipboard analyses (or sample archiving).

3.2 Shipboard pore water ion analysis

Shipboard ion analysis of pore waters followed protocols outlined in Gieskes et al. [1991], Murray et al. [2000], and the International Ocean Discovery Program user manual for shipboard instrumentation. Major cation (Na, Ca, Mg, K) and anion (Cl^- and SO_4^{2-}) concentrations were measured using a shipboard Metrohm 850 professional ion chromatographer (IC). Dissolved ammonium (NH_4^+) concentrations were determined using an Agilent Cary Series 100 UV-visible spectrophotometer fitted with an Agilent SPS3 autosampler. Alkalinity was determined immediately after squeezing by Gran titration with an autotitrator (Metrohm 794 basic Titrino) using 0.1M HCl at 25°C. Certain trace element (Li, Sr, B, dissolved silica (DSi)) concentrations were measured using a shipboard Agilent 5110 SVDV ICP-AES. Precision (1σ) based on repeated measurements of IAPSO and internal standards were <3.5% for IC measurements, <3.4% for NH_4^+ , and <2% for alkalinity. Reproducibility for ICP-AES measurements was ~1% for all elements. We refer the reader to the Expedition 379T Preliminary Report for additional details on shipboard geochemical analysis of pore water and sediment samples [Bova et al., 2019].

3.3 Pore water oxygen and hydrogen isotope analysis

Pore water $\delta^{18}\text{O}$ and δD composition was determined using a Picarro L2130-*i* cavity ringdown laser spectrometer light isotope instrument in triplicate at the University at Buffalo following methods in van Geldern and Barth [2012] (J1005, n=13; J1006, n=22). Samples were injected four times; each injection was corrected for memory, drift, and were then normalized to Vienna Standard Mean Ocean Water (VSMOW). The first injection was discarded for each sample and the remaining three analyses were aggregated into an average value with associated replicate uncertainty. Average replicate standard deviation (1 SD) was 0.03‰ for $\delta^{18}\text{O}$ measurements and 0.11‰ for δD measurements.

Additional pore water $\delta^{18}\text{O}$ measurements (J1005, n=24; J1006, n=39) were made at the Rutgers University Stable Isotope Laboratory using a FISIONS OPTIMA Mass Spectrometer equipped with a MicroMass multiprep automatic sample processing system after 1-minute water equilibration with CO_2 in a sealed glove bag using standard methods [Epstein and Mayeda, 1953; Fairbanks, 1982]. All samples were run in duplicate. Reproducibility is estimated to be $\pm 0.04\text{‰}$ (1 SD) as determined by multiple (n=12) daily analyses of laboratory standards. Accuracy is estimated to be within 0.03‰ by comparison of North Atlantic Bottom Water with VSMOW.

Lastly, a ~5 cm methane hydrate nodule was recovered from Hole C at Site J1006 (Figure S1) and subsequently processed, archived, and analyzed for its $\delta^{18}\text{O}$ (Picarro and IR-MS) and δD (Picarro only) composition following the protocols outlined above.

3.4 Pore water strontium isotope analysis

Pore water strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) analysis followed the Sr separation protocol of Horwitz et al. [1992] (J1005, n=12; J1006, n=12). Sample volumes were calculated from shipboard elemental concentrations, targeting at least 1 μg Sr for each sample. Pore water samples were acidified to 2N strength with calculated volumes of 7N HNO_3 prior to separation. Strontium was chromatographically separated from the pore water matrix using Eichrom 50-100 μm Sr Resin and different concentrations of HNO_3 . Strontium was collected in 0.05N HNO_3 in acid cleaned 3 mL Savillex vials, dried down, and then dissolved in 2% by volume HNO_3 for analysis. Samples were analyzed in a wet plasma using a ThermoScientific Neptune Plus MC-ICP-MS at Rutgers University. Sr isotopes were corrected for fractionation using the measured $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 8.3752. NIST SRM 987, which was analyzed multiple times during sample analyses, yielded an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710274 ± 0.000008 (2 SD, n=13).

3.5 Headspace hydrocarbon gas analysis

Sediment gas composition was determined at a resolution of 1 sample per core for J1005 (n=11) and J1006 (n=11). A 3 cm^3 bulk sediment sample was collected from the freshly exposed top end of a core section using a brass boring tool immediately after core recovery on the catwalk. The sediment plug was placed in a glass vial and sealed with an aluminum cap fitted with a PTFE/silicon septa for transfer to the shipboard geochemistry laboratory. The vial was heated to 70°C for 30 minutes to evolve hydrocarbon gases from the sediment. A 5 cm^3 volume of headspace gas was extracted from the sealed vial using a gas-tight 5 mL PTFE Luer lock glass syringe and injected into the Agilent/HP 6890 Series II Gas Chromatograph fitted with a flame ionization detector for analysis. Concentrations of methane (CH_4) and higher molecular weight hydrocarbons (e.g., ethane, propane) were determined and reported as parts per million by volume (ppmv) of the injected sample.

4. Results and Discussion

Pore water geochemical profiles for Sites J1005 and J1006 are shown in Figure 2 and Figure 3, respectively [Clementi *et al.*, 2022b]. Despite the proximity of the two sites (<5 km), there exists substantial spatial heterogeneity in pore water chemistry. Most notable is the difference in chloride (Cl⁻) concentration, which at J1006 decreases from seawater values by ~200 mM with depth but undergoes relatively little change at J1005. This ~37 percent decrease in Cl⁻ concentration suggests mixing with a freshwater source. The freshening signal occurs concomitantly with marked changes in the concentrations of Ca, Mg, K, B, DSi, Li, and Sr (Figure 3). Normalizing elemental concentrations to Cl⁻ allows for comparison between the sites and reveals the conservative behavior in pore fluid chemistry at J1005 compared with J1006 (Figure 2). Site J1005 is positioned slightly upslope from J1006 and farther from the mound, and the pore water composition here suggests minimal influence from deeper fluid sources in the cored strata. As such, we treat J1005 pore water as a reference site for pore waters near the mound venting structure, which provides context for observed changes at J1006. In contrast, the non-conservative nature of pore waters at J1006 suggests a complex sedimentary environment. Site J1006 is closest to the mound and the strong freshening signal implies a dominant influence from venting-associated fluids on pore water chemistry. However, downcore changes in elemental concentrations are not homogeneous (e.g., Mg/Cl and B/Cl) and potentially highlight multiple source fluids.

In the following sections, we use pore water $\delta^{18}\text{O}$ and δD to identify the source of low-Cl⁻ fluid at Site J1006. Changes in the radiogenic strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) can be independent from changes in O/H isotopes and provide constraints on additional source fluids. Comparison with elemental data from ODP Site 1233 offers context for spatial heterogeneity near the venting structure. Finally, we use this information to address implications for fluid and gas migration in the accretionary prism and how such processes might influence methane hydrate formation in the region.

4.1 Source(s) of low Cl⁻ at J1006

Pore water freshening in convergent margin settings is often attributed to methane hydrate dissociation and mineral dehydration (e.g., smectite to illite transformation, also referred to as illitization), although clay membrane ion filtration, low-temperature crustal alteration, anaerobic oxidation of methane, mixing with meteoric water have all been shown to yield Cl⁻ concentrations lower than seawater in convergent margin sediments from Nankai Trough, the Cascadia and Peru margins, Barbados, and the Mediterranean Sea [Dahlmann and de Lange, 2003; Kastner *et al.*, 1991; Kastner *et al.*, 1990; Toki *et al.*, 2017]. Indeed, prior pore water studies in this study region, paired with lithologic evidence for abundant smectite content and recovered hydrate nodules, have prompted hypotheses that documented freshening signals are primarily attributable to clay dehydration or methane hydrate dissociation [Bova *et al.*, 2019; Mix *et al.*, 2003; Scholz *et al.*, 2013]. However, a 200 mM reduction in Cl⁻ concentration (similar in magnitude to Site J1006) at a site offshore Patagonia was recently attributable to the deep submarine infiltration of fossil groundwaters [Clementi *et al.*, 2022a]. This new finding challenges the basis of the longstanding

hypotheses in this region and implies that low Cl^- concentrations in pore waters cannot alone be used to diagnose influences from illitization or methane hydrate dissociation, regardless of additional sedimentary evidence.

The alteration processes that can yield low- Cl^- pore fluids isotopically fractionate oxygen and hydrogen in distinct ways, which can enrich or deplete pore water $\delta^{18}\text{O}$ and δD relative to seawater (Table S1). For example, compaction and increasing temperature (60-150°C) during slab subduction promotes the dehydration of hydrous minerals, such as the alteration of smectite to illite clays [Perry, 1970]. Relative to seawater, this mineral-bound water is enriched in $\delta^{18}\text{O}$ and depleted in δD and is released to the surrounding sediments during dehydration reactions [Savin and Epstein, 1970], which increases $\delta^{18}\text{O}$ and decreases δD in the pore water [Kastner et al., 1991]. In contrast, methane hydrate dissociation increases both $\delta^{18}\text{O}$ and δD owing to fractionation of the heavier isotopes into the hydrate matrix [Hesse and Harrison, 1981; Ussler and Paull, 1995]. Methane hydrate dissociation typically occurs from hydrostatic pressure decreases during core recovery, which can result in anomalous pore water $\delta^{18}\text{O}$ and δD increases (and Cl^- decreases) from otherwise conservative profiles (e.g., [Egeberg and Dickens, 1999; Matsumoto and Borowski, 2000; Torres et al., 2004]). In certain instances, however, *in situ* dissociation can occur and produces more gradual changes in the downcore profiles (e.g., [Vargas-Cordero et al., 2020]).

