

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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2 methane hydrate near a seafloor mound venting structure on the south Chilean Margin (41°S)

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13 **Key Points:**

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

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

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

19 **Abstract**

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

38

39 **Plain Language Summary**

40 The Chilean Margin is one of the world's largest subduction zones and has a substantial methane
41 hydrate reservoir at shallow depths in the sediment column. However, it is still poorly understood
42 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.

47 **1. Introduction**

48 Compressional tectonics, sediment loading, and the subsequent reductions in porosity are the
49 principal processes controlling the vertical migration of fluids and gas through accreted sediments
50 at convergent margins [Moore and Vrolijk, 1992]. Within these forearc complexes, the circulation
51 and alteration of fluids can influence subduction mechanics and the cycling of elements between
52 the ocean, lithosphere, and mantle [Chan and Kastner, 2000; Peacock, 1990; Saffer and Tobin,
53 2011]. At the sediment-seawater interface, fluids and gas can be expelled to the ocean through
54 various seafloor venting structures like cold seeps and submarine mud volcanoes, which have been
55 documented globally [Brown, 1990; Kopf, 2002; Milkov, 2000]. Provided sufficient volumetric
56 fluxes, the transfer of fluid from sedimentary to oceanic regimes through these structures could
57 exert influence on marine elemental and isotopic budgets [Elderfield et al., 1990; Gieskes et al.,
58 1989; Kastner et al., 1991].

59 Prior examination of pore water chemistry near seafloor venting structures have offered a better
60 understanding of the hydrogeological and geochemical processes taking place well beyond the
61 limits of modern ocean drilling [Dahmann and de Lange, 2003]. The elemental and isotopic
62 composition of these fluids often reflect subduction mechanics, diagenetic reactions, and mineral
63 dehydration processes taking place deep within the accretionary prism. Indeed, pore water studies
64 on the Barbados, Mediterranean, Nankai, Gulf of Cadiz, and Taiwan accretionary prisms (among
65 others) have provided critical insight on the roles of dewatering in megathrust tectonism, fluid
66 expulsion in oceanic geochemical budgets, and deep gas migration in supporting methane hydrate
67 formation [Chen et al., 2020; Deyhle and Kopf, 2001; Dia et al., 1999; Godon et al., 2004; Haese
68 et al., 2006; Hensen et al., 2007; Kopf and Deyhle, 2002; Martin et al., 1996; Menapace et al.,
69 2017; Nishio et al., 2015; Scholz et al., 2009; Vanneste et al., 2011].

70 Despite these advances, the south Chilean Margin—a 1500 km convergent plate boundary and one
71 of the most tectonically-active regions on Earth [Melnick et al., 2006; Völker et al., 2013]—
72 remains one such setting where cold seeps and mud volcanoes have only been documented within
73 a limited sector of the margin near the Concepción Methane Seep Area (36°S) [Sellanes et al.,
74 2004; Vargas-Cordero et al., 2020]. Recently, cold seeps have also been observed near the Chile
75 Triple Junction in the south (46°S) [Villar-Muñoz et al., 2021]. The scarcity of documented venting
76 systems is in stark contrast with fluid budget estimates in the forearc complex, which remain
77 unbalanced and require transfer of fluid and volatiles from subducted sediments back to the ocean
78 [Völker et al., 2014]. Moreover, pore water studies near sites of active fluid and gas discharge on
79 the Chilean Margin are limited [Coffin et al., 2007; Scholz et al., 2013; Zheng et al., 1995]; thus,
80 a comprehensive geochemical characterization of deep fluids remains incomplete. Addressing this
81 deficiency can provide critical insight on a number of fronts, including the interaction between
82 deep-seated fluids and tectonism on the Chilean Margin [Contreras-Reyes et al., 2013; Saffer and
83 Tobin, 2011; Völker and Stipp, 2015] and how fluid and gas migration within this accretionary
84 prism supports a robust methane hydrate reservoir in shallow margin sediments despite relatively

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

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

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

108 **2. Study Area**

109 **2.1 Geologic and tectonic setting**

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

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

124 Active subduction and frequent megathrust earthquakes have manifested in normal and splay
125 faulting throughout the forearc complex [*Völker et al.*, 2014]. Gas seepage on the south Chilean
126 Margin was first reported by Sellanes *et al.* [2004] in what is now called the Concepción Methane
127 Seepage Area (CMSA), with more recent evidence for active and paleo seepage [*Klaucke et al.*,
128 2012]. Seepage of methane-rich fluids typically cluster near these faults and support robust
129 chemosynthetic communities near the seafloor [*Munoz et al.*, 2016; *Sellanes et al.*, 2008]. It has
130 been suggested that onset of seepage in this region may be linked to the tectonic history of the
131 margin, potentially as recent as the 2010 Maule earthquake in some sectors of the margin [*Geersen*
132 *et al.*, 2016; *Villar-Muñoz et al.*, 2021]. Low pore water chloride concentrations in a small set of
133 multicores near the CMSA were interpreted to reflect freshening from deep fluids released during
134 clay dehydration processes at depth, potentially providing a mechanism for vertical migration of
135 gas saturated fluids at these seeps [*Scholz et al.*, 2013]. However, pore water freshening is not a
136 necessarily widespread feature at venting sites [*Coffin et al.*, 2007]. In contrast, high $^{18}\text{O}/^{16}\text{O}$ and
137 $^2\text{H}/^1\text{H}$ ratios ($\delta^{18}\text{O}$ and δD , respectively) in pore waters near a newly discovered chain of small
138 (meter-scale) mud volcanoes upslope and just south of the CMSA indicate that regional fluid
139 migration and discharge may be linked to methane hydrate dissociation [*Vargas-Cordero et al.*,
140 2020].

141 Methane hydrates are ubiquitous on the south Chilean Margin and have often, but not only, been
142 observed near sites of active venting [*Bangs et al.*, 1993; *Behrmann et al.*, 1992; *Coffin et al.*,
143 2007; *Vargas-Cordero et al.*, 2010; *Vargas-Cordero et al.*, 2017; *Villar-Muñoz et al.*, 2018; *Villar-*
144 *Muñoz et al.*, 2019]. Steep redox gradients indicate that marine sediments in the region are highly
145 reducing owing to sediment loading and microbial degradation of organic carbon (~0.5-2 wt%)
146 [*Bova et al.*, 2019; *Mix et al.*, 2003; *Scholz et al.*, 2013]. Anaerobic oxidation of methane (AOM)
147 from sulfate reduction typically occurs in the upper few meters of the sediment column, with
148 methanogenic conditions below [*Bova et al.*, 2019; *Coffin et al.*, 2007; *Mix et al.*, 2003; *Scholz et*
149 *al.*, 2013]. A widespread bottom simulating reflector marks the transition between methane
150 hydrate-rich sediments and free gas below [*Rodrigo et al.*, 2009]. On the Chilean Margin, this
151 horizon is relatively shallow, typically less than 150 meters below sea floor (mbsf), with methane
152 hydrate occupying 5-15% of the pore space [*Alessandrini et al.*, 2019; *Vargas-Cordero et al.*,
153 2017]. Sites of active venting often have the shallowest sulfate-methane transition zone, which can
154 be <1 mbsf or even at the sediment-seawater interface itself owing to high vertical fluxes of gas-
155 saturated fluids [*Coffin et al.*, 2007]. Elevated pore water alkalinity concentrations have been
156 observed throughout much of the margin, which likely reflect AOM via sulfate reduction but could
157 also be attributed to marine silicate weathering in the anoxic sedimentary system [*Torres et al.*,
158 2020; *Wallmann et al.*, 2008]. The alkalinity generated by these processes promote authigenic
159 carbonate precipitation below the SMTZ or even on the seafloor [*Bohrmann et al.*, 1998; *Klaucke*

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

162 **2.2 Study sites**

163 D/V *JOIDES Resolution* Expedition 379T (JR100) cored two sites at 41°S on the Chilean Margin.
164 Sites J1005 and J1006 are located on a bench in the upper continental slope ~38 km offshore at
165 807- and 824-meters water depth, respectively (Figure 1; Table 1). Three holes (A, B, and C) were
166 cored at each site using the advanced piston coring system, yielding complete stratigraphic sections
167 of 118 mbsf at J1005 and 120 mbsf at J1006. Sediment at both sites are assigned to single lithologic
168 units comprising of Pleistocene silty clay, with varying contributions from biogenic, volcanogenic,
169 and authigenic (sulfidic, silicate, carbonate) components. Despite the proximity of the sites, the
170 respective sediment columns have different bottom ages as indicated by shipboard correlation of
171 paleomagnetic and physical properties data [Bova *et al.*, 2019] (Table 1).

