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# Geochemistry, Geophysics, Geosystems

## REPLY

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This article is a reply to a comment by Sultan (2020), <https://doi.org/10.1029/2019gc008846>.

### Key Points:

- Site U1517 gas hydrate inferred pore-water chloride concentrations are supported by geophysical evidence
- Unsteady-state temperature profiles in subseafloor sediments can affect estimates of gas hydrate stability
- Sedimentation can bury methane hydrates below the base of gas hydrate stability

### Correspondence to:

E. J. Screaton,  
[screaton@ufl.edu](mailto:screaton@ufl.edu)







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## Reply to Comments by N. Sultan on “Sedimentation Controls on Methane-Hydrate Dynamics Across Glacial/Interglacial Stages: An Example From International Ocean Discovery Program Site U1517, Hikurangi Margin”

E. J. Screaton<sup>1</sup> , M. E. Torres<sup>2</sup> , B. Dugan<sup>3</sup> , K. U. Heeschen<sup>4</sup>, J. J. Mountjoy<sup>5</sup>, C. Ayres<sup>2</sup>, P. S. Rose<sup>6</sup> , I. A. Pecher<sup>7</sup> , P. M. Barnes<sup>6</sup>, and L. J. LeVay<sup>8</sup> 

<sup>1</sup>Department of Geological Sciences, University of Florida, Gainesville, FL, USA, <sup>2</sup>College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis, OR, USA, <sup>3</sup>Department of Geophysics, Colorado School of Mines, Golden, CO, USA, <sup>4</sup>GFZ German Research Centre for Geosciences, Potsdam, Germany, <sup>5</sup>National Institute of Water and Atmospheric Research, Wellington, New Zealand, <sup>6</sup>Department of Physical and Environmental Sciences, Texas A&M University Corpus Christi, Corpus Christi, TX, USA, <sup>7</sup>School of Environmental and Marine Sciences, University of Auckland, Auckland, New Zealand, <sup>8</sup>International Ocean Discovery Program, Texas A&M University, College Station, TX, USA

**Abstract** Screaton et al. (2019, <https://doi.org/10.1029/2019GC008603>) examined the role of sedimentation, sea level, and bottom water temperature (BWT) changes due to glaciation as drivers for the downward migration of the base of gas hydrate stability and gas hydrate formation. International Ocean Discovery Program (IODP) Site U1517 in the Hikurangi margin was used as a case study because data at this site document a marked increase in chloride over a broad depth range, which was attributed to recent gas hydrate formation. In a comment on Screaton et al. (2019, <https://doi.org/10.1029/2019GC008603>), Sultan (2020, <https://doi.org/10.1029/2019gc008846>) used a linear thermal profile to argue that inferences and characterization of methane hydrate at IODP Site U1517 were incorrect because some occur below his estimated base of gas hydrate stability (BGHS). Based on this apparent discrepancy, Sultan (2020, <https://doi.org/10.1029/2019gc008846>) further stated that low-chloride spikes may be unreliable indicators of methane hydrate occurrence. In this reply, we emphasize that unsteady-state, and thus nonlinear, thermal profiles are likely in areas experiencing active sedimentation and bottom-water temperature (BWT) changes. The resulting deviation from steady-state temperature profile shifts the BGHS downward. In addition, sedimentation has the potential to bury methane hydrate more rapidly than it dissociates, helping to explain how methane hydrate could be observed below the BGHS. We also review the supporting evidence for gas-hydrate occurrence at Site U1517 and the criteria used for Site U1517 site selection.