Methane hydrate nodules were only recovered at J1006, where there was substantial cracking and expansion of core material from gas expansion (Figure S1). As such, we initially hypothesized that the linear decrease in Cl^- with depth was attributable to *in situ* methane hydrate dissociation [Bova et al., 2019]. Indeed, decreases in Cl^- concentrations below 60 mbsf at ODP Site 1233 were also attributed to active hydrate dissociation [Mix et al., 2003]. The downcore $\delta^{18}\text{O}$ increase (0.5‰) at J1006 is consistent with mixing between seawater and dissociated fluid as evidenced by a $\delta^{18}\text{O}$ value of 3.02‰ in the recovered methane hydrate nodule; this hydrate endmember value is in agreement with observations in both laboratory and natural settings [Davidson et al., 1983; Kvenvolden and Kastner, 1990; Martin et al., 1996]. In contrast, δD decreases by ~2‰ from seawater values (Figure 3). Notwithstanding a few anomalously enriched $\delta^{18}\text{O}$ and δD values ~85-90 mbsf, which most likely reflect hydrate dissociation upon recovery (i.e., hydrate δD value of 19.7‰), the robust downcore δD decrease appears to rule out a primary influence from *in situ* methane hydrate dissociation on pore water freshening in the region. This requires an alternate fluid source for low Cl^- concentrations at J1006 and ODP Site 1233.

We assess the relationship between pore water freshening (i.e., decreasing Cl^- concentrations) and $\delta^{18}\text{O}$ increases and δD decreases at J1006 by comparing observed downcore changes (Cl_{obs} , $\delta^{18}\text{O}_{\text{obs}}$, and $\delta\text{D}_{\text{obs}}$) with seawater reference values (Cl_{ref} , $\delta^{18}\text{O}_{\text{ref}}$, and $\delta\text{D}_{\text{ref}}$) [Tomaru et al., 2006]. Downcore Cl^- concentration is normalized to seawater, yielding a freshening factor, $f([\text{Cl}_{\text{obs}}]/[\text{Cl}_{\text{ref}}])$; the changes in $\delta^{18}\text{O}$ and δD ($\Delta\delta^{18}\text{O}$ and $\Delta\delta\text{D}$, respectively) are derived as $\delta_{\text{obs}} - \delta_{\text{ref}}$

[Hong *et al.*, 2021]. At Site J1006, this approach demonstrates that the observed $\delta^{18}\text{O}$ increase (higher $\Delta\delta^{18}\text{O}$) and δD decrease (lower $\Delta\delta\text{D}$) with depth occurs as a function of pore water freshening, as denoted by lower f (Figure 4), which suggests that the fresh mound-associated pore fluid is primarily sourced from clay dehydration reactions at depth (Table S1). The alteration of smectite to illite often involves the consumption of K from surrounding pore waters and release of Li, B, DSi with the mineral bound water [Chao *et al.*, 2011; Hüpers and Kopf, 2012]. At J1006, the linear K/Cl increase between 0-50 mbsf is driven by the marked decrease in Cl^- concentrations, whereas the greatest consumption of K occurs below ~ 50 mbsf and results in a cessation of the K/Cl increase (Figure 3; Figure S2). The increase in Li above seawater concentrations tracks the decrease in Cl^- concentration, which results in an overall increase in Li/Cl and implies a deep Li source. Similarly, downcore DSi and B concentrations increase substantially above seawater values. These elemental profiles substantiate the robust isotopic evidence for dehydration reactions sourcing the low- Cl^- fluids at Site J1006, and now adds the Chilean Margin to the large body of evidence linking illitization to venting structures along convergent margins (e.g., [Chao *et al.*, 2011; Chen *et al.*, 2020; Dahlmann and de Lange, 2003; Martin *et al.*, 1996]).

At J1006, fluid endmember estimates by linear extrapolation of $\delta^{18}\text{O}$ and δD to zero Cl^- concentration yield values of approximately +1‰ and -11.5‰ (Figure S3). Although fluid isotopic endmembers for illitization on the Chilean Margin have not yet been established, these estimates are different than the clay dehydration endmember derived using pore waters from the Mediterranean Sea ($\delta^{18}\text{O}$: +10‰, δD : -32‰) [Dahlmann and de Lange, 2003]. This discrepancy suggests that there may be additional fluid sources acting to modify pore water chemistry near the mound. The bottom 20-30 m at J1006 is characterized by marked shifts in elemental concentrations (e.g., Ca, Sr, Na, and B) and less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 3). The high Sr/Cl and low $^{87}\text{Sr}/^{86}\text{Sr}$ at depth are characteristic of ash alteration, although apparent consumption of Sr (and Ca) with little change in $^{87}\text{Sr}/^{86}\text{Sr}$ between 10-80 mbsf (also at J1005) highlights a likely influence from authigenic carbonate precipitation [Elderfield and Gieskes, 1982] (Figure 5).

Volcanogenic material comprised less than 10 percent of bulk sediment composition in cores recovered during this expedition [Bova *et al.*, 2019]. However, even minor ash diagenesis can impart large changes in pore water Sr and its isotopes [Hong *et al.*, 2020], as well as $\delta^{18}\text{O}$ and δD [Egeberg *et al.*, 1990; Lawrence and Gieskes, 1981]. In contrast to clay dehydration, the formation of hydrous minerals during ash diagenesis should decrease $\delta^{18}\text{O}$ and increase δD in surround pore water [Kastner *et al.*, 1991] (Table S1). We suggest that an overprinting of ash alteration on the primary signal from clay dehydration explains the discrepancy between endmember $\delta^{18}\text{O}$ and δD estimates at J1006 and expected endmember values from the Mediterranean Sea, as well as the abrupt changes in certain elemental concentration at depths greater than 100 mbsf. Low pore water $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ were also reported at ODP Sites 859 and 860 offshore Patagonia (46°S) and were attributed to ash diagenesis [Zheng *et al.*, 1995], which suggests that diagenetic alteration of

volcanogenic material may be a common process on the south Chilean Margin but does not appear to be occurring uniformly throughout the sediment column.

The lack of a similar elemental and isotopic signals at Site J1005 highlights the spatial heterogeneity in regional pore fluid composition and migration. Here, $\delta^{18}\text{O}$ and δD have a prominent maxima at ~25 mbsf (Figure 2), which is attributable to the downward diffusion of isotopically heavier seawater during the last glacial period [Adkins *et al.*, 2002]. This feature is also present at Site J1006, but the relatively higher $\delta^{18}\text{O}$ and lower δD peaks suggest active migration of deep fluids with a distinct isotopic signature has likely attenuated the glacial signal. That this signal is even present at J1006 might indicate that fluid discharge at this MV initiated at some point since the last glaciation. Alternatively, enriched pore water $\delta^{18}\text{O}$ and δD paired with low Cl^- concentrations could indicate *in situ* dissociation of methane hydrate, which would be consistent with observations offshore Patagonia and near mud volcanoes proximal to the CMSA [Clementi *et al.*, 2022a; Ussler and Paull, 1995; Vargas-Cordero *et al.*, 2020]. It is worth noting that $\delta^{18}\text{O}$ and δD abruptly increase and decrease, respectively, at the very base of J1005 (Figure 2). These values agree with those at J1006 and suggest that deeply sourced fluids from clay dehydration may also be influencing sediments farther from the mound. However, Cl^- (and other elemental) concentrations near seawater values at this same depth indicate minimal influence on pore water freshening (Figure 2; Figure S2), or that the locus of freshening at J1005 is deeper than the recovered sediment column. Taken together, the new pore water elemental, $\delta^{18}\text{O}$, δD , and $^{87}\text{Sr}/^{86}\text{Sr}$ profiles highlight a complex diagenetic environment and for the first time characterize deep fluids being expelled at a seafloor venting structure on the Chilean Margin.

4.2 Constraints on fluid migration

Although no pore water isotope data have been reported for ODP Site 1233, the decreasing Cl^- concentrations below 60 mbsf are paired with decreasing K and Li concentrations above seawater concentrations [Mix *et al.*, 2003] (Figure 6). These downcore changes are consistent with profiles at Site J1006 (Figure 3), which is located less than 5 km to the south. From this, we infer that low Cl^- concentrations at ODP Site 1233 also reflect deep freshening influences from clay dehydration. Indeed, the depth at which pore water Cl^- starts decreasing at ODP Site 1233 coincides with depths in the sediment column at which seafloor reflectors begin dipping upwards; these horizons intersect the seafloor near Site J1006 and implies a link between seafloor geometry and fluid flow (Figure 1). The diminishing freshening signal with increasing distance from the mound (J1006>ODP 1233>J1005) suggests that the migration of mound-associated fluids may be focused, potentially aided by faults and the anticlinal sediment structure.

