Geochemistry, Geophysics, Geosystems

COMMENT
10.1029/2019GC008846

This article is a comment on Screaton et al. (2019), https://doi.org/10.1029/2019GC008603.

Comment on "Sedimentation Controls on Methane-Hydrate Dynamics Across Glacial/Interglacial Stages: An Example From International Ocean Discovery Program Site U1517, Hikurangi Margin" by E. J. Screaton et al.

Nabil Sultan[1]

[1]Ifremer, REM/GM/LAD, Plouzané, France

Key Points:
- The IODP U1517 site was selected based on an initial hypothesis neglecting the effect of salt on the methane hydrate stability law
- Reported chloride anomalies are deeper than the methane hydrate stability zone at site U1517
- Predicted methane hydrate (up to 68%) is not confirmed by direct evidence of the presence of gas hydrate nor by indirect seismic velocity

Correspondence to:
N. Sultan,
nabil.sultan@ifremer.fr

Citation:
Sultan, N. (2020). Comment on "Sedimentation controls on methane-hydrate dynamics across glacial/interglacial stages: An example from International Ocean Discovery Program Site U1517, Hikurangi margin" by E. J. Screaton et al. *Geochemistry, Geophysics, Geosystems*, *21*, e2019GC008846. https://doi.org/10.1029/2019GC008846

Received 25 NOV 2019
Accepted 27 JAN 2020
Accepted article online 11 MAY 2020

Abstract In the IODP 372A proposal, working hypotheses used with respect to actively deforming gas hydrate-bearing landslides were based on an initial calculation considering gas hydrate to occur in fresh water. This initial inaccuracy leads to predict the base of methane hydrate stability zone (MHSZ) to be at around 162 m below the seafloor (mbsf) at site U1517 while it is expected to be between 85 and 128 mbsf. It is most interesting that important negative chloride anomalies were measured well below the theoretical MHSZ without direct evidence of the presence of gas hydrate. These anomalies are usually a strong indication of gas hydrate occurrence. This initial inaccurate hypothesis provides the opportunity to evaluate the effectiveness of the indirect salinity detection method to quantify gas hydrate.

1. Site Selection and Gas Hydrate Stability Conditions

The paper by Screaton et al. (2019) concerns IODP U1517 drilling hole which is located in the Tuaheni Landslide Complex and was intended to help understand actively deforming gas hydrate-bearing landslides (Barnes et al., 2019). The target depth of the U1517 hole was defined to cross a landslide mass suspected to be the result of gas hydrate creeping and the base of the gas hydrate stability (BGHS) which was estimated to be at 162 mbsf (Barnes et al., 2019). The 162 mbsf depth seems to be mistakenly calculated by using a methane hydrate stability law (MHSL) for fresh water (Mountjoy et al., 2014, figure 8; Pecher et al., 2005, figure 3b; and Figure 1a). For comparison, the HSL corresponding to gas composition (96.3% CH_4, 2.6% CO_2, 1.1% C_2H_6, mole fractions) obtained by Giggenbach et al. (1993) from onshore vent sites on the East Coast of New Zealand is shown in Figure 1a. In the Screaton et al. (2019) paper, the use of a thermal gradient of 27°/km (Screaton et al., 2019, figure 1d) instead of the measured 39.8°/km (Screaton et al., 2019, figure 1f) and a high thermal conductivity in the numerical calculations (33% higher than the shipboard measured value) led to results fitting with the initial hypothesis of Barnes et al. (2019).

I argue that the Screaton et al. (2019) thermal conditions are in disagreement with the in situ nonlinear temperature profile which crosses the MHSL at 110 mbsf and indicates a transient thermal regime (Figure 2). The salinity-hydrate interpretation carried out in the Screaton et al. (2019) paper is therefore not fully justified. However, this initial inaccurate hypothesis provides the opportunity to evaluate the effectiveness of the indirect salinity method to quantify gas hydrate.