## 1. Temperature Profiles and Methane Hydrate Stability

Relative to the Site U1517 report (Barnes et al., 2019), Screaton et al. (2019) used a higher present-day BWT (6.5°C) and a lower heat flow. In the simulations described by Screaton et al. (2019), basal heat flow was 0.043 to 0.050 W/m<sup>2</sup>. For a uniform thermal conductivity of 1.6 W/(m·°C), heat flow of 0.050 W/m<sup>2</sup>, and steady-state conditions, the resulting temperature depth equation would be

$$T=6.5^{\circ}\text{C} + 0.03125^{\circ}\text{C}/\text{m} \times \text{subseafloor depth (m)}$$

For comparison the best-fit Site U1517 equation from Barnes et al. (2019) was

$$T=5.32^{\circ}\text{C} + 0.0398^{\circ}\text{C}/\text{m} \times \text{subseafloor depth (m)}$$

As explained in Screaton et al. (2019), this change was made because the extrapolated BWT of 5.32°C was considerably lower than reported in the region. For illustration, the two lines are plotted with the methane-hydrate stability relationship in seawater from Dickens and Quinby-Hunt (1994). The two linear profiles yield very similar temperatures in the depth range near the BGHS. They intersect the stability

curve at depths of 127 to 130 mbsf (Figure 1). As a result, the choice of current-day BWT and heat flow was not a major factor in the simulations.

As was discussed in Screaton et al. (2019), the temperature profiles resulting from the simulations were not identical to steady-state profiles. The simulated temperatures for constant sedimentation at a rate of 0.8 mm/yr and applying a 2°C cooler BWT at the LGM were lower than the linear profiles. For example, at 138 mbsf, the simulation results yielded a temperature 0.36°C cooler. The lower temperatures shifted the BGHS downward to 145 mbsf (Figure 1). With a BGHS at 145 mbsf, methane hydrate could form above this depth, increasing pore-water chloride concentrations. Formation of methane hydrate above 145 mbsf is consistent with the Site U1517 observations showing the highest chloride concentrations were in the interval between 130 and 140 mbsf.

Sultan (2020) implies that the chloride dilution method must be incorrect because it indicates that Site U1517 methane hydrate occurs below the BGHS. However, the simulations described in Screaton et al. (2019) provided a key insight that could help to reconcile the BGHS at 145 mbsf and methane hydrate at greater depths; in areas of active sedimentation, methane hydrate could be buried below the BGHS more rapidly than it dissociates. In the simulation with constant 0.8 mm/yr sedimentation, gas hydrate saturations above 1% were predicted to depths of 164 mbsf, or 19 m deeper than the BGHS.

We acknowledge that overpressure could affect the position of the BGHS, as suggested by Sultan (2020), and that gas hydrate stability could be influenced by local salinity variations or by the incorporation of other components such as higher hydrocarbons. Dickens and Quinby-Hunt (1994) noted that the incorporation of other gases could increase hydrate stability. Analyses of onland seeps on the East Coast of New Zealand suggest the possible occurrence of other gases (Giggenbach et al., 1995). However, the composition of fluids from land seeps can greatly differ from those offshore (e.g. Torres et al., 2009), and the shipboard results did not indicate significant concentrations of higher hydrocarbons. Similarly, shipboard data did not provide clear evidence for elevated pore pressures. Thus, adding these complexities to the simulations was not warranted. The simplified model used in Screaton et al. (2019) also did not include capillary effects, which could shift the phase boundary to higher temperatures (You et al., 2019).