The alteration of smectite to illite takes place at sedimentary temperatures between 60-150°C [Perry, 1970]. We apply the Na/K geothermometer to constrain temperatures at the depth of illitization ($Z_{\text{S} \rightarrow \text{I}}$) [Martin *et al.*, 1996; Nieva and Nieva, 1987], which yield a consistent equilibrium alteration temperature of $142 \pm 6^\circ\text{C}$ amongst the three sites (Table 2). We refrained

from using Mg- or Ca-based geothermometers owing to the precipitation of authigenic carbonate at Sites J1005 and J1006 [Bova *et al.*, 2019], which could bias the temperature estimate. The lack of continuous Li enrichment with depth suggests that alteration temperatures are <150°C, in agreement with our Na/K estimates [Hensen *et al.*, 2007]. Applying the Na/K-derived alteration temperatures to geothermal gradients at the three sites demonstrates that $Z_{S \rightarrow I}$ is achieved 2.5±0.6 kmbsf, although different Na/K geothermometers provide a range of $Z_{S \rightarrow I}$ estimates between 2.4±0.6 and 2.7±0.7 kmbsf [Fournier, 1979; Tonani, 1980] (Table 2). Nonetheless, the $Z_{S \rightarrow I}$ estimates are more or less consistent with each other and thermal modeling estimates near the CMSA ($Z_{S \rightarrow I}$ = 2-5 kmbsf) [Scholz *et al.*, 2013]. This places the locus of smectite dehydration towards the base of the trench fill package near the décollement [Völker *et al.*, 2013], as observed in the Barbados and Mediterranean accretionary complexes [Martin *et al.*, 1996; Scholz *et al.*, 2009].

Vertical fluid migration in accretionary prisms typically follows fault or fractures in the thrustsediment [Moore and Vrolijk, 1992]. We surmise that faults in this sector of the forearc complex act as a conduit for deeply sourced fluids to vent at the seafloor. The mound near our sites appears to be the seafloor manifestation of such migration and discharge. However, the observed variability in downcore freshening at J1005, J1006, and ODP Site 1233 suggest that despite their proximity, fluid migration pathways are potentially narrow.

4.3 Implications for Chilean Margin methane hydrate formation

Methane hydrate is ubiquitous on the south Chilean Margin, occupying ~7.5 percent of the pore space on average but can range from 5-15 percent [Alessandrini *et al.*, 2019; Villar-Muñoz *et al.*, 2018; Villar-Muñoz *et al.*, 2019], with higher hydrate saturation (S_h) often reported near faults in the forearc sediments [Vargas-Cordero *et al.*, 2018]. Methane hydrate typically forms in marine sediments with relatively high total organic carbon (TOC) content (>2%) to supply sufficient material for biogenic methane production [Hesse and Harrison, 1981; Kvenvolden, 1993]. In contrast, TOC in sediments along the Chilean Margin is relatively low (0.2-2%, average of 0.87% at the three sites) owing to high sedimentation rates and burial, with the highest TOC content limited to the sediment-seawater interface [Bova *et al.*, 2019; Mix *et al.*, 2003; Scholz *et al.*, 2013] (Figure S4). TOC can be used to provide a first-order approximation of S_h linked to *in situ* biogenic methane production following:

$$S_h = 3.45 \cdot \text{TOC} - 1.77$$

[Waseda, 1998]. Average TOC content at the three sites would yield 1.2 percent of the pore space occupied by methane hydrate, which is substantially lower than margin estimates (Figure S4). Moreover, methane hydrate nodules were only recovered at Site J1006 but not at Site J1005 [Bova *et al.*, 2019]; nor were they reported at ODP Site 1233 [Mix *et al.*, 2003]. This suggests that an additional methane supply (independent from *in situ* biogenic generation) may be needed to

account for observed S_h estimates in the region, and that this additional source might also account for spatially heterogeneous methane hydrate formation near the mound.

Deep fluids are often enriched in methane and the vertical migration of these fluids has been suggested to facilitate the formation of methane hydrate near cold seep and mud volcano structures globally [Milkov, 2000; You *et al.*, 2019]. On the Chilean Margin, AOM via sulfate reduction is the dominant diagenetic pathway for deposited organic matter [Treude *et al.*, 2005], which leads to rapid decreases in pore water sulfate concentration and increases in methane concentration, resulting in shallow SMTZ depths as observed at our sites (Figure 6; Table 3). SMTZ depths follow a similar pattern as downcore freshening, with the shallowest SMTZ at J1006, followed by ODP Site 1233, and J1005 with the deepest (Table 3). Below the SMTZ, methane concentrations also yield a similar trend, with the highest CH₄ concentrations at J1006 occurring as a sharp peak just below the SMTZ, whereas broader and deeper maxima are observed at the more distal sites (Figure 6).

Assuming steady state conditions, the downward diffusion and consumption of pore water sulfate is controlled by the upward diffusion of methane, allowing us to approximate the vertical methane flux at each site [Borowski *et al.*, 1996]. Diffusive sulfate fluxes can be calculated following Fick's first law:

$$J = -\phi \cdot D_s \cdot \frac{dC}{dz}$$

where J represents the downward sulfate flux (mmol m⁻² yr⁻¹), ϕ is the average porosity between the sediment-seawater interface and the SMTZ (dimensionless), D_s is the sediment diffusion coefficient (cm² s⁻¹), and $\frac{dC}{dz}$ is the pore water sulfate concentration gradient between the sediment-seawater interface and the SMTZ (mM cm⁻¹) [Berner, 1980]. D_s was corrected for tortuosity and calculated assuming a tracer diffusion coefficient for sulfate following Boudreau [1997]:

$$D_s = \frac{D_0}{1 - \ln(\phi)^2}$$

where D_0 , the diffusion coefficient for sulfate in seawater, is 5.8x10⁻⁶ cm² s⁻¹ [Li and Gregory, 1974]. We assume a linear decrease in sulfate concentration between the sediment-seawater interface and the SMTZ (Figure 6). Although sampling resolution in the upper few meters of J1005, J1006, and ODP Site 1233 is relatively low, this assumption is substantiated by pore water sulfate profiles from gravity cores taken near seep sites in the CMSA [Coffin *et al.*, 2007]. As such, our calculated diffusion rates are taken as conservative flux estimates since complete sulfate reduction near venting sites can occur even shallower than J1006 indicates, resulting in steeper sulfate gradients in the upper few meters of the sediment column and higher flux estimates.

Downward sulfate diffusion rates range between -67.40 and -306.96 mmol m⁻² yr⁻¹, with the highest flux at J1006 and lowest at J1005 (Table 3). As expected, sulfate fluxes at ODP Site 1233 (-164.63 mmol m⁻² yr⁻¹) fall between the other two sites. The sulfate flux at J1006 is consistent with estimates from a seep site in the CMSA (-361.91 mmol m⁻² yr⁻¹), which had a much shallower SMTZ (33 cm) [Coffin *et al.*, 2007]. Assuming a 1:1 stoichiometric consumption of sulfate and methane [Borowski *et al.*, 1996], and neglecting influences from advection that would likely enhance the migration of deep fluids, we can infer that methane fluxes at J1006 are at least ~2 and 5 times greater than ODP Site 1233 and J1005, respectively. This provides a mechanism to supplement the low methane concentrations/hydrate saturation solely from organic matter degradation to concentrations that are likely sufficient to support the higher hydrate saturations estimated in this region [Alessandrini *et al.*, 2019; Vargas-Cordero *et al.*, 2018; Villar-Muñoz *et al.*, 2018; Villar-Muñoz *et al.*, 2019]. It is important to note that the lack of recovered methane hydrate at J1005 and J1006 does not imply that they are not present. It is plausible, given the widespread bottom simulating reflector along the Chilean Margin [Rodrigo *et al.*, 2009], that methane hydrate could have simply been missed during coring operations at these sites or that they could be limited to deeper sections of the sediment column than were cored. Nonetheless, pore water elemental, isotopic, and hydrocarbon data from J1006 provide robust evidence that the vertical migration of fresh, gas saturated fluids from deep within the forearc complex may be a primary factor in the formation of shallower methane hydrate on the Chilean Margin (Figure 7).

The abundance of authigenic dolomitic concretions, as confirmed by shipboard XRD, at J1006 further supports active gas migration at this site. The absence of radiogenic pore water ⁸⁷Sr/⁸⁶Sr appears to rule out influences from anoxic marine silicate weathering as a control on alkalinity production [Torres *et al.*, 2020; Wallmann *et al.*, 2008] (Figure 5). Instead, AOM via sulfate reduction yields high pore water alkalinity concentrations at depth (Figure 6) following:



[Reeburgh, 1980]. Marked downcore decreases in pore water Ca/Cl, Mg/Cl, and Sr/Cl ratios (Figure 3) suggests that authigenic carbonate formation is also a sink for these divalent cations, in particular between 50-100 mbsf where the highest density of concretions was documented [Bova *et al.*, 2019]. Authigenic carbonates were also recovered at J1005 and ODP Site 1233 despite much less (or no) pore water freshening (i.e., venting signals). Thus, migration pathways and/or advective rates for gas saturated fluids at these sites may have been different in the past, with the distribution of authigenic carbonates serving as potential paleo-horizons of shallow SMTZ depths and venting [Sample, 1996]. Indeed, recovery of fossil *Lucinidae* shells and authigenic carbonate nodules from ~55 mbsf at Site J1005 potentially indicate more active seepage in the past at this site despite a lack of pore water freshening in the sediment column today [Holmes *et al.*, 2005]

(Figure S1). Geochemical characterization of authigenic carbonates and other minerals (e.g., sulfides) may provide valuable insight on the evolution of fluid venting on the Chilean Margin.