2. Chloride Anomalies and Gas Hydrate Occurrence

Chloride anomaly data suggest that the main Gas Hydrate Occurrence Zone (GHOZ) is between 135 and 165 mbsf with hydrate saturation between 2% and 68% (Screaton et al., 2019, figure 1). Despite this high predicted hydrate concentration (up to 68%), no direct observation of the presence of hydrates has been reported (Barnes et al., 2019). This derived GHOZ is outside the MHSZ for seawater conditions and in situ temperature data (Figure 1b). Indeed, for methane gas and a salinity of around 34 g/L, the gas-hydrate phase boundary is expected to cross the natural geothermal gradient between 85 and 128 mbsf, well above the chlorinity anomalies (Figure 1). Consequently, how can one explain these important chloride anomalies outside the

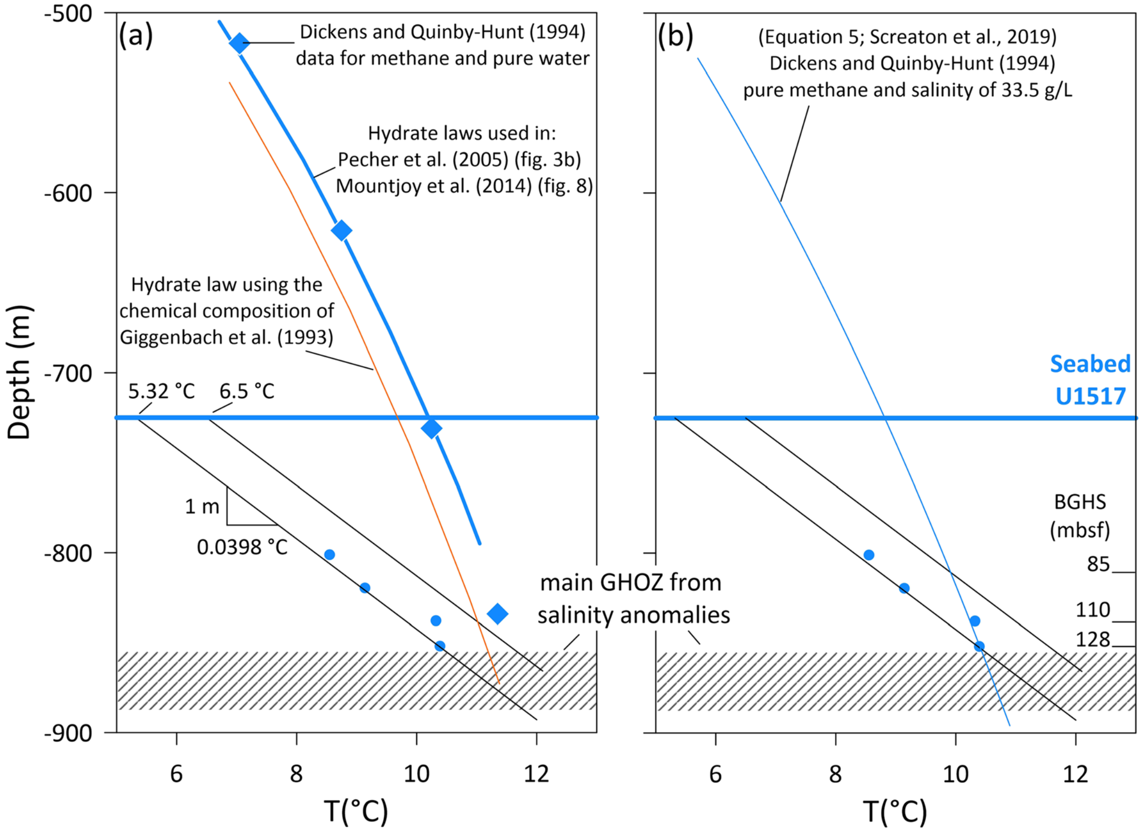

Figure 1. Methane hydrate stability diagrams at hole U1517 for (a) fresh water fitting with the MHSL used by Pecher et al. (2005) and Mountjoy et al. (2014) and (b) seawater conditions. Blue diamonds are data from Dickens and Quinby-Hunt (1994). Orange curve, obtained using CSMHYD (Sloan, 1998), corresponds to the gas hydrate law with the chemical composition of Giggenbach et al. (1993) and 3.5 weight-percent of NaCl. The geothermal gradients, seabed temperatures, and in situ temperature data (blue dots) are from Screaton et al. (2019). The base of the MHSZ for seawater conditions is expected to be between 85 and 128 mbsf. For seawater conditions, the chloride anomaly data are outside the MHSZ.