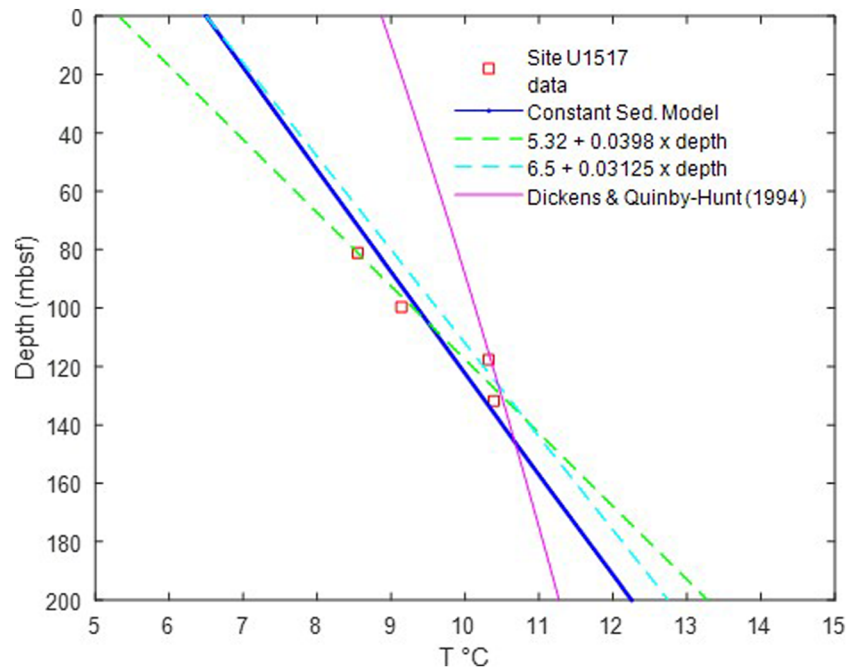
Sultan (2020) also suggested that the simulations used a thermal conductivity that was too high. As explained in Screaton et al. (2019), the thermal conductivity was based on the measured porosity of 0.46. The choice of thermal conductivity would not affect the linear profiles shown in Figure 1; when the heat flow and thermal conductivity values are changed proportionally, the same linear thermal profile will result for steady-state conditions. On the other hand, transient deviations from the steady-state profile due to sedimentation would have been greater if thermal conductivity were lower.

To confirm that using a different BWT and heat flow would not influence our conclusions, Screaton et al. (2019) compared results to a simulation with the 5.32°C BWT and a heat flow consistent with the 0.0398°C/km temperature-depth relationship. The modeling results were not significantly affected. This was noted in the text of Screaton et al. (2019), and resulting figures were included in the supplementary material.

We note that no BWT measurement and only four successful seafloor temperature measurements were taken at Site U1517. Two deepest measurements were taken with the half-length APC core barrel. The dissipation curves of these deepest measurements show some noise, and the dissipation profiles were not as complete as the shallow two measurements (Barnes et al., 2019). Given the uncertainty associated with these curves, we suggest that they provide some guidance on the in situ temperature but not exact values. Our transient models align with these data given their uncertainty.

## 2. Evidence for Methane Hydrate Occurrence

Although low chloride concentrations are an indirect indicator of methane hydrate, their use at Site U1517 was corroborated by the geophysical evidence (Figure 2). Sultan (2020) suggested that gas provides an alternate explanation for the high resistivity intervals. These intervals were described at 113.0–113.3, 117.5–121.0, and 128.0–145.5 mbsf (Barnes et al., 2019) and were associated with increased seismic velocity. The high seismic velocity precludes gas as the cause of high resistivity and is consistent with gas hydrate occurrence.