5. Conclusions

Pore waters from sediment cores at sites proximal to a mound venting structure on the south Chilean Margin were collected and analyzed for their elemental and isotopic composition. The downcore patterns of $\delta^{18}\text{O}$ and δD reveal the influence from deeply-rooted fluids linked to smectite dehydration as a source of freshening in marine sediments. Strontium isotope systematics highlight secondary influences from ash diagenesis on pore water chemistry. The extent of pore water freshening and intensity of methane fluxes are a function of a site's distance to a regional seafloor mound, with the largest decreases in Cl^- concentration and highest methane fluxes occurring closest to this venting structure where methane hydrate was documented. This not only suggests that subsurface fluid and gas migration within the accretionary prism may be directly linked to venting structures, but also that delivery of fresh, gas-saturated fluids from deeper in the sediment column may be a critical component of higher than estimate methane hydrate saturations on the Chilean Margin. Together, the data paint a clearer picture of the mechanisms of fluid and gas migration within the forearc complex.

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581 **Data Availability Statement**

582 The pore water, headspace, and sediment geochemical data for J1005 and J1006 can be found
 583 online at the Zenodo repository (<https://doi.org/10.5281/zenodo.7160921>). All correspondence
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Figure 1: Study Setting. A) Bathymetric map of regional study area with the location of Sites J1005 (blue), J1006 (dark grey), and ODP Site 1233 (yellow) denoted by the colored symbols. Dotted line represents the seismic profile in C and D. Red symbol represents the general location of a gas flare shown in panel D. B) Downcore pore water chloride (Cl^-) concentration at the three sites, with the same color assignment in A. Depth scale in meters below sea floor (mbsf). Black arrow marks seawater concentration. C) Underway seismic profile of the study area along the A-A' line shown in subpanel A. Site J1006 is located on a ~4 km wide, 25 m tall seafloor mound, with ODP Site 1233 slightly to the north and Site J1005 positioned just upslope to the south. D) Underway seismic profile of the study area along the B-B' line shown in subpanel A, with ODP Site 1233, the observed gas flare, and seismic blanking feature shown. For C and D, images have been modified with permission after Hebbeln et al. [1995].

Figure 2: Pore water geochemistry at Site J1005. Downcore profiles for SO_4^{2-} , headspace CH_4 concentrations, alkalinity, NH_4^+ , Cl^- , Na/Cl , Ca/Cl , Mg/Cl , K/Cl , B/Cl , DSi/Cl , Li/Cl , Sr/Cl , $\delta^{18}\text{O}$, δD , and $^{87}\text{Sr}/^{86}\text{Sr}$. For $\delta^{18}\text{O}$, squares are samples measured via Picarro and open circles are samples measured via mass spectrometer. Reported errors for $\delta^{18}\text{O}$, δD , and $^{87}\text{Sr}/^{86}\text{Sr}$ represent 1 SD; uncertainty is smaller than the symbol size.

Figure 3: Pore water geochemistry at Site J1006. Downcore profiles for SO_4^{2-} , headspace CH_4 concentrations, alkalinity, NH_4^+ , Cl^- , Na/Cl , Ca/Cl , Mg/Cl , K/Cl , B/Cl , DSi/Cl , Li/Cl , Sr/Cl , $\delta^{18}\text{O}$, δD , and $^{87}\text{Sr}/^{86}\text{Sr}$. For $\delta^{18}\text{O}$, squares are samples measured via Picarro and open circles are samples measured via mass spectrometer. Reported errors for $\delta^{18}\text{O}$, δD , and $^{87}\text{Sr}/^{86}\text{Sr}$ represent 1 SD; uncertainty is smaller than the symbol size.

Figure 4: Changes in pore water $\delta^{18}\text{O}$ and δD as a function of freshening. Differences in $\delta^{18}\text{O}$ (A) and δD (B) between downcore observations (δ_{obs}) and seawater reference (δ_{ref}) values ($\Delta\delta^{18}\text{O}$ and $\Delta\delta\text{D}$, respectively) plotted against pore water Cl^- normalized to seawater ($f([\text{Cl}_{\text{obs}}]/[\text{Cl}_{\text{ref}}])$). Site J1005 (blue) and J1006 (dark grey) are shown. Seawater reference values are denoted by the red star.

Figure 5: Strontium systematics at Sites J1005 and J1006. Pore water $^{87}\text{Sr}/^{86}\text{Sr}$ plotted against the inverse Sr concentration for Site J1005 (blue) and J1006 (dark grey). The seawater reference value is denoted by the red star. The schematic inset indicates the general direction of change associated with marine silicate weathering (MSiW), authigenic carbonate precipitation, and ash diagenesis.

Figure 6: Spatially variable pore water geochemistry near the mound. Downcore profiles for concentrations of SO_4^{2-} (A), headspace methane (B), alkalinity (C), Cl^- (D), K (E), and Li (F) at Sites J1005 (blue), J1006 (dark grey), and ODP Site 1233 (yellow). In A, the inset figure shows

SO_4^{2-} concentrations between the seafloor and 15 mbsf. Solid lines denote linear gradients used in sulfate diffusion calculations.

Figure 7: A conceptual schematic for fluid migration and methane hydrate formation near the regional venting structure. The location of J1005, J1006, and ODP 1233 are shown in proximity to the mound feature. The red line marks the assumed shape of the mound feature based on sediment and pore water data. Large blue arrows denote the vertical migration of deep-sourced fluids from clay dehydration at depth with its characteristic low- Cl^- , high $\delta^{18}\text{O}$, and low δD signatures. The white symbols with “GH” represent approximate depths that methane hydrate was recovered at Site J1006, for which their occurrence might be linked to high methane fluxes close to the mound (see inset CH_4 flux plot). Dotted blue lines denote additional likely pathways for fluid being expelled at the venting structure based on low- Cl^- below 60 mbsf at ODP Site 1233 and high $\delta^{18}\text{O}$ /low δD in the deepest data point at J1005. However, the lack of concomitant freshening in this sample leaves this pathway relatively unconstrained. This figure has been modified with permission after Hebbeln et al. [1995].