172 Site J1006 is located near the apex of a seafloor mound, with Site J1005 positioned just upslope
173 from this feature. Authigenic carbonate nodules were recovered at both sites (Figure S1); at J1005,
174 small (1-3 cm) concretions were recovered ~30-60 mbsf, with larger concretions (5-13 cm) and an
175 order of magnitude greater abundance at Site J1006 between 75-115 mbsf. Shipboard x-ray
176 diffraction (XRD) analysis indicates that these authigenic carbonates are primarily dolomitic in
177 composition [Bova *et al.*, 2019]. Likewise, methane hydrate nodules were recovered at Site J1006
178 ~85 mbsf (Figure S1). Sediment in the core sections within ±10 m of the hydrate interval was
179 heavily cracked and expanded owing to depressurization of gas (and potentially methane hydrate
180 dissociation) upon recovery (Figure S1). As a result, a substantial void between 88-104 mbsf exists
181 at J1006. Intact bivalve fossils were recovered at Sites J1005 and J1006 and were identified to
182 belong to the *Lucinidae* family of seawater clams (Figure S1). These burrowing bivalves live in
183 reducing, sulfur-rich sediments and can be indicative of active (or past) seepage of gas-saturated
184 fluids from the seafloor [Holmes *et al.*, 2005]. Full site reports are provided in the Expedition 379T
185 Preliminary Report [Bova *et al.*, 2019].

186 Sites J1005 and J1006 were cored 10 km and 5 km SSE of ODP Site 1233, respectively, which
187 was previously cored during ODP Leg 202 [Mix *et al.*, 2003]. Collectively, the three sites comprise
188 a lateral transect across the mound structure, with J1006 the most proximal, followed by ODP Site
189 1233 (<5 km), and J1005 being the most distal (~10 km) (Table 1). Like the JR100 sites, a shallow
190 SMTZ, methanogenic sediments, and authigenic carbonates were reported at ODP Site 1233 but
191 methane hydrate was not recovered despite strong reductions in pore water chloride concentration
192 >60 mbsf [Mix *et al.*, 2003]. The proximity of the three sites to the mound, similar lithologic and
193 depositional features, and similar redox conditions but distinct pore water chemistry makes these
194 sites uniquely suited to address the targeted research objectives outlined above.

195 **3. Materials and Methods**

196 **3.1 Pore water sample collection for Sites J1005 and J1006**

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

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

210 **3.2 Shipboard pore water ion analysis**

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

224 **3.3 Pore water oxygen and hydrogen isotope analysis**

225 Pore water $\delta^{18}\text{O}$ and δD composition was determined using a Picarro L2130-*i* cavity ringdown
226 laser spectrometer light isotope instrument in triplicate at the University at Buffalo following
227 methods in van Geldern and Barth [2012] (J1005, n=13; J1006, n=22). Samples were injected four
228 times; each injection was corrected for memory, drift, and were then normalized to Vienna
229 Standard Mean Ocean Water (VSMOW). The first injection was discarded for each sample and
230 the remaining three analyses were aggregated into an average value with associated replicate
231 uncertainty. Average replicate standard deviation (1 SD) was 0.03‰ for $\delta^{18}\text{O}$ measurements and
232 0.11‰ for δD measurements.

233 Additional pore water $\delta^{18}\text{O}$ measurements (J1005, n=24; J1006, n=39) were made at the Rutgers
234 University Stable Isotope Laboratory using a FISIONS OPTIMA Mass Spectrometer equipped with
235 a MicroMass multiprep automatic sample processing system after 1-minute water equilibration
236 with CO_2 in a sealed glove bag using standard methods [Epstein and Mayeda, 1953; Fairbanks,
237 1982]. All samples were run in duplicate. Reproducibility is estimated to be $\pm 0.04\text{‰}$ (1 SD) as
238 determined by multiple (n=12) daily analyses of laboratory standards. Accuracy is estimated to be
239 within 0.03‰ by comparison of North Atlantic Bottom Water with VSMOW.

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

243 **3.4 Pore water strontium isotope analysis**

244 Pore water strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) analysis followed the Sr separation protocol of Horwitz et
245 al. [1992] (J1005, n=12; J1006, n=12). Sample volumes were calculated from shipboard elemental
246 concentrations, targeting at least $1\ \mu\text{g}$ Sr for each sample. Pore water samples were acidified to 2N
247 strength with calculated volumes of 7N HNO_3 prior to separation. Strontium was
248 chromatographically separated from the pore water matrix using Eichrom 50-100 μm Sr Resin and
249 different concentrations of HNO_3 . Strontium was collected in 0.05N HNO_3 in acid cleaned 3 mL
250 Savillex vials, dried down, and then dissolved in 2% by volume HNO_3 for analysis. Samples were
251 analyzed in a wet plasma using a ThermoScientific Neptune Plus MC-ICP-MS at Rutgers
252 University. Sr isotopes were corrected for fractionation using the measured $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of
253 8.3752. NIST SRM 987, which was analyzed multiple times during sample analyses, yielded an
254 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710274 ± 0.000008 (2 SD, n=13).

255 **3.5 Headspace hydrocarbon gas analysis**

256 Sediment gas composition was determined at a resolution of 1 sample per core for J1005 (n=11)
257 and J1006 (n=11). A $3\ \text{cm}^3$ bulk sediment sample was collected from the freshly exposed top end
258 of a core section using a brass boring tool immediately after core recovery on the catwalk. The
259 sediment plug was placed in a glass vial and sealed with an aluminum cap fitted with a
260 PTFE/silicon septa for transfer to the shipboard geochemistry laboratory. The vial was heated to
261 70°C for 30 minutes to evolve hydrocarbon gases from the sediment. A $5\ \text{cm}^3$ volume of headspace
262 gas was extracted from the sealed vial using a gas-tight 5 mL PTFE Luer lock glass syringe and
263 injected into the Agilent/HP 6890 Series II Gas Chromatograph fitted with a flame ionization
264 detector for analysis. Concentrations of methane (CH_4) and higher molecular weight hydrocarbons
265 (e.g., ethane, propane) were determined and reported as parts per million by volume (ppmv) of the
266 injected sample.

267 **4. Results and Discussion**

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

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

292 **4.1 Source(s) of low Cl⁻ at J1006**

293 Pore water freshening in convergent margin settings is often attributed to methane hydrate
294 dissociation and mineral dehydration (e.g., smectite to illite transformation, also referred to as
295 illitization), although clay membrane ion filtration, low-temperature crustal alteration, anaerobic
296 oxidation of methane, mixing with meteoric water have all been shown to yield Cl⁻ concentrations
297 lower than seawater in convergent margin sediments from Nankai Trough, the Cascadia and Peru
298 margins, Barbados, and the Mediterranean Sea [Dahlmann and de Lange, 2003; Kastner *et al.*,
299 1991; Kastner *et al.*, 1990; Toki *et al.*, 2017]. Indeed, prior pore water studies in this study region,
300 paired with lithologic evidence for abundant smectite content and recovered hydrate nodules, have
301 prompted hypotheses that documented freshening signals are primarily attributable to clay
302 dehydration or methane hydrate dissociation [Bova *et al.*, 2019; Mix *et al.*, 2003; Scholz *et al.*,
303 2013]. However, a 200 mM reduction in Cl⁻ concentration (similar in magnitude to Site J1006) at
304 a site offshore Patagonia was recently attributable to the deep submarine infiltration of fossil
305 groundwaters [Clementi *et al.*, 2022a]. This new finding challenges the basis of the longstanding

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

309 The alteration processes that can yield low-Cl⁻ pore fluids isotopically fractionate oxygen and
310 hydrogen in distinct ways, which can enrich or deplete pore water δ¹⁸O and δD relative to seawater
311 (Table S1). For example, compaction and increasing temperature (60-150°C) during slab
312 subduction promotes the dehydration of hydrous minerals, such as the alteration of smectite to
313 illite clays [Perry, 1970]. Relative to seawater, this mineral-bound water is enriched in δ¹⁸O and
314 depleted in δD and is released to the surrounding sediments during dehydration reactions [Savin
315 and Epstein, 1970], which increases δ¹⁸O and decreases δD in the pore water [Kastner et al., 1991].
316 In contrast, methane hydrate dissociation increases both δ¹⁸O and δD owing to fractionation of the
317 heavier isotopes into the hydrate matrix [Hesse and Harrison, 1981; Ussler and Paull, 1995].
318 Methane hydrate dissociation typically occurs from hydrostatic pressure decreases during core
319 recovery, which can result in anomalous pore water δ¹⁸O and δD increases (and Cl⁻ decreases)
320 from otherwise conservative profiles (e.g., [Egeberg and Dickens, 1999; Matsumoto and
321 Borowski, 2000; Torres et al., 2004]). In certain instances, however, *in situ* dissociation can occur
322 and produces more gradual changes in the downcore profiles (e.g., [Vargas-Cordero et al., 2020]).