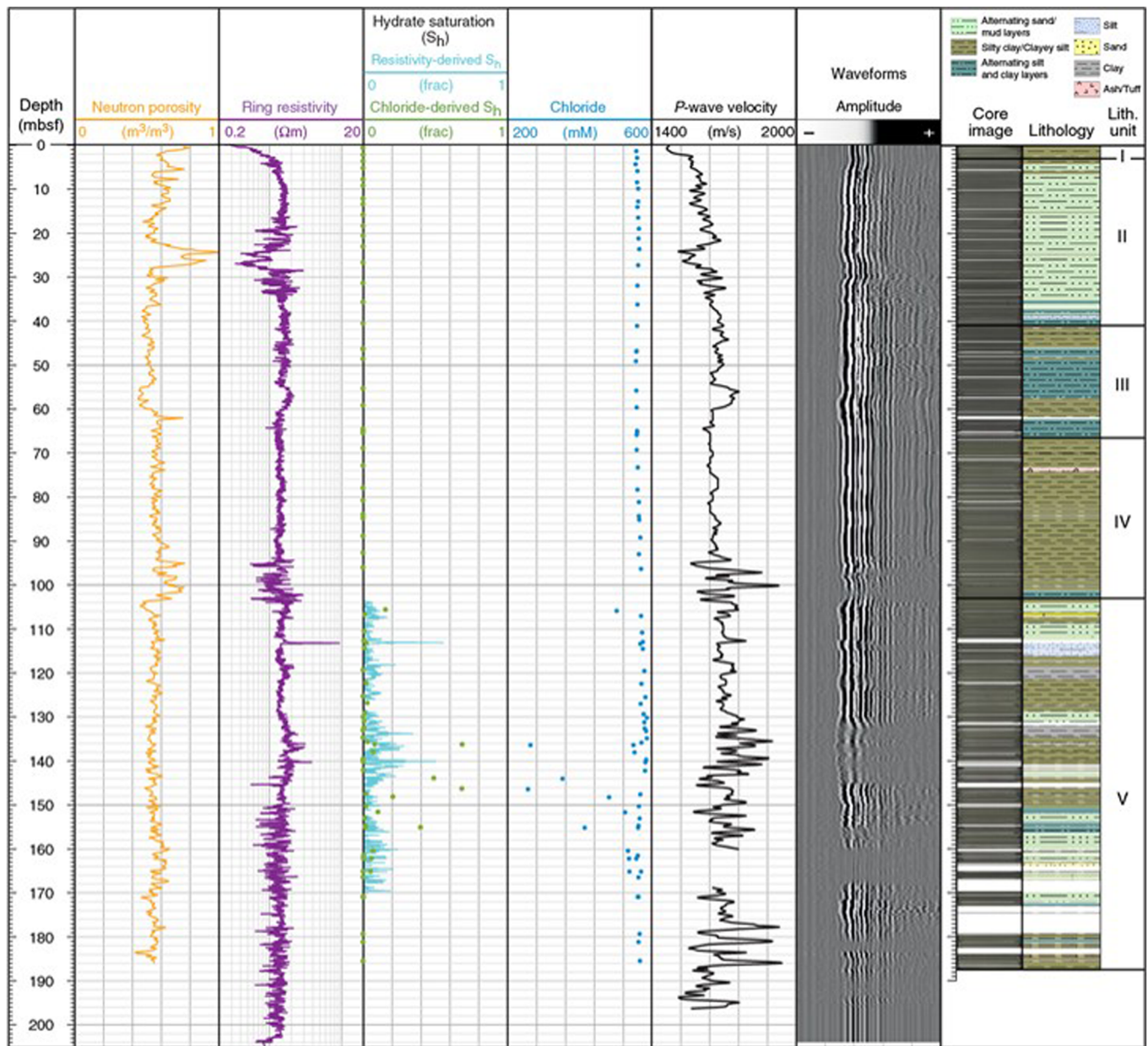
**Figure 1.** Steady-state (linear) and simulated temperature profiles and methane-hydrate stability. The simulation results shown in solid blue are for constant sedimentation of 0.8 mm/yr, and BWT that was 2°C cooler during the last glacial maximum. See Sreaton et al. (2019) for simulation details.

Gas hydrate occurrence was further supported by the cold temperatures from the infrared imagery of the recovered cores. Sultan (2020) suggested that gas expansion might explain the cold IR temperatures; however, the areas with gas expansion cracks did not correlate with colder temperatures (Figure 2). The occurrence of hydrate to depths of ~160 mbsf was also consistent with seismic observations of a bottom simulated reflector (BSR) that cuts across bedding. The BSR generally indicates a transition from hydrate to free gas and is estimated to lie at a depth of 160 mbsf based on a seismic velocity of 1,700 m/s (Barnes et al., 2019).