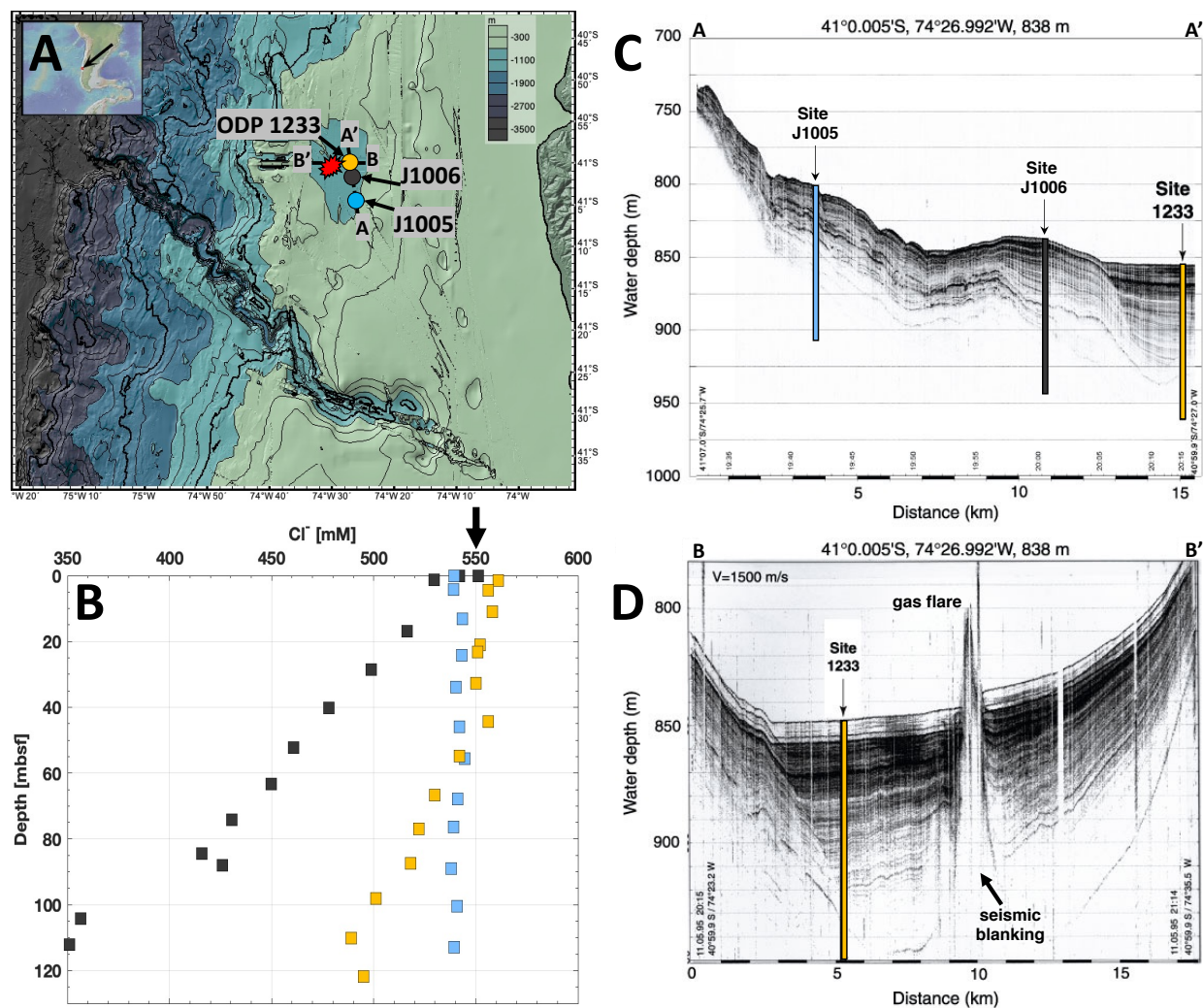


Figure 1

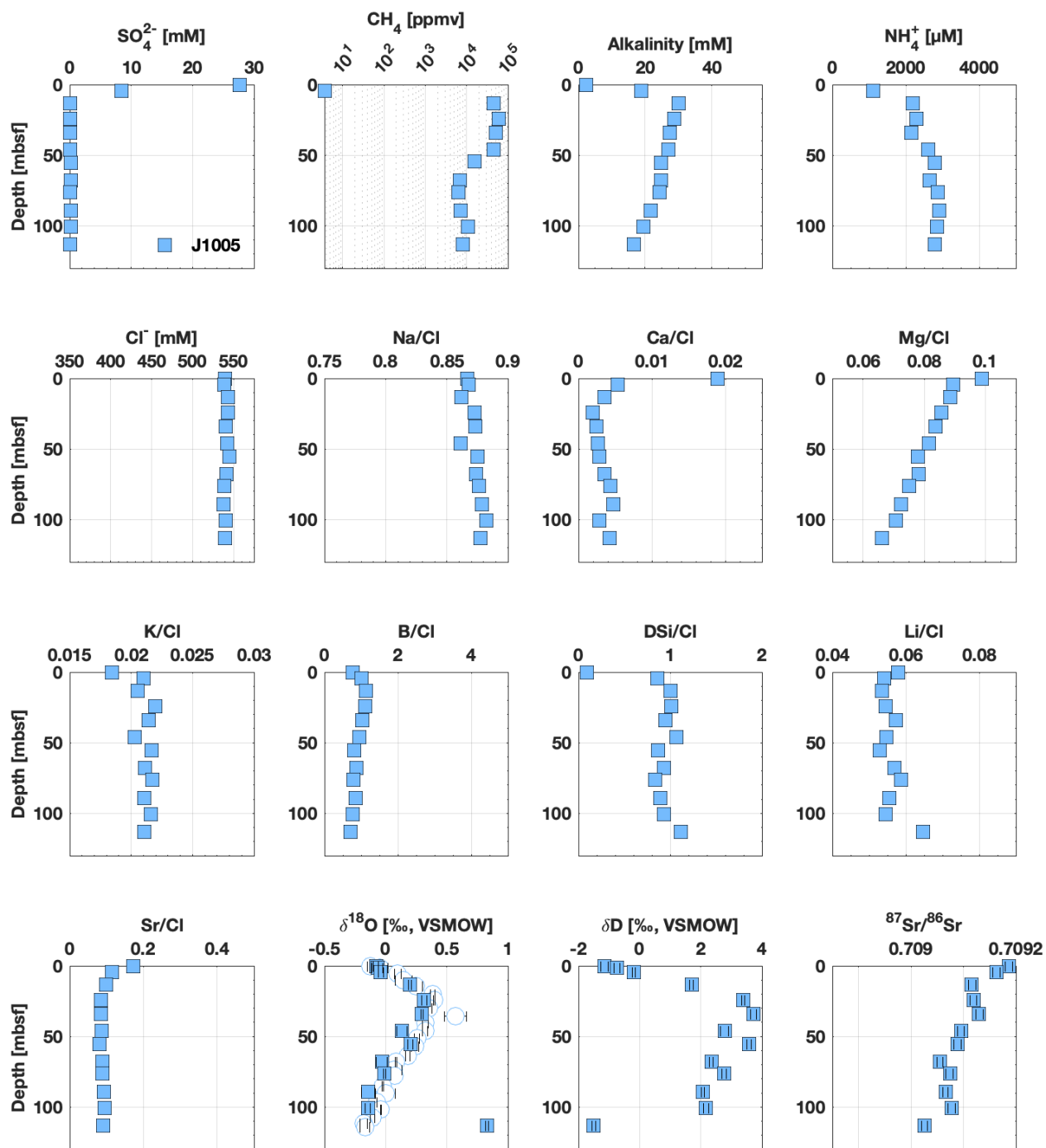


Figure 2

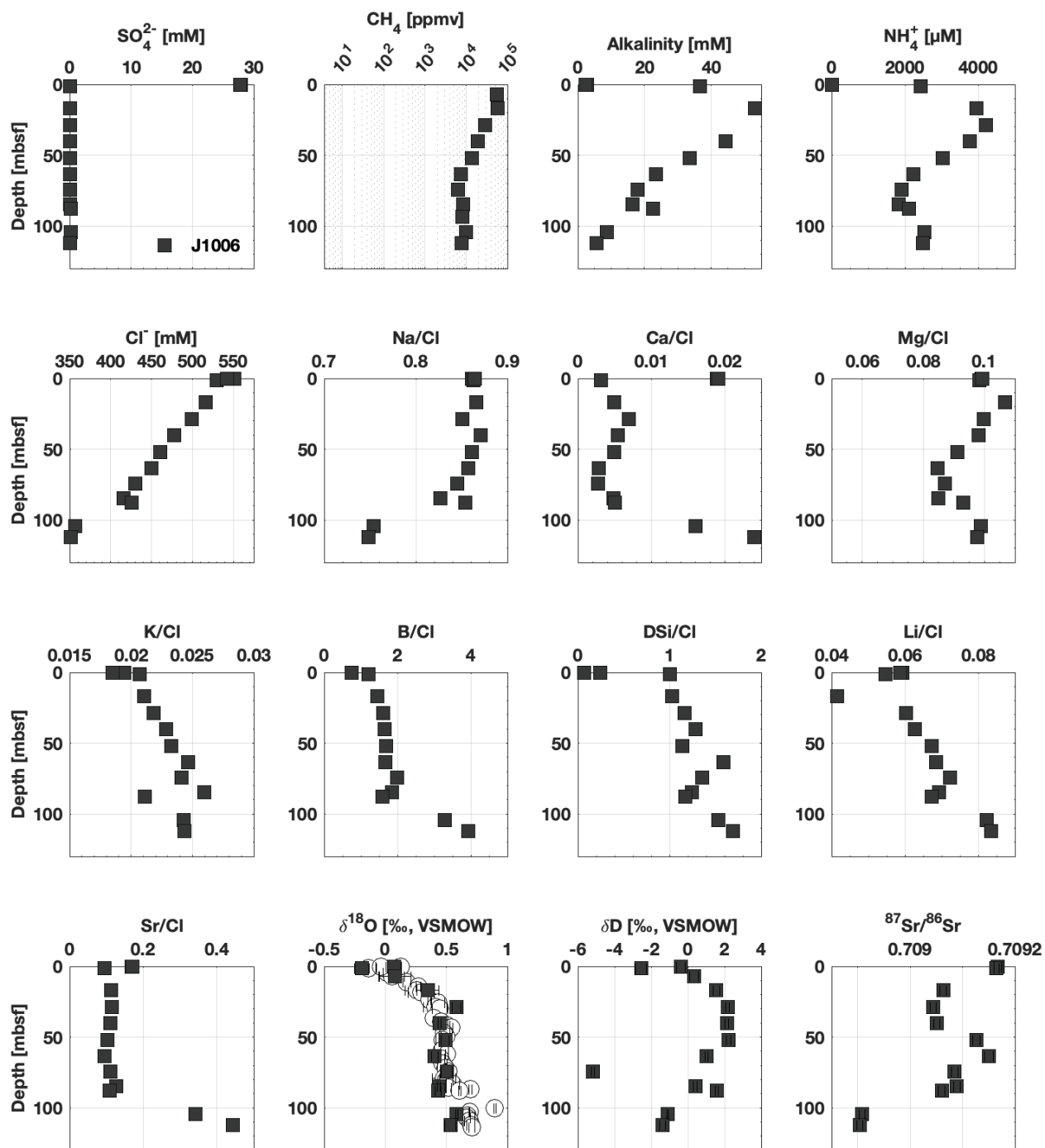


Figure 3

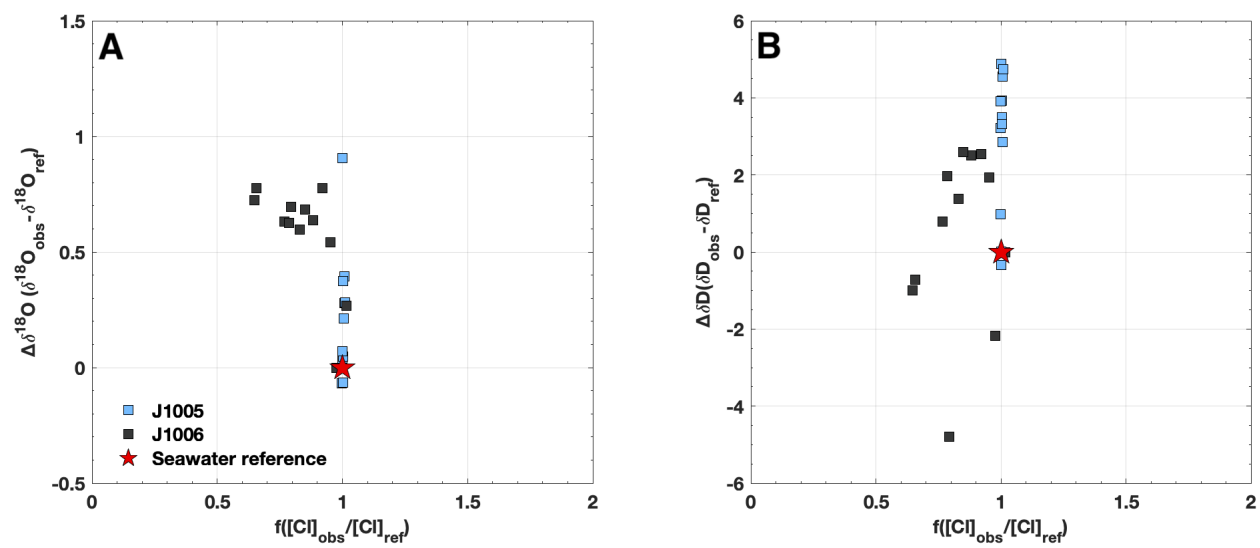


Figure 4

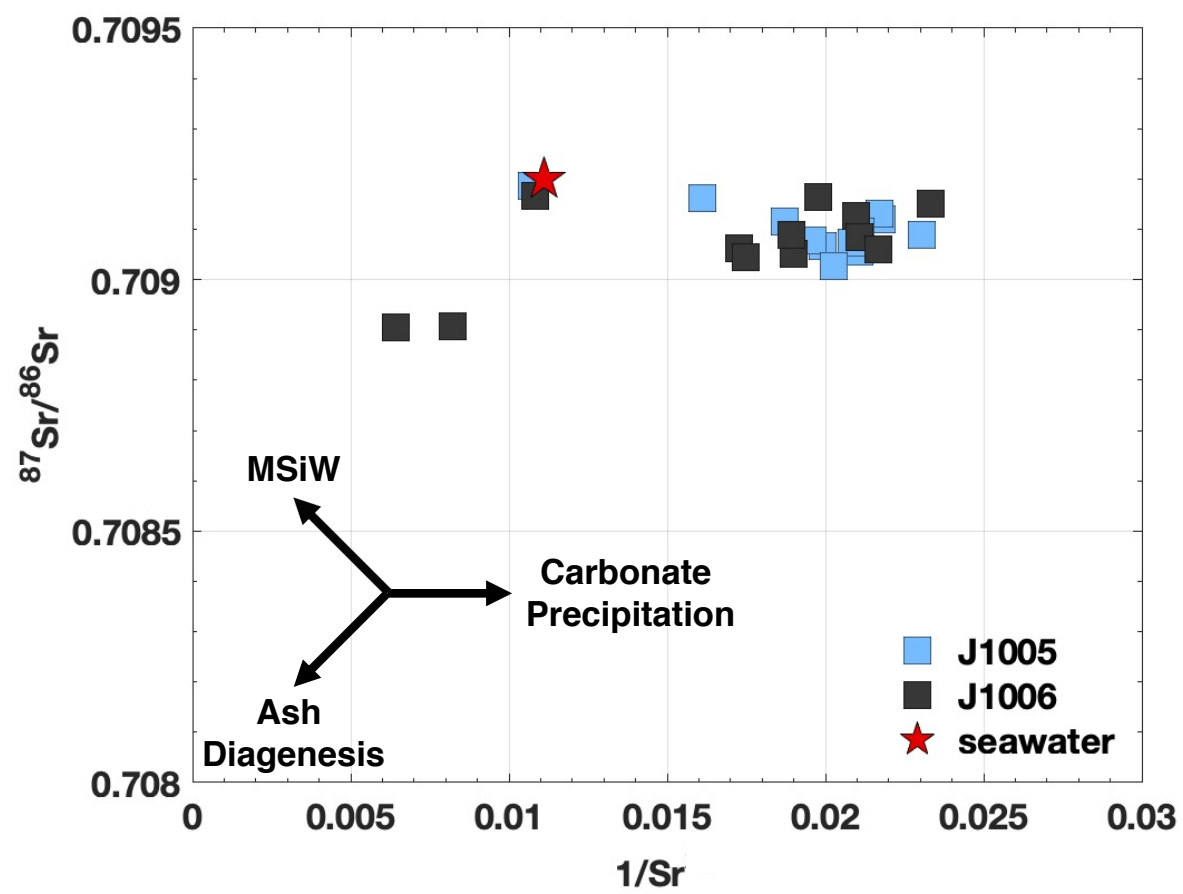


Figure 5

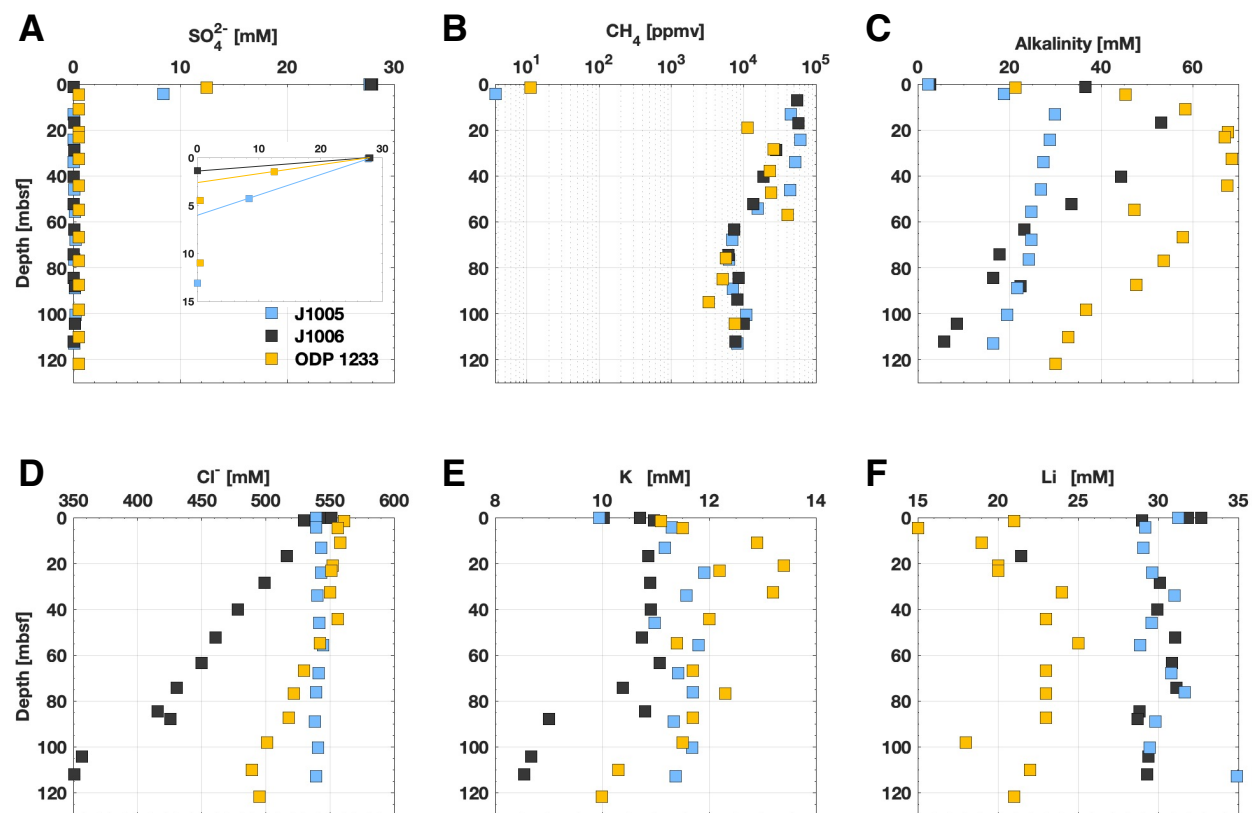


Figure 6

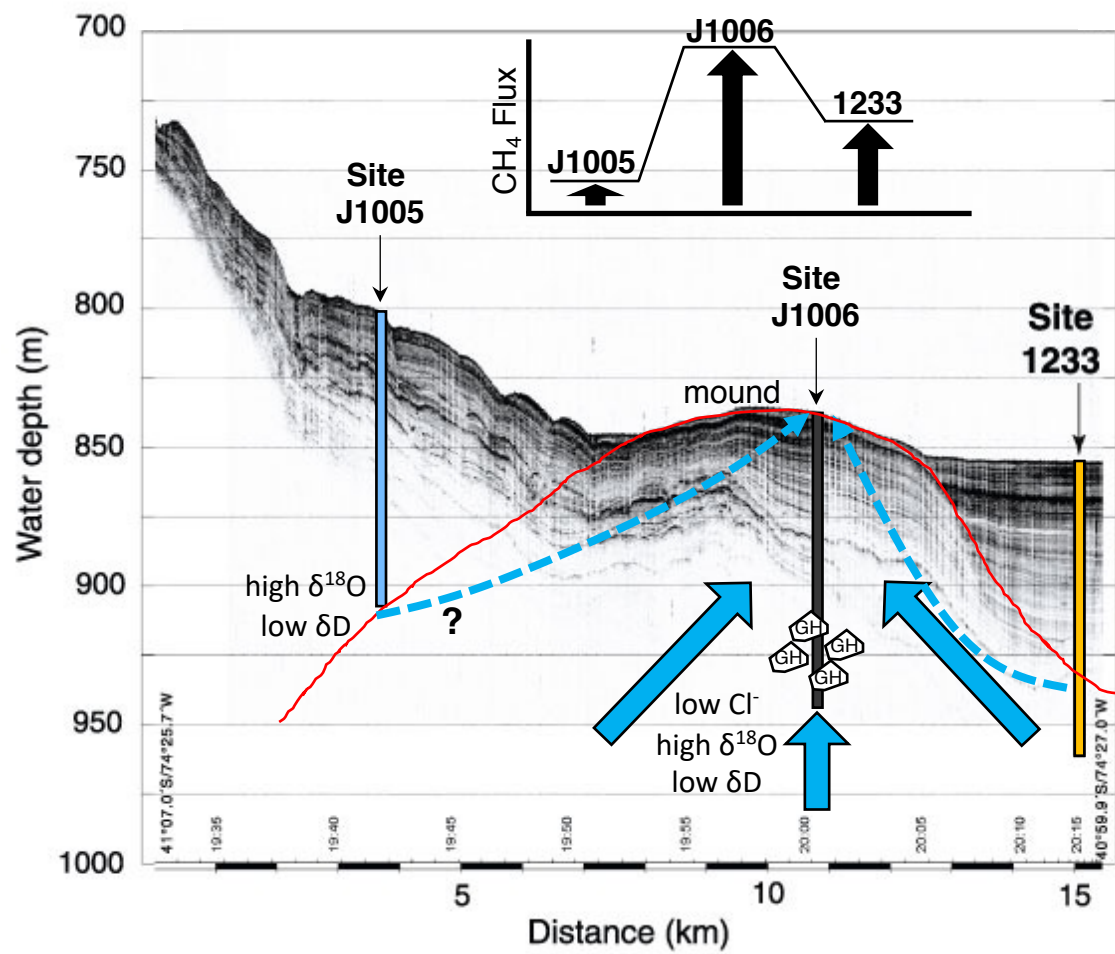


Figure 7

Table 1: Core locations, water depth, and proximity to the mound venting structure at 41°S						
Site	Latitude	Longitude	Water Depth (m)	Distance to Mound (km)	Estimated Bottom Age (kyr)	Reference
J1005	41°4.58'S	74°26.70'W	807	5-10	170	This Study
J1006	41°1.56'S	74°26.70'W	824	~0	70	This Study
ODP 1233	41°0.00'S	74°26.99'W	838	<5	70	Mix et al. [2003]