323 Methane hydrate nodules were only recovered at J1006, where there was substantial cracking and
324 expansion of core material from gas expansion (Figure S1). As such, we initially hypothesized that
325 the linear decrease in Cl⁻ with depth was attributable to *in situ* methane hydrate dissociation [Bova
326 et al., 2019]. Indeed, decreases in Cl⁻ concentrations below 60 mbsf at ODP Site 1233 were also
327 attributed to active hydrate dissociation [Mix et al., 2003]. The downcore δ¹⁸O increase (0.5‰) at
328 J1006 is consistent with mixing between seawater and dissociated fluid as evidenced by a δ¹⁸O
329 value of 3.02‰ in the recovered methane hydrate nodule; this hydrate endmember value is in
330 agreement with observations in both laboratory and natural settings [Davidson et al., 1983;
331 Kvenvolden and Kastner, 1990; Martin et al., 1996]. In contrast, δD decreases by ~2‰ from
332 seawater values (Figure 3). Notwithstanding a few anomalously enriched δ¹⁸O and δD values ~85-
333 90 mbsf, which most likely reflect hydrate dissociation upon recovery (i.e., hydrate δD value of
334 19.7‰), the robust downcore δD decrease appears to rule out a primary influence from *in situ*
335 methane hydrate dissociation on pore water freshening in the region. This requires an alternate
336 fluid source for low Cl⁻ concentrations at J1006 and ODP Site 1233.

337 We assess the relationship between pore water freshening (i.e., decreasing Cl⁻ concentrations) and
338 δ¹⁸O increases and δD decreases at J1006 by comparing observed downcore changes (Cl_{obs},
339 δ¹⁸O_{obs}, and δD_{obs}) with seawater reference values (Cl_{ref}, δ¹⁸O_{ref}, and δD_{ref}) [Tomaru et al., 2006].
340 Downcore Cl⁻ concentration is normalized to seawater, yielding a freshening factor,
341 $f([\text{Cl}_{\text{obs}}]/[\text{Cl}_{\text{ref}}])$; the changes in δ¹⁸O and δD (Δδ¹⁸O and ΔδD, respectively) are derived as δ_{obs}-δ_{ref}

342 [Hong *et al.*, 2021]. At Site J1006, this approach demonstrates that the observed $\delta^{18}\text{O}$ increase
343 (higher $\Delta\delta^{18}\text{O}$) and δD decrease (lower $\Delta\delta\text{D}$) with depth occurs as a function of pore water
344 freshening, as denoted by lower f (Figure 4), which suggests that the fresh mound-associated pore
345 fluid is primarily sourced from clay dehydration reactions at depth (Table S1). The alteration of
346 smectite to illite often involves the consumption of K from surrounding pore waters and release of
347 Li, B, DSi with the mineral bound water [Chao *et al.*, 2011; Hüpers and Kopf, 2012]. At J1006,
348 the linear K/Cl increase between 0-50 mbsf is driven by the marked decrease in Cl^- concentrations,
349 whereas the greatest consumption of K occurs below ~ 50 mbsf and results in a cessation of the
350 K/Cl increase (Figure 3; Figure S2). The increase in Li above seawater concentrations tracks the
351 decrease in Cl^- concentration, which results in an overall increase in Li/Cl and implies a deep Li
352 source. Similarly, downcore DSi and B concentrations increase substantially above seawater
353 values. These elemental profiles substantiate the robust isotopic evidence for dehydration reactions
354 sourcing the low- Cl^- fluids at Site J1006, and now adds the Chilean Margin to the large body of
355 evidence linking illitization to venting structures along convergent margins (e.g., [Chao *et al.*,
356 2011; Chen *et al.*, 2020; Dahlmann and de Lange, 2003; Martin *et al.*, 1996]).

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

368 Volcanogenic material comprised less than 10 percent of bulk sediment composition in cores
369 recovered during this expedition [Bova *et al.*, 2019]. However, even minor ash diagenesis can
370 impart large changes in pore water Sr and its isotopes [Hong *et al.*, 2020], as well as $\delta^{18}\text{O}$ and δD
371 [Egeberg *et al.*, 1990; Lawrence and Gieskes, 1981]. In contrast to clay dehydration, the formation
372 of hydrous minerals during ash diagenesis should decrease $\delta^{18}\text{O}$ and increase δD in surround pore
373 water [Kastner *et al.*, 1991] (Table S1). We suggest that an overprinting of ash alteration on the
374 primary signal from clay dehydration explains the discrepancy between endmember $\delta^{18}\text{O}$ and δD
375 estimates at J1006 and expected endmember values from the Mediterranean Sea, as well as the
376 abrupt changes in certain elemental concentration at depths greater than 100 mbsf. Low pore water
377 $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ were also reported at ODP Sites 859 and 860 offshore Patagonia (46°S) and
378 were attributed to ash diagenesis [Zheng *et al.*, 1995], which suggests that diagenetic alteration of

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

381 The lack of a similar elemental and isotopic signals at Site J1005 highlights the spatial
382 heterogeneity in regional pore fluid composition and migration. Here, $\delta^{18}\text{O}$ and δD have a
383 prominent maxima at ~25 mbsf (Figure 2), which is attributable to the downward diffusion of
384 isotopically heavier seawater during the last glacial period [Adkins *et al.*, 2002]. This feature is
385 also present at Site J1006, but the relatively higher $\delta^{18}\text{O}$ and lower δD peaks suggest active
386 migration of deep fluids with a distinct isotopic signature has likely attenuated the glacial signal.
387 That this signal is even present at J1006 might indicate that fluid discharge at this MV initiated at
388 some point since the last glaciation. Alternatively, enriched pore water $\delta^{18}\text{O}$ and δD paired with
389 low Cl^- concentrations could indicate *in situ* dissociation of methane hydrate, which would be
390 consistent with observations offshore Patagonia and near mud volcanoes proximal to the CMSA
391 [Clementi *et al.*, 2022a; Ussler and Paull, 1995; Vargas-Cordero *et al.*, 2020]. It is worth noting
392 that $\delta^{18}\text{O}$ and δD abruptly increase and decrease, respectively, at the very base of J1005 (Figure
393 2). These values agree with those at J1006 and suggest that deeply sourced fluids from clay
394 dehydration may also be influencing sediments farther from the mound. However, Cl^- (and other
395 elemental) concentrations near seawater values at this same depth indicate minimal influence on
396 pore water freshening (Figure 2; Figure S2), or that the locus of freshening at J1005 is deeper than
397 the recovered sediment column. Taken together, the new pore water elemental, $\delta^{18}\text{O}$, δD , and
398 $^{87}\text{Sr}/^{86}\text{Sr}$ profiles highlight a complex diagenetic environment and for the first time characterize
399 deep fluids being expelled at a seafloor venting structure on the Chilean Margin.

400 **4.2 Constraints on fluid migration**

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

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

416 from using Mg- or Ca-based geothermometers owing to the precipitation of authigenic carbonate
417 at Sites J1005 and J1006 [Bova *et al.*, 2019], which could bias the temperature estimate. The lack
418 of continuous Li enrichment with depth suggests that alteration temperatures are <150°C, in
419 agreement with our Na/K estimates [Hensen *et al.*, 2007]. Applying the Na/K-derived alteration
420 temperatures to geothermal gradients at the three sites demonstrates that $Z_{S \rightarrow I}$ is achieved 2.5±0.6
421 kmbsf, although different Na/K geothermometers provide a range of $Z_{S \rightarrow I}$ estimates between
422 2.4±0.6 and 2.7±0.7 kmbsf [Fournier, 1979; Tonani, 1980] (Table 2). Nonetheless, the $Z_{S \rightarrow I}$
423 estimates are more or less consistent with each other and thermal modeling estimates near the
424 CMSA ($Z_{S \rightarrow I} = 2\text{-}5$ kmbsf) [Scholz *et al.*, 2013]. This places the locus of smectite dehydration
425 towards the base of the trench fill package near the décollement [Völker *et al.*, 2013], as observed
426 in the Barbados and Mediterranean accretionary complexes [Martin *et al.*, 1996; Scholz *et al.*,
427 2009].