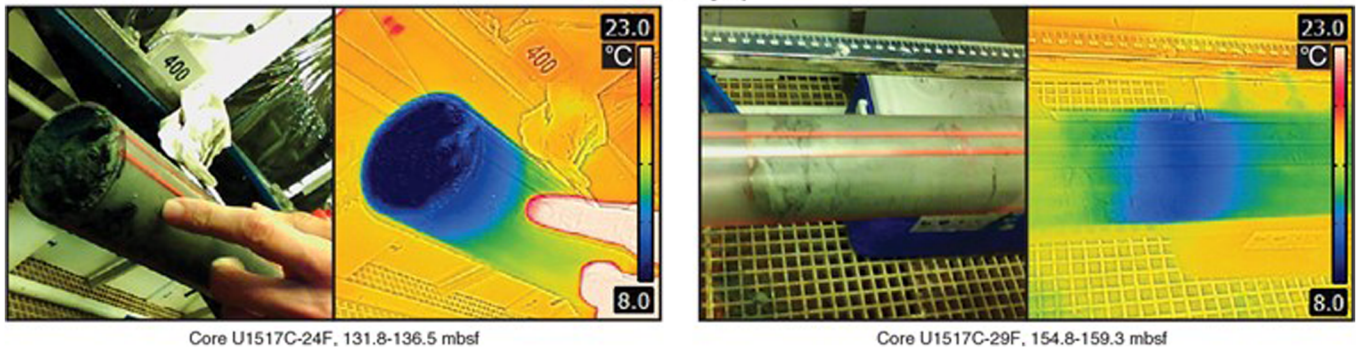
Thus, hydrate occurrence as the cause of the low-chloride spikes is supported by the borehole logs, the IR temperature scans, and seismic observation. In contrast, there is no clear alternate explanation for the low-chloride concentration spikes, as acknowledged in the comment. Sultan (2020) raised the possibility of squeezing artifacts but, at the same time, recognized that this seemed unlikely to produce the low-chloride spikes. We agree with that conclusion. The same protocol for pore-water squeezing was used consistently throughout Site U1517. Spikes of low chloride would therefore need to have been caused by significantly higher content of clay minerals with interlayer water. In contrast, the observed negative anomalies occurred primarily in the coarse-grained (less clay-rich) intervals of the core (Barnes et al., 2019). Squeezing the clay fraction immediately in contact with the coarse-grained sediment yielded less or no indication of freshening; thus, the observation was not associated with clay squeezing artifacts (Barnes et al., 2019). We further emphasize that the pore-water squeezing procedure has been used consistently in ocean drilling and that studies comparing pore-water solute concentrations from squeezing and an alternative sampling method suggest minor differences (Dickens et al., 2007).

### 2.1. Site Selection

Finally, Sultan (2020) asserted that Site U1517 was incorrectly selected based on the gas hydrate stability analysis of Mountjoy et al. (2014) assuming fresh rather than saltwater. Although this point is not closely tied to the usefulness of the Site U1517 drilling observations or the insights provided by the modeling of Sreaton et al. (2019), we nonetheless address this concern. Site U1517 was chosen to understand the potential interplay of hydrates, free gas, and the landslide complex. The proximity of the observed BSR and landslide was based on seismic observations. These criteria for site selection were independent of any details of any phase boundary calculations.



Infrared imagery



**Figure 2.** Top: Neutron porosity and resistivity used to derive LWD-based estimate of hydrate saturation and chlorinity used to estimate hydrate saturation from core samples, site U1517. *P* wave velocity and waveforms are also shown. Bottom: IR imaging used as diagnostic indicators of potential gas hydrate occurrences during core retrieval. Figure from Barnes et al. (2019); CC BY 4.0 license.

As stated in the supplementary information of Mountjoy et al. (2014), the hydrate stability analysis followed the approach by Pecher et al. (2005) who investigated possible seafloor erosion associated with gas hydrate formation and dissociation at similar water depths on Rock Garden, ~140 km to the south of the Tuaheni Landslide Complex. The models assume methane hydrate with an admixture of small fractions of other Structure-I hydrate forming gases based on chemistry from onshore seeps along the East Coast of New Zealand (2.6% CO<sub>2</sub>, 1.1% ethane; Giggenbach et al., 1995) and 3.5 weight-percent of NaCl as inhibitor using CSMHYD (Sloan, 1998).

#### Data Availability Statement

This research used samples and data provided by the International Ocean Discovery Program (IODP). Data from cores can be accessed at <http://web.iodp.tamu.edu/OVERVIEW/>. Data from logging tools can be accessed at <http://mlp.ldeo.columbia.edu/logdb/>.

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