Table 2: Estimates for the depth of illitization at 41°S based on Na/K geothermometry

Site	Geothermal Gradient (°C km ⁻¹)	Na/K (°C) ^c	$Z_{S \rightarrow I}$ (kmbsf) ^c	Na/K (°C) ^d	$Z_{S \rightarrow I}$ (kmbsf) ^d	Na/K (°C) ^e	$Z_{S \rightarrow I}$ (kmbsf) ^e
J1005 ^a	57	138±3	2.4	133±4	2.3	150±3	2.6
J1006 ^a	76	146±9	1.9	143±11	1.9	158±9	2.1
ODP 1233 ^b	45	142±4	3.2	138±5	3.1	154±4	3.4

^a[Bova et al., 2019] ^b[Grevemeyer et al., 2003] ^c[Nieva and Nieva, 1987] ^d[Tonani, 1980] ^e[Fournier, 1979]
Note: All concentrations in mg/L. Reported errors represent 1 SD.

Table 3: SMTZ depth, changes in pore water sulfate concentration, diffusive sulfate fluxes, near the mound			
Site	SMTZ (mbsf)	$\Delta[\text{SO}_4^{2-}]$ (mM)	Flux ($\text{mM SO}_4^{2-} \text{ m}^{-2} \text{ yr}^{-1}$)