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

434 **4.3 Implications for Chilean Margin methane hydrate formation**

435 Methane hydrate is ubiquitous on the south Chilean Margin, occupying ~7.5 percent of the pore
436 space on average but can range from 5-15 percent [Alessandrini *et al.*, 2019; Villar-Muñoz *et al.*,
437 2018; Villar-Muñoz *et al.*, 2019], with higher hydrate saturation (S_h) often reported near faults in
438 the forearc sediments [Vargas-Cordero *et al.*, 2018]. Methane hydrate typically forms in marine
439 sediments with relatively high total organic carbon (TOC) content (>2%) to supply sufficient
440 material for biogenic methane production [Hesse and Harrison, 1981; Kvenvolden, 1993]. In
441 contrast, TOC in sediments along the Chilean Margin is relatively low (0.2-2%, average of 0.87%
442 at the three sites) owing to high sedimentation rates and burial, with the highest TOC content
443 limited to the sediment-seawater interface [Bova *et al.*, 2019; Mix *et al.*, 2003; Scholz *et al.*, 2013]
444 (Figure S4). TOC can be used to provide a first-order approximation of S_h linked to *in situ* biogenic
445 methane production following:

$$446 \quad S_h = 3.45 \cdot \text{TOC} - 1.77$$

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

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

454 Deep fluids are often enriched in methane and the vertical migration of these fluids has been
455 suggested to facilitate the formation of methane hydrate near cold seep and mud volcano structures
456 globally [Milkov, 2000; You *et al.*, 2019]. On the Chilean Margin, AOM via sulfate reduction is
457 the dominant diagenetic pathway for deposited organic matter [Treude *et al.*, 2005], which leads
458 to rapid decreases in pore water sulfate concentration and increases in methane concentration,
459 resulting in shallow SMTZ depths as observed at our sites (Figure 6; Table 3). SMTZ depths follow
460 a similar pattern as downcore freshening, with the shallowest SMTZ at J1006, followed by ODP
461 Site 1233, and J1005 with the deepest (Table 3). Below the SMTZ, methane concentrations also
462 yield a similar trend, with the highest CH₄ concentrations at J1006 occurring as a sharp peak just
463 below the SMTZ, whereas broader and deeper maxima are observed at the more distal sites (Figure
464 6).

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

$$469 \quad J = -\phi \cdot D_s \cdot \frac{dC}{dz}$$

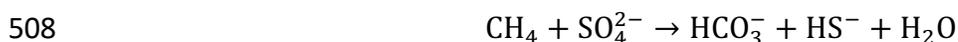
470 where J represents the downward sulfate flux (mmol m⁻² yr⁻¹), ϕ is the average porosity between
471 the sediment-seawater interface and the SMTZ (dimensionless), D_s is the sediment diffusion
472 coefficient (cm² s⁻¹), and $\frac{dC}{dz}$ is the pore water sulfate concentration gradient between the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

$$475 \quad D_s = \frac{D_0}{1 - \ln(\phi)^2}$$

476 where D_0 , the diffusion coefficient for sulfate in seawater, is 5.8x10⁻⁶ cm² s⁻¹ [Li and Gregory,
477 1974]. We assume a linear decrease in sulfate concentration between the sediment-seawater
478 interface and the SMTZ (Figure 6). Although sampling resolution in the upper few meters of
479 J1005, J1006, and ODP Site 1233 is relatively low, this assumption is substantiated by pore water
480 sulfate profiles from gravity cores taken near seep sites in the CMSA [Coffin *et al.*, 2007]. As such,
481 our calculated diffusion rates are taken as conservative flux estimates since complete sulfate
482 reduction near venting sites can occur even shallower than J1006 indicates, resulting in steeper
483 sulfate gradients in the upper few meters of the sediment column and higher flux estimates.

484 Downward sulfate diffusion rates range between -67.40 and -306.96 mmol m⁻² yr⁻¹, with the
485 highest flux at J1006 and lowest at J1005 (Table 3). As expected, sulfate fluxes at ODP Site 1233
486 (-164.63 mmol m⁻² yr⁻¹) fall between the other two sites. The sulfate flux at J1006 is consistent
487 with estimates from a seep site in the CMSA (-361.91 mmol m⁻² yr⁻¹), which had a much shallower
488 SMTZ (33 cm) [Coffin *et al.*, 2007]. Assuming a 1:1 stoichiometric consumption of sulfate and
489 methane [Borowski *et al.*, 1996], and neglecting influences from advection that would likely
490 enhance the migration of deep fluids, we can infer that methane fluxes at J1006 are at least ~2 and
491 5 times greater than ODP Site 1233 and J1005, respectively. This provides a mechanism to
492 supplement the low methane concentrations/hydrate saturation solely from organic matter
493 degradation to concentrations that are likely sufficient to support the higher hydrate saturations
494 estimated in this region [Alessandrini *et al.*, 2019; Vargas-Cordero *et al.*, 2018; Villar-Muñoz *et al.*
495 *et al.*, 2018; Villar-Muñoz *et al.*, 2019]. It is important to note that the lack of recovered methane
496 hydrate at J1005 and J1006 does not imply that they are not present. It is plausible, given the
497 widespread bottom simulating reflector along the Chilean Margin [Rodrigo *et al.*, 2009], that
498 methane hydrate could have simply been missed during coring operations at these sites or that they
499 could be limited to deeper sections of the sediment column than were cored. Nonetheless, pore
500 water elemental, isotopic, and hydrocarbon data from J1006 provide robust evidence that the
501 vertical migration of fresh, gas saturated fluids from deep within the forearc complex may be a
502 primary factor in the formation of shallower methane hydrate on the Chilean Margin (Figure 7).

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



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

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

521 5. Conclusions

522 Pore waters from sediment cores at sites proximal to a mound venting structure on the south
523 Chilean Margin were collected and analyzed for their elemental and isotopic composition. The
524 downcore patterns of $\delta^{18}\text{O}$ and δD reveal the influence from deeply-rooted fluids linked to smectite
525 dehydration as a source of freshening in marine sediments. Strontium isotope systematics highlight
526 secondary influences from ash diagenesis on pore water chemistry. The extent of pore water
527 freshening and intensity of methane fluxes are a function of a site's distance to a regional seafloor
528 mound, with the largest decreases in Cl^- concentration and highest methane fluxes occurring
529 closest to this venting structure where methane hydrate was documented. This not only suggests
530 that subsurface fluid and gas migration within the accretionary prism may be directly linked to
531 venting structures, but also that delivery of fresh, gas-saturated fluids from deeper in the sediment
532 column may be a critical component of higher than estimate methane hydrate saturations on the
533 Chilean Margin. Together, the data paint a clearer picture of the mechanisms of fluid and gas
534 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
584 and additional data requests should be addressed to V.J.C.

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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].