MHSZ? In numerous previous IODP drilling holes, chlorinity measurements were proved to be a relevant method to detect and quantify gas hydrate (for instance, IODP expedition 311).

These results suggest that either the hydrate law used to evaluate the stability of gas hydrate is inappropriate (gas composition, excess pore pressure, capillary effects …), or the chloride anomalies are linked to a phenomenon other than the presence of hydrates.

For the first case and to obtain the base of the GHOZ at 165 mbsf, it is necessary to have either fresh pore water or a very high excess pore pressure exceeding the lithostatic stress (around 2 MPa according to the method proposed by Sultan, 2007 and Ker et al., 2019). The geological conditions and data from hole U1517 (gas composition, salinity, temperature, and in situ pore pressure) lead us to reject this hypothesis (see data from Barnes et al., 2019).

For the second case, a combination of both free-gas exsolution/expansion and pore water expulsion during core recovery and squeezing adsorbed water with lower electrolytes can explain some chloride negative anomalies (Engelhardt & Gaida, 1963) but not as low as the ones shown by Screaton et al. (2019). Volume ratio between squeezed water and theoretical pore water obtained from porosity can provide an indication on the nature of analyzed water. Nevertheless, this second scenario fits well with the modest temperature anomaly detected by infrared (IR) thermal scanning (gas expansion is endothermic reaction), the resistivity anomalies, the seismic *P* wave velocity negative peaks (between 140 and 152 mbsf in figure 42; Barnes et al., 2019) and the location of the observed Bottom Simulating Reflector (BSR) (data in Barnes et al., 2019). Indeed, BSR, which is considered to result from free gas in sedimentary layers below the GHOZ, could also indicate the presence of free gas trapped in specific sedimentary layers (through capillarity for instance). It is

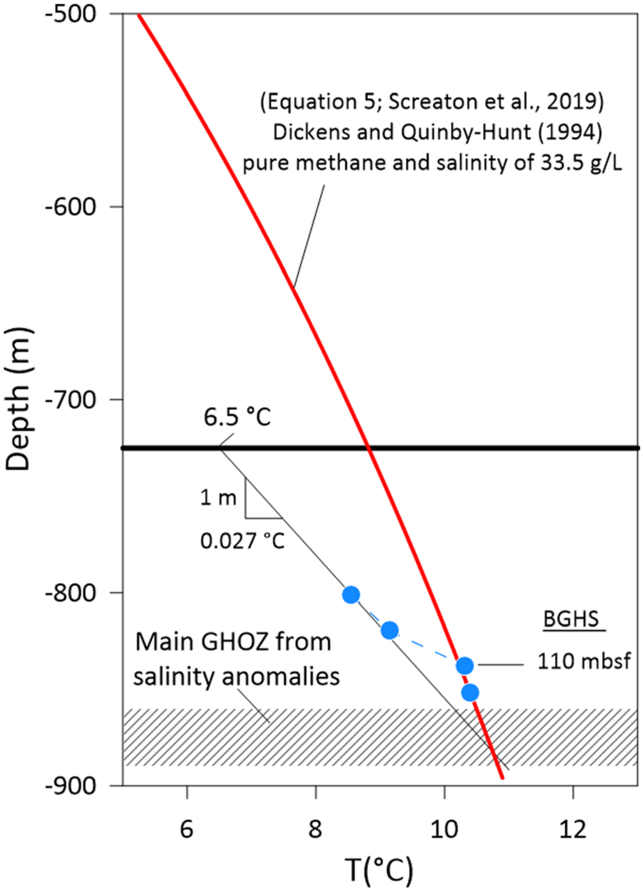

Figure 2. Methane hydrate stability diagrams at hole U1517 used in Screaton et al. (2019). The geothermal gradient and seabed temperature used by Screaton et al. (2019) in the numerical calculations are in disagreement with the in situ temperature data, which cross the MHSL at 110 mbsf.

also interesting to note that the highest measured seismic *P* wave velocity peaks was observed between 176 and 186 mbsf (Barnes et al., 2019, figure 42) well below the Screaton et al. (2019) MHSZ.