J1005	6	27.712	-67.40
J1006	1.35	27.965	-306.96
ODP 1233	2.5	27.5	-164.63

Supplemental Information:

Links between spatially heterogeneous pore water geochemistry, fluid migration, and methane hydrate near a seafloor mound venting structure on the south Chilean Margin (41°S)

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Contents:

- 1) Supplemental Figures 1-4
- 2) Supplemental Table 1
- 3) Supplemental References

Introduction

We provide four supplemental figures and a supplemental table describing expected changes in pore water chemistry from relevant processes.

Figures S1-S4.

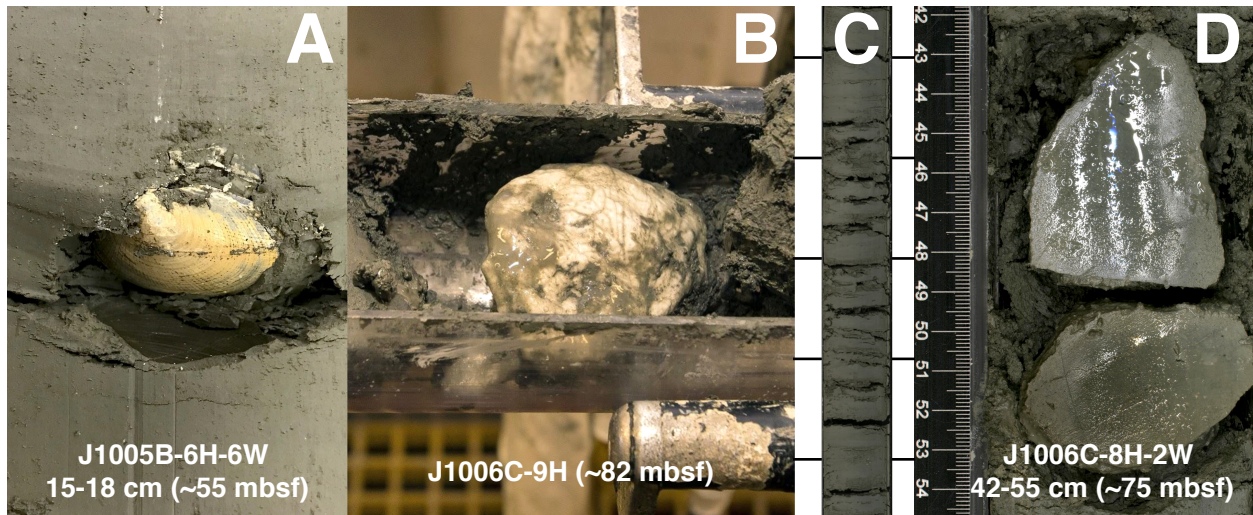
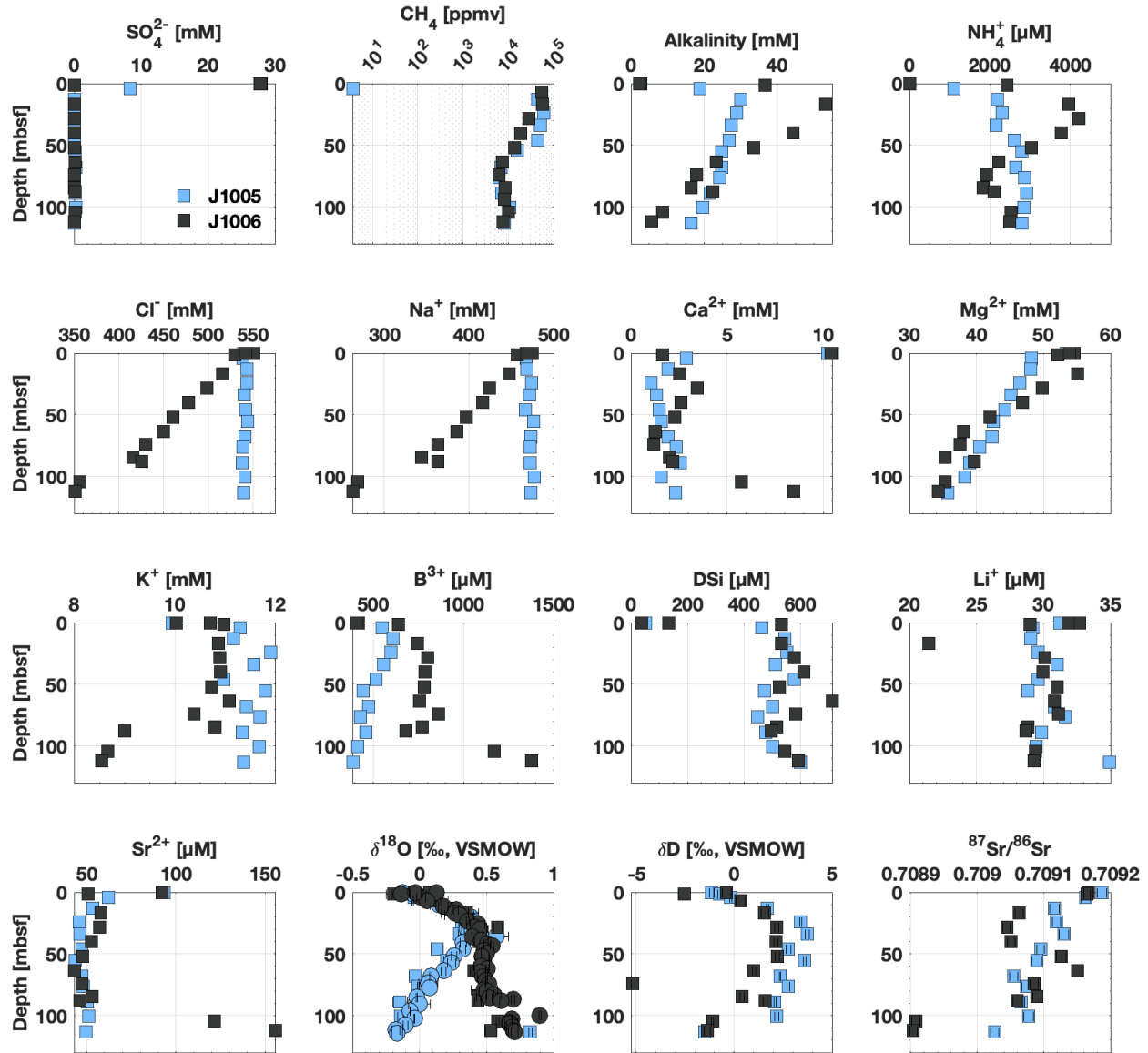