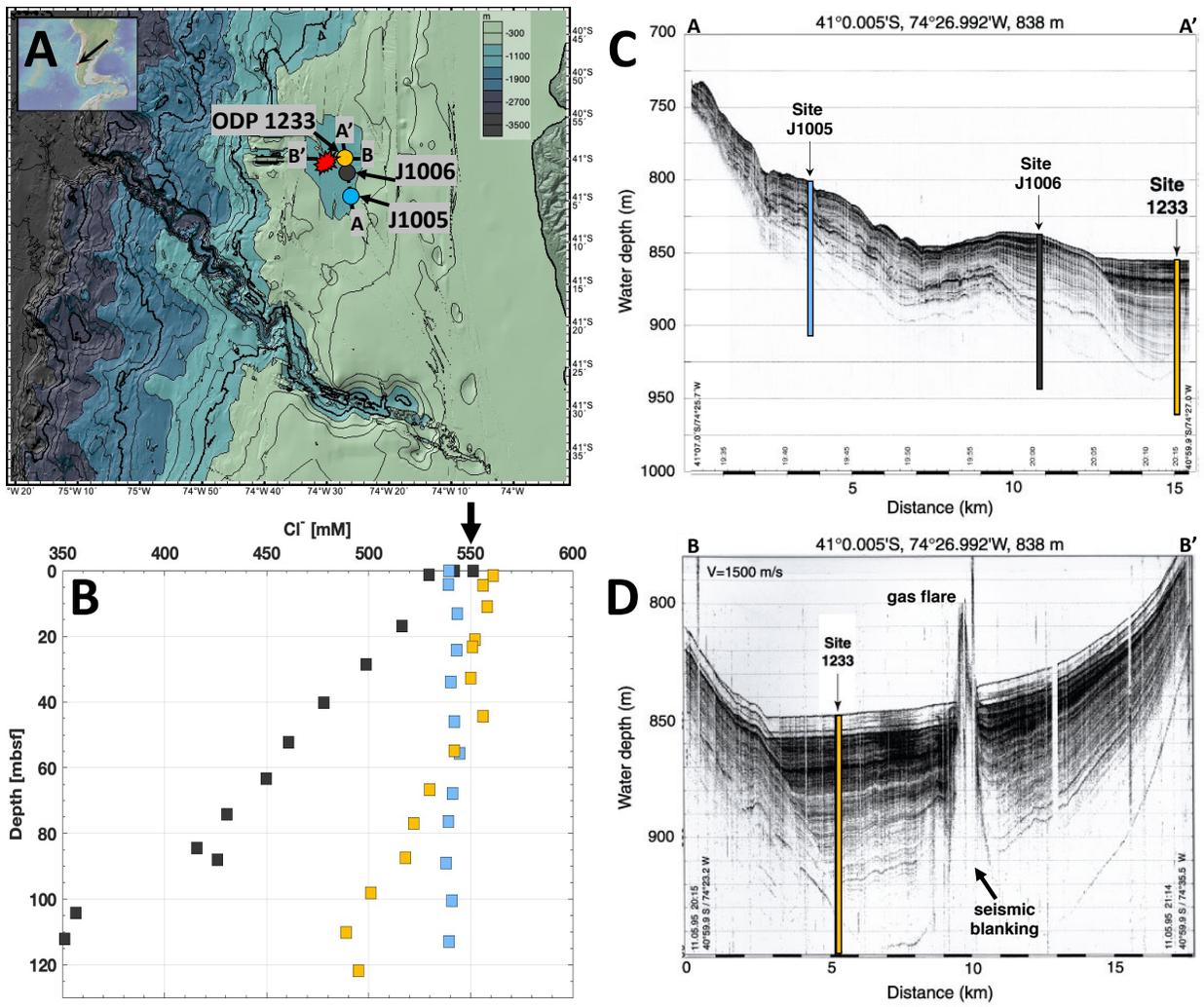


Figure 1

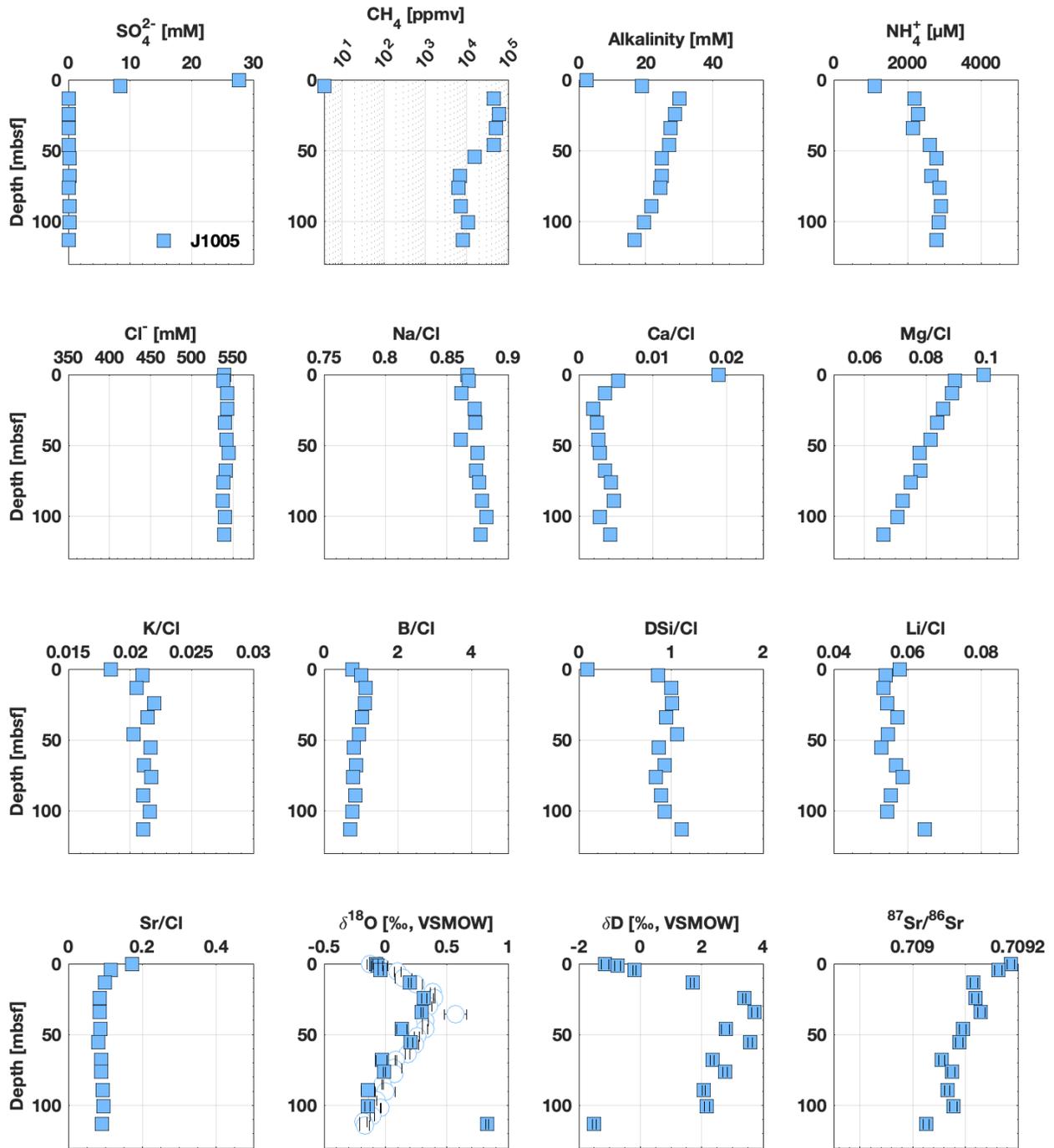


Figure 2

