Pore water evidence for methane hydrates and fluid origins in the Mahanadi Basin, offshore India

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The driving question behind the study of submarine natural gas hydrates (NGH), which has implication for energy and climate sciences, is how much exists? Because gas hydrates are enriched in both δ^{18}O (3.5‰) and δD (21‰) and depleted in Cl-, pore water chemical analyses provide the best tools for constraining NGH pore volume occupancy. 31 NGH occurrences were identified at Site U1445 of IODP Expedition 353 by infrared scanning for thermal anomalies >3.5°C below background temperatures within whole cores on the catwalk, or the presence of soupy structures in split cores. Pore water was collected from all 31 occurrences, by squeezing or Rhizon sampling, then analyzed for Cl- concentrations. The Cl- values fell between 400 µM and 104 µM which corresponds to 31% - 84% NGH pore space occupancy, assuming a Cl- baseline of 546 µM; however, the Cl- background at U1445 exhibited a strong decreasing trend with depth. Dilution of Cl- can occur as a result of hydrate dissociation or hydrous silica dehydration. To better understand the Cl- depth profile, the local hydrologic regime, and to more accurately constrain hydrate occurrence, 114 down-core interstitial water samples, including routine shipboard splits and hydrate-bearing splits, were analyzed for their δ^{18}O and δD values.

We report our values in ‰ relative to VSMOW. δ^{18}O values range from 0.1 to -2.12, while δD values range from 6.31 to -13.38. Hydrate bearing samples show expected enrichments in ^{18}O and D. An inverse relationship between δ^{18}O and δD is exhibited below 400 m, and is characteristic of mineral dehydration. The geothermal gradient at this site is 50°C/km, which means our termination depth of 660mbsf is well above the thermal boundary for clay mineral dewatering. This suggests that advection is likely delivering Cl- depleted waters and methane to charge the NGH stability zone at this site. Discrete excursions to heavier waters concomitant with deceases in Cl- concentrations reflect hydrate dissociation within the cores upon recovery. A plot of δD vs δ^{18}O reveals a slope consistent with fractionation during active hydrate formation, and further, the isotope data support far more abundant NGH occurrence in the upper 300 meters than the 31 occurrences detected by shipboard visual identification. We therefore conclude an advection-driven hydrologic regime with abundant gas hydrate occurrence and active hydrate formation occurring in the uppermost 300 m.