Figure S1: Evidence for (paleo) seepage, methane hydrate presence, and authigenesis. A) *Lucinidae* bivalve shells from ~55 mbsf at Site J1005 (also recovered from ~85 mbsf at Site J1006). B) methane hydrate nodule from ~82 mbsf at Site J1006. C) Example of gas cracks, which resulted in loss of sediment between 88-104 mbsf, in core sections at Site J1006. D) Examples of authigenic carbonate concretions at Site J1006.



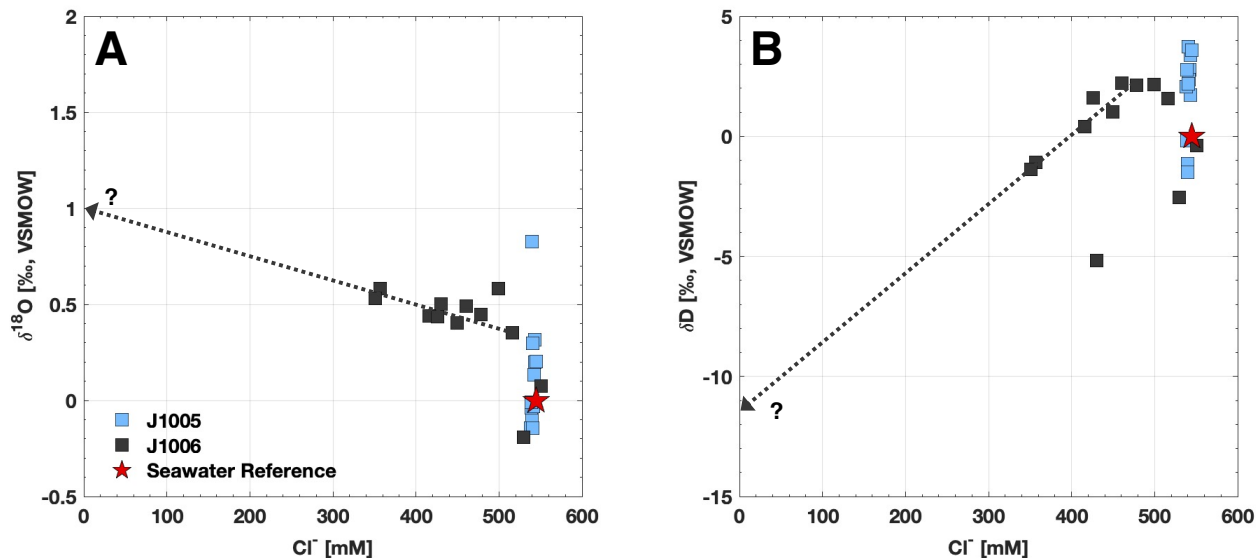


Figure S3: A comparison between pore water $\delta^{18}\text{O}$ and δD and Cl^- concentration. A) $\delta^{18}\text{O}$ versus Cl^- . B) δD versus Cl^- . Sites J1005 (blue), J1006 (dark grey), and seawater reference (red) are shown. Dotted lines represent approximated linear extrapolation to freshened endmember at $\text{Cl}^- = 0$ ($\delta^{18}\text{O} = +1.0\text{‰}$, $\delta\text{D} = -11.5\text{‰}$), though the apparent non-linearity adds some uncertainty to these estimates.

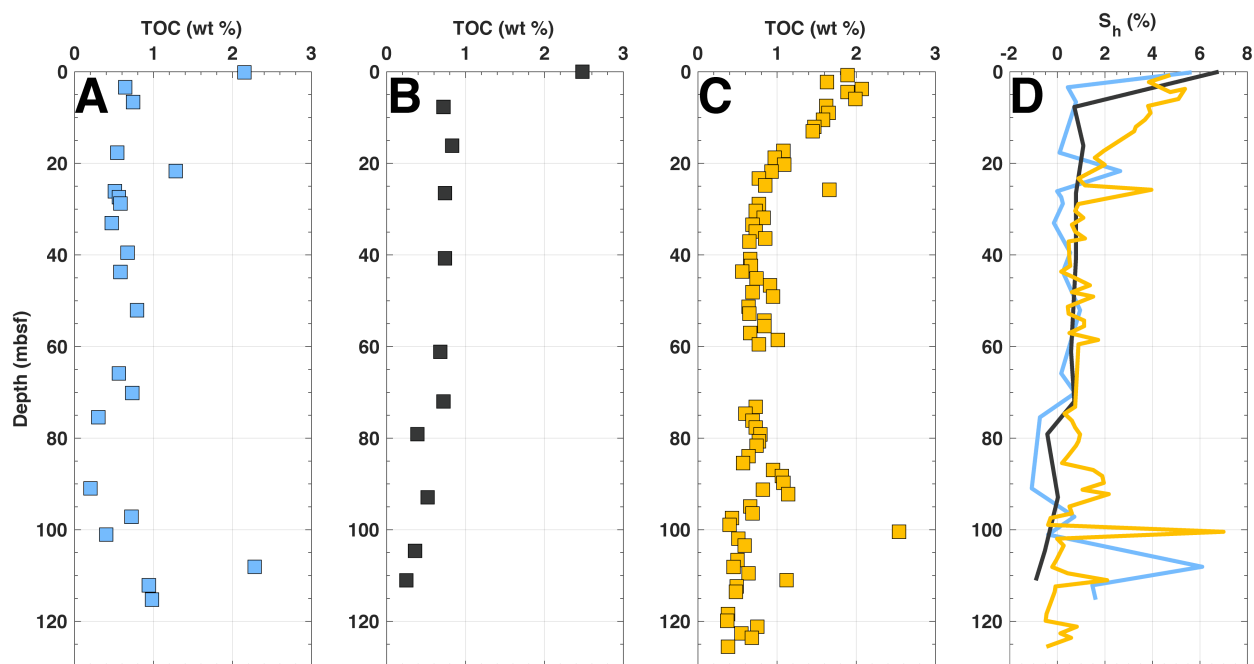


Figure S4: TOC-based methane hydrate saturation. A-C) Downcore bulk sediment TOC for J1005 (blue), J1006 (dark grey), and ODP Site 1233 (yellow). D) Methane hydrate saturation index (S_h) derived using the following equation: $S_h = 3.45 \cdot (\text{TOC}) - 1.77$ [Waseda, 1998]. Methane hydrate saturation is $<1\%$ omitting the highest TOC content, which is generally limited to the upper few mbsf, though discrete horizons are also found at depth at sites J1005 and ODP 1233.

Supplementary Table

Table S1: Changes in pore water Cl⁻, $\delta^{18}\text{O}$, and $\delta^2\text{H}$ from different sedimentary or diagenetic processes. Adapted from Kastner et al. [1991], Dahlmann and de Lange [2003], and references therein.			
Process	Cl ⁻	$\delta^{18}\text{O}$	$\delta^2\text{H}$
Gas hydrate dissociation	-	+	+
Clay mineral dehydration	-	+	-
Ash alteration	o/+	-	+
Oceanic crust alteration (<200°C)	-	-	+
Anaerobic oxidation of methane	-	o	-
Meteoric water infiltration	-	-	-
Clay membrane filtration	-	-	-
(-) decrease in value (+) increase in value (o) no change			

Supplementary References

- Dahlmann, A., and G. J. de Lange (2003), Fluid-sediment interactions at Eastern Mediterranean mud volcanoes: a stable isotope study from ODP Leg 160, *Earth and Planetary Science Letters*, 212(3-4), 377-391, doi:10.1016/s0012-821x(03)00227-9.
- Kastner, M., H. Elderfield, and J. B. Martin (1991), FLUIDS IN CONVERGENT MARGINS - WHAT DO WE KNOW ABOUT THEIR COMPOSITION, ORIGIN, ROLE IN DIAGENESIS AND IMPORTANCE FOR OCEANIC CHEMICAL FLUXES, *Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences*, 335(1638), 243-259, doi:10.1098/rsta.1991.0045.
- Waseda, A. (1998), Organic carbon content, bacterial methanogenesis, and accumulation processes of gas hydrates in marine sediments., *GEOCHEMICAL JOURNAL*, 32(3), 143-157, doi:10.2343/geochemj.32.143.