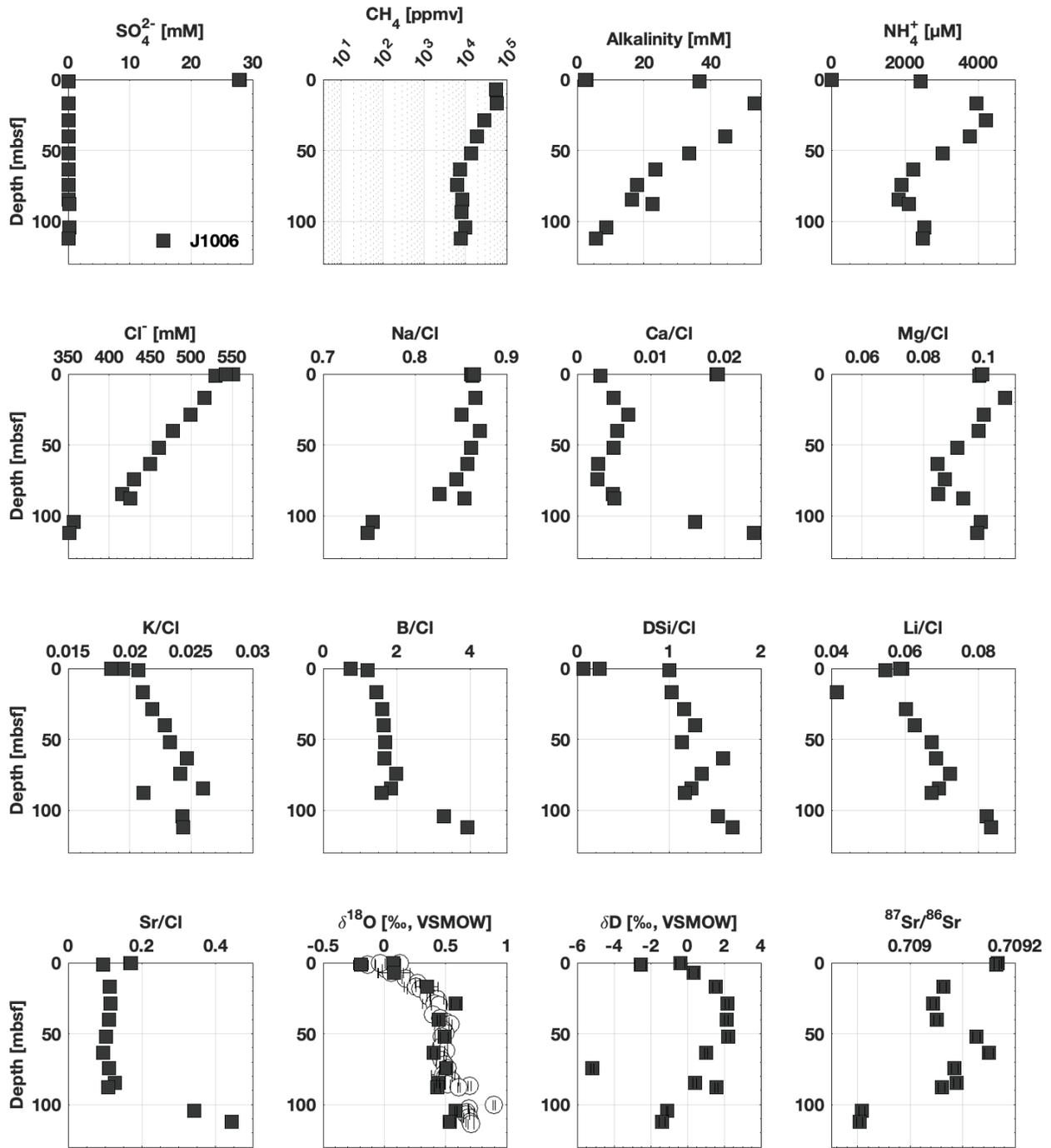


Figure 3

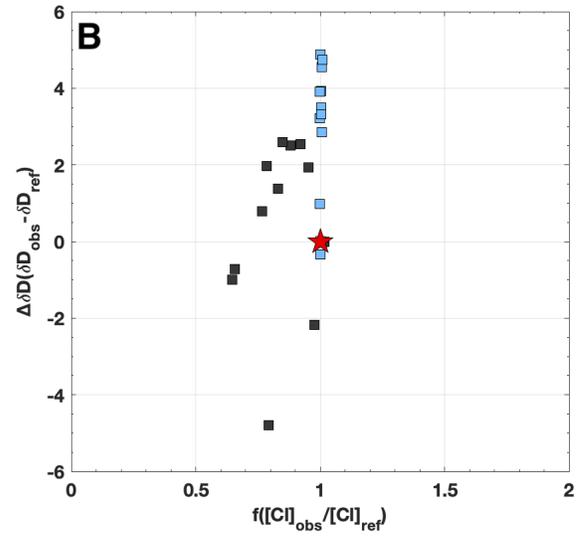
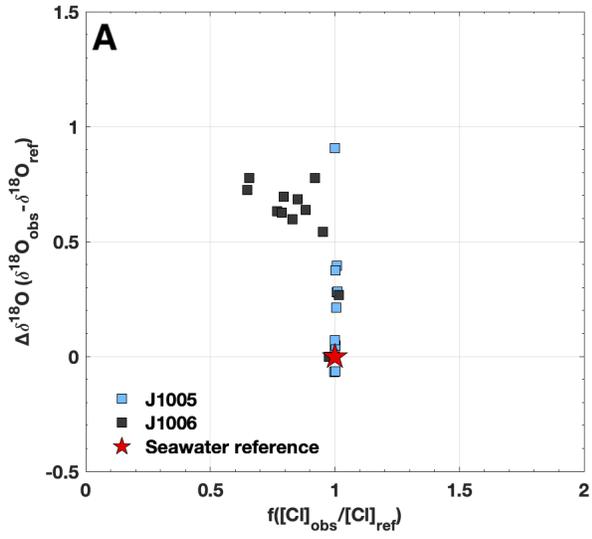