3. Summary

The purpose of this comment is to show that the chloride anomaly method, which is often used as a robust technique to detect and quantify gas hydrate, seems to be questionable in the case of IODP expedition 372A-U1517. Other hypotheses must be considered and verified and mainly the role of free gas and squeezing methods used to recover pore water. Resolving the paradox related to chloride anomalies below the MHSZ seems essential to analyze the role of gas hydrate as a trigger of the Tuaheni Landslide Complex.

Acknowledgments
Author thanks Dr Héctor Marín Moreno and an anonymous reviewer for their comments and constructive reviews. English editing by Alison Chalm is gratefully acknowledged.

References

Barnes, P. M., Pecher, I. A., LeVay, L. J., Bourlange, S. M., Brunet, M. M. Y., Cardona, S., et al. (2019). Site U1517. In Pecher, I. A., Barnes, P. M., LeVay, L. J., and the Expedition 372A Scientists, 2019. *Creeping gas hydrate slides. Proceedings of the International Ocean Discovery Program, 372A* (40 pp.). College Station, TX: International Ocean Discovery Program. https://doi.org/10.14379/iodp.proc.372A.103.2019

Dickens, G. R., & Quinby-Hunt, M. S. (1994). Methane hydrate stability in seawater. *Geophysical Research Letters*, *21*(19), 2115–2118. https://doi.org/10.1029/94GL01858

Engelhardt, W. V., & Gaida, K. H. (1963). Concentration changes of pore solutions during the compaction of clay sediments. *Journal of Sedimentary Petrology*, *33*, 919–930. https://doi.org/10.1306/74d70f74-2b21-11d7-8648000102c1865d

Giggenbach, W. F., Stewart, M. K., Sano, Y., Goguel, R. L., & Lyon, G. L. (1993). Isotopic and chemical composition of the waters and gases from the East Coast accretionary prism, New Zealand. In *Paper Presented at Final Research Coordination Meeting on the Application of Isotope and Geochemical Techniques to Geothermal Exploration in the Middle East, Asia, the Pacific, and Africa, Dumaguete, Philippines* (pp. 209–231). Vienna, Austria: International Atomic Energy Agency (IAEA).

Ker, S., Thomas, Y., Riboulot, V., Sultan, N., Bernard, C., Scalabrin, C., et al. (2019). Anomalously deep BSR related to a transient state of the gas hydrate system in the western Black Sea. *Geochemistry, Geophysics, Geosystems*, *20*, 442–459. https://doi.org/10.1029/2018GC007861

Mountjoy, J. J., Pecher, I., Henrys, S., Crutchley, G., Barnes, P. M., & Plaza-Faverola, A. (2014). Shallow methane hydrate system controls ongoing, downslope sediment transport in a low-velocity active submarine landslide complex, Hikurangi margin, New Zealand. *Geochemistry, Geophysics, Geosystems*, *15*, 4137–4156. https://doi.org/10.1002/2014GC005379

Pecher, I. A., Henrys, S. A., Ellis, S., Chiswell, S. M., & Kukowski, N. (2005). Erosion of the seafloor at the top of the gas hydrate stability zone on the Hikurangi margin, New Zealand. *Geophysical Research Letters*, *32*, L24603. https://doi.org/10.1029/2005GL024687

Screaton, E. J., Torres, M. E., Dugan, B., Heeschen, K. U., Mountjoy, J. J., Ayres, C., et al. (2019). Sedimentation controls on methane-hydrate dynamics across glacial/interglacial stages: An example from International Ocean Discovery Program Site U1517, Hikurangi Margin. *Geochemistry, Geophysics, Geosystems*, *20*, 4906-4921. https://doi.org/10.1029/2019GC008603

Sloan, E. D. (1998). *Clathrate hydrates of natural gases*. New York: Marcel Dekker.

Sultan, N. (2007). Comment on “Excess pore pressure resulting from methane hydrate dissociation in marine sediments: A theoretical approach” by Wenyue Xu and Leonid N. Germanovich. *Journal of Geophysical Research*, *112*, B02103. https://doi.org/10.1029/2006JB004527