Figure 4

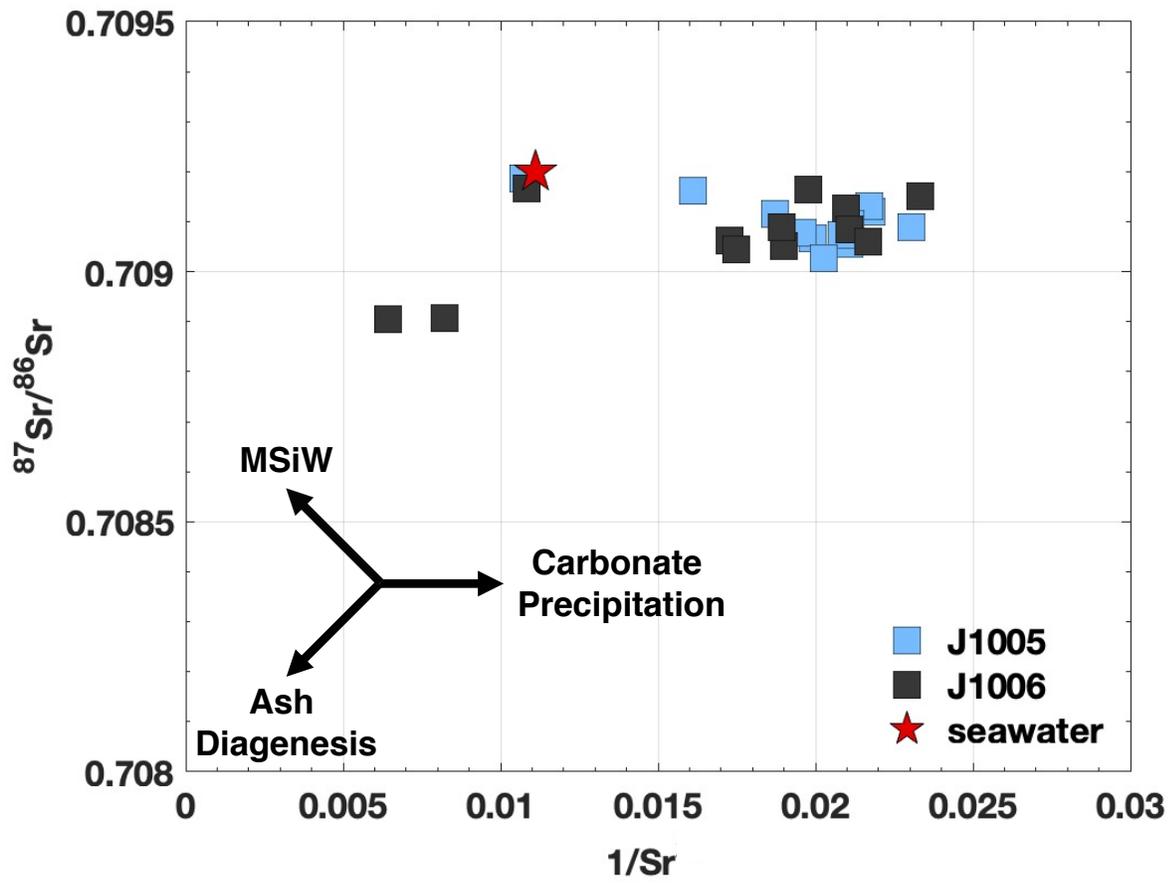


Figure 5

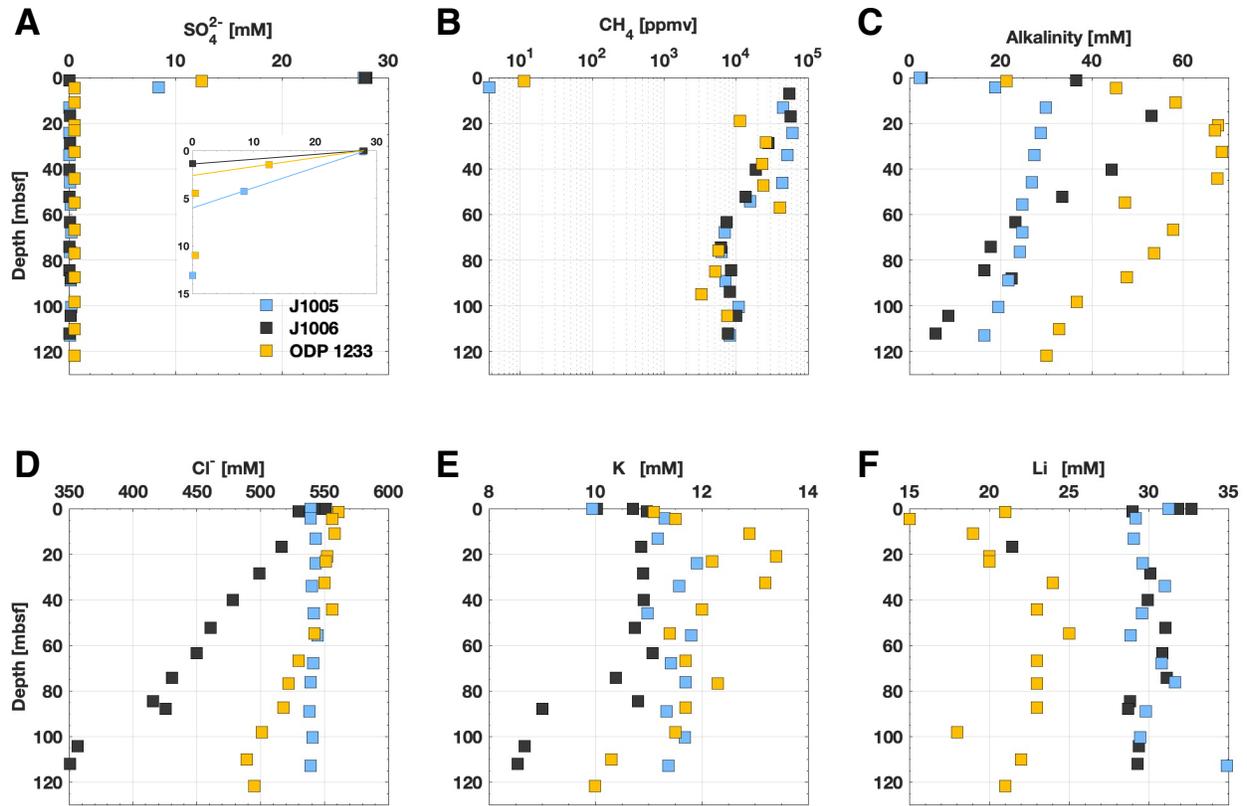


Figure 6

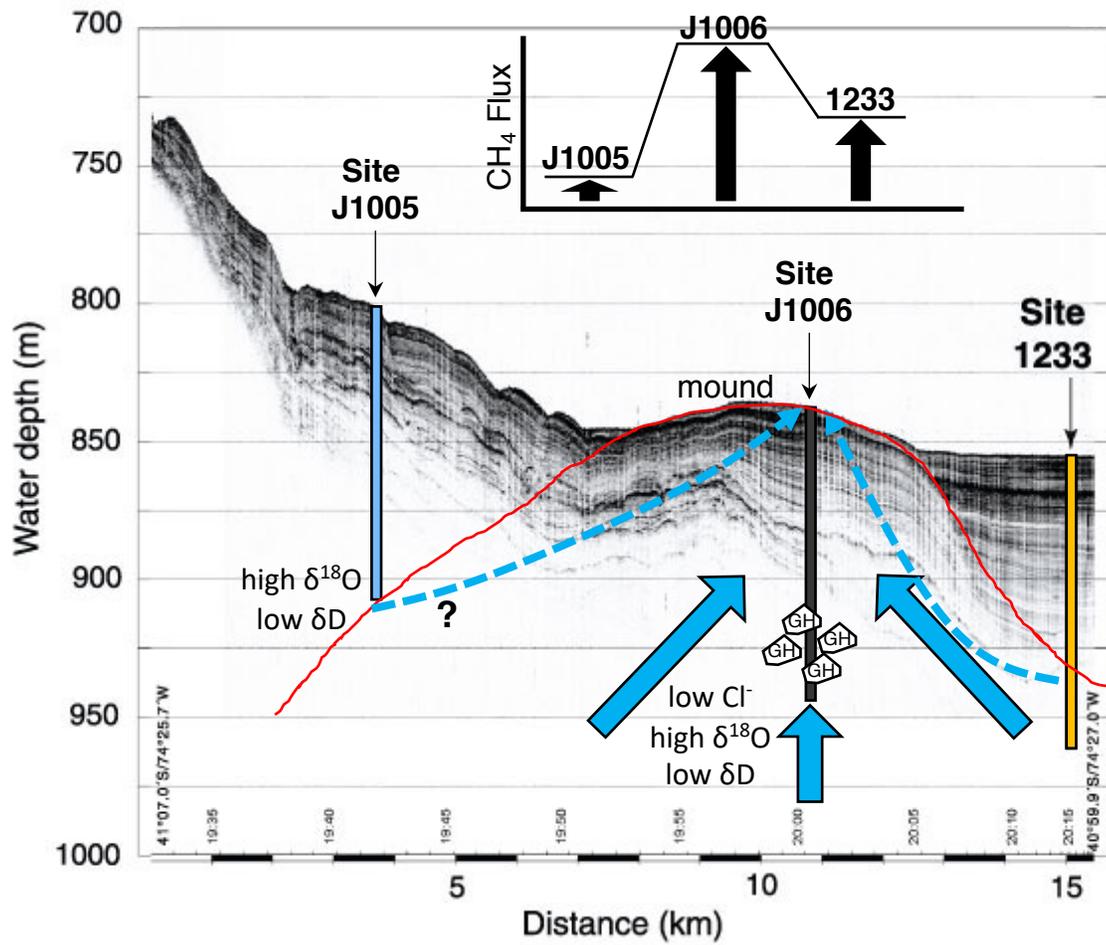


Figure 7

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] <i>Note: All concentrations in mg/L. Reported errors represent 1 SD.</i>							

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.

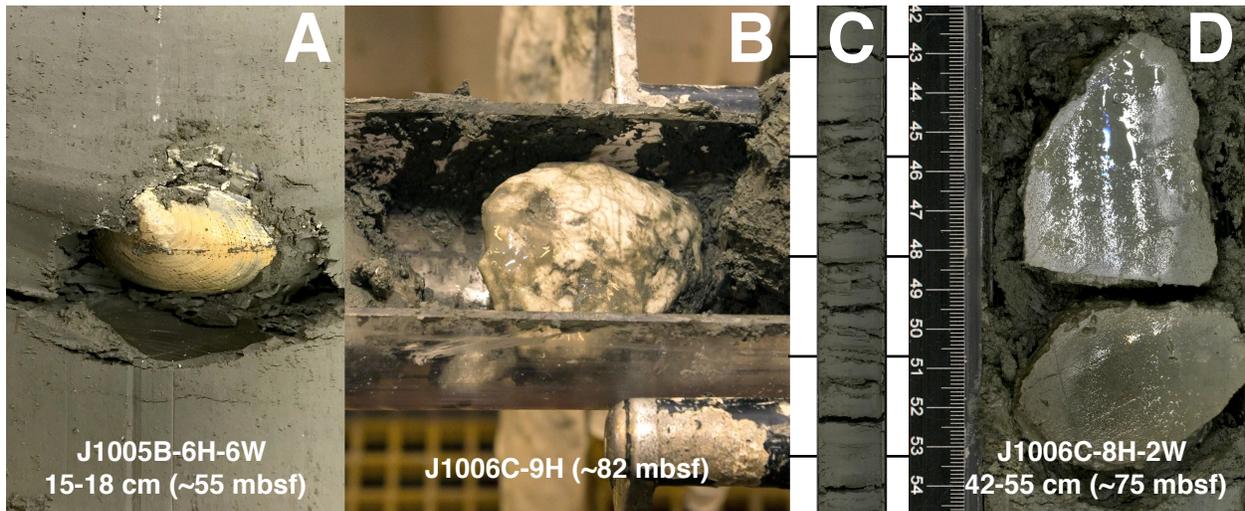


Figure S1: Evidence for (paleo) seepage, methane hydrate presence, and authigenesis. A) *Lucinidae* bivalve shells from ~55 mbsf at Site J1005 (also recovered from ~85 mbsf at Site J1006). B) methane hydrate nodule from ~82 mbsf at Site J1006. C) Example of gas cracks, which resulted in loss of sediment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

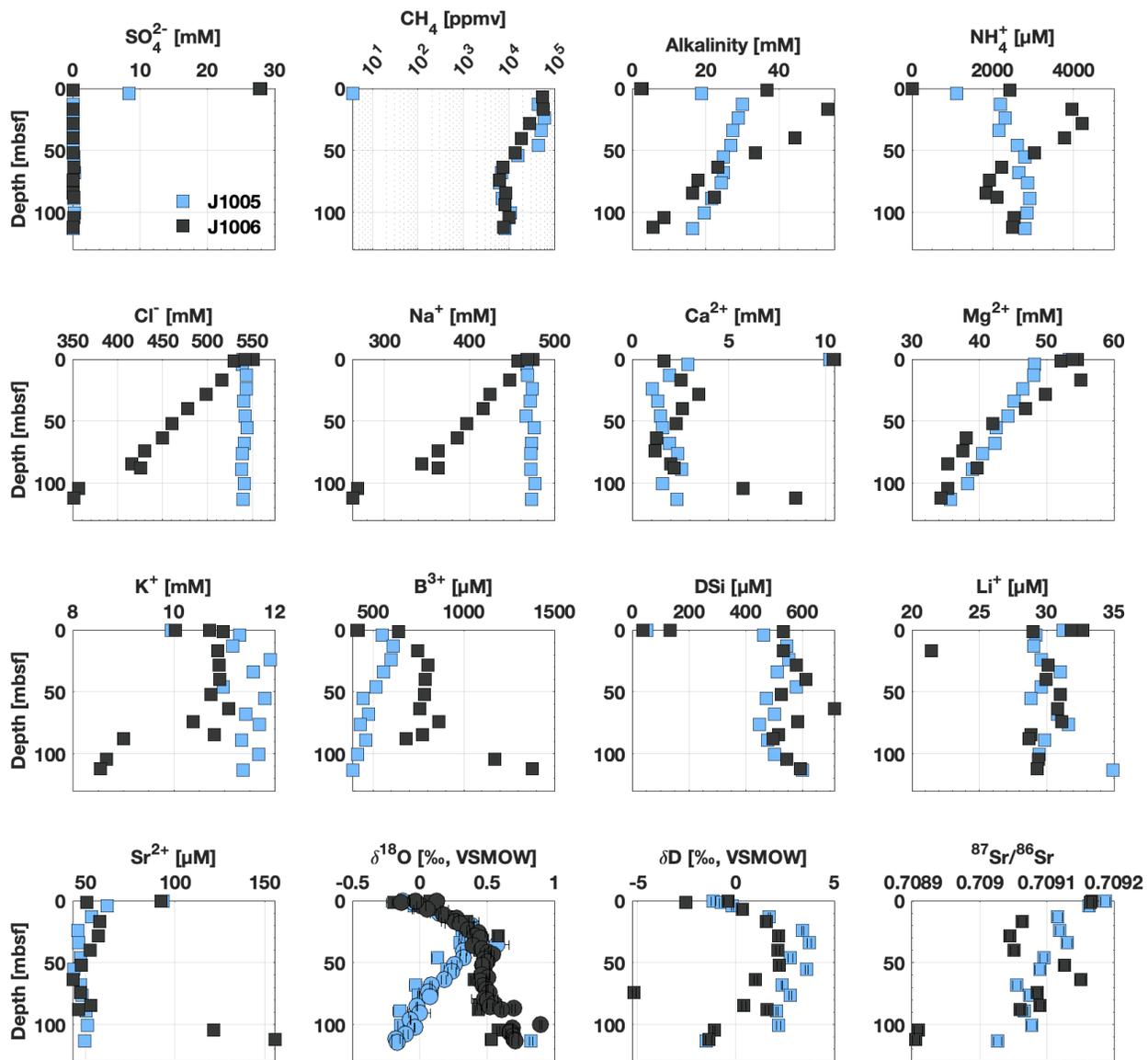


Figure S2: Pore water geochemical profiles for Site J1005 (blue) and J1006 (dark grey). Downcore profiles for SO_4^{2-} , headspace CH_4 concentrations, alkalinity, NH_4^+ , Cl^- , Na^+ , Ca^{2+} , Mg^{2+} , K^+ , B^{3+} , DSi , Li^+ , Sr^{2+} , $\delta^{18}\text{O}$, δD , and $^{87}\text{Sr}/^{86}\text{Sr}$. 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. Non-normalized profiles provide context for changes in ion/ Cl^- profiles in Figures 2 and 3 in the main paper.

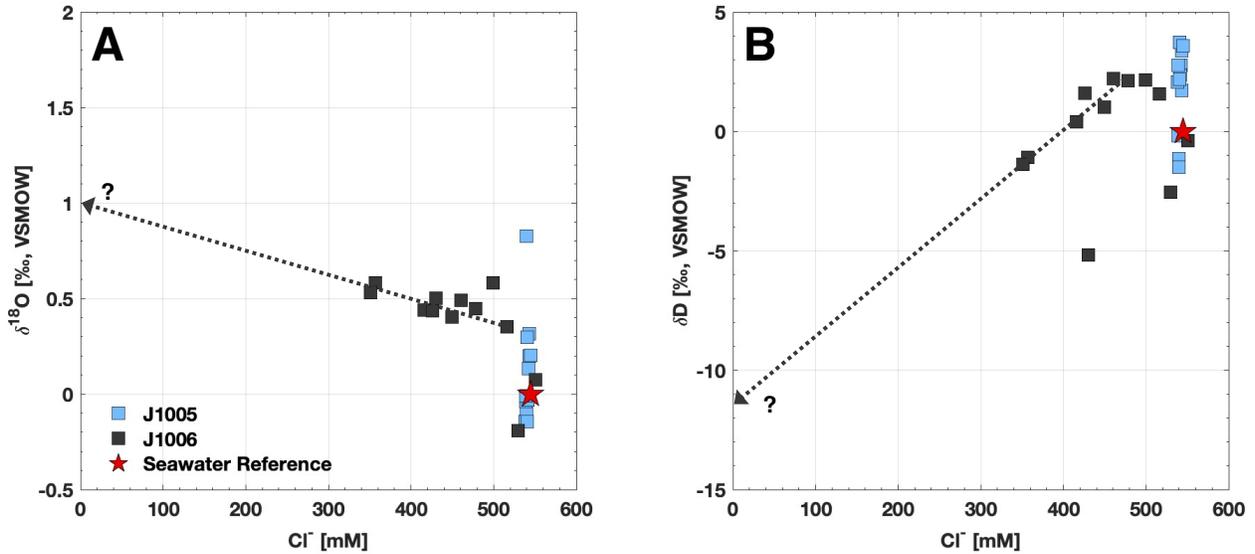


Figure S3: A comparison between pore water $\delta^{18}\text{O}$ and δD and Cl^- concentration. A) $\delta^{18}\text{O}$ versus Cl^- . B) δD versus Cl^- . Sites J1005 (blue), J1006 (dark grey), and seawater reference (red) are shown. Dotted lines represent approximated linear extrapolation to freshened 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.

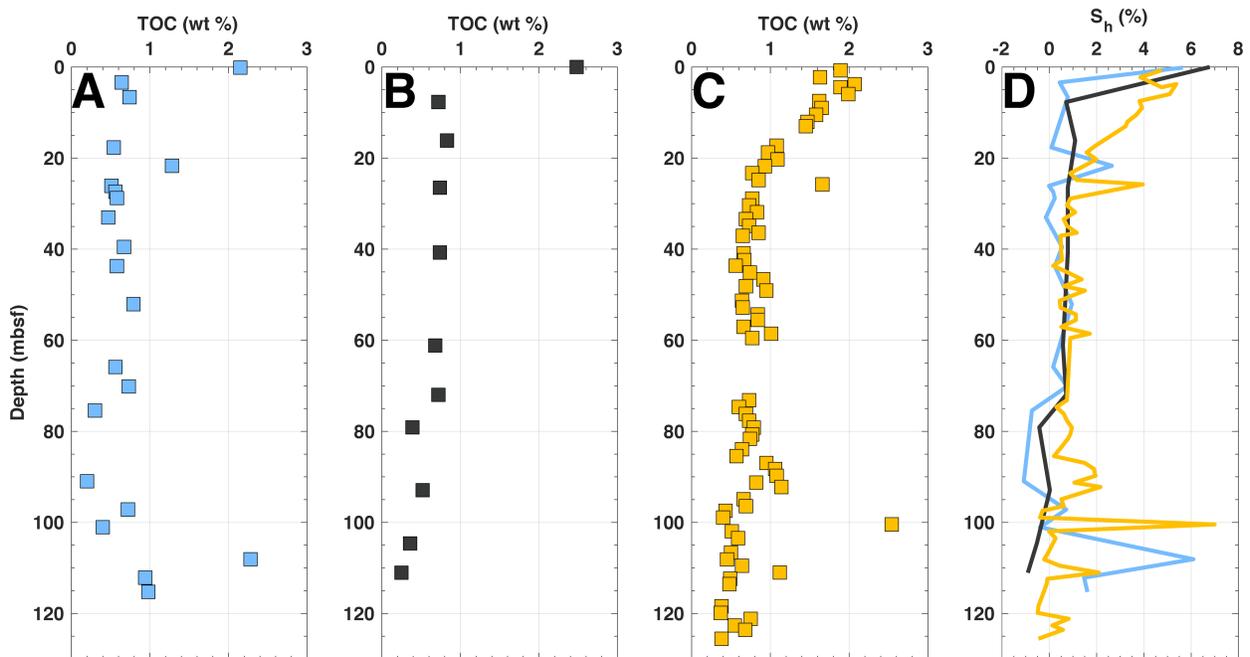


Figure S4: TOC-based methane hydrate saturation. A-C) Downcore bulk sediment TOC for J1005 (blue), J1006 (dark grey), and ODP Site 1233 (yellow). D) Methane hydrate saturation index (S_h) derived using the following equation: $S_h = 3.45 \cdot (\text{TOC}) - 1.77$ [Waseda, 1998]. Methane hydrate saturation 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

Process	Cl ⁻	δ ¹⁸ O	δD
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.
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- 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.