

Changes of pore water geochemistry constrained by gas hydrate formation/dissociation in the Japan Sea

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Gas hydrate is composed of water and gas, mostly methane in natural environment, its formation and dissociation must change the geochemical signature of pore water in sediment in response to the amount, rate, and sedimentary environment of the gas hydrate. The eastern margin of the Japan Sea is one of the places where very active methane accumulation through the gas chimney structure sustains the formation of dense and thick gas hydrates near the seafloor. We have collected large number of sediment cores on and around the gas chimneys and have measured the geochemistry of pore waters to examine the existence and potential of gas hydrate, material transfer via fluid, and relationship with biological activities and mineral precipitations. The profiles, however, have not reached well down to or below the massive accumulation zone of gas hydrates, the entire model of pore water changes has not been discussed well. We report the analytical results of pore waters collected successfully from the sediments within/deeper than the gas hydrate stability during the HR14 expedition and show that the pore water geochemistry has been modified strongly by the formation/dissociation of gas hydrate through the gas chimney structures compared to that outside the chimney.

The sulfate concentration of pore water at the site outside the gas chimney progressively decreases with depth, reaching 0 mM at 10 mbsf (sulfate-methane interface; SMI), and is stable at very low level. The chloride concentration is close to the seawater level throughout the sediment. The high concentration anomaly only of sulfate occurs exceptionally at 42 mbsf where the sediment core looked “wet/loose”, reflecting contamination of seawater during coring. The significant concentration of sulfate below the SMI is therefore useful for the correction of contamination with seawater/drilling mud. Contrary, the sulfate concentrations at two sites within the gas chimney are strongly variable below the SMI through the gas hydrate stability, indicating the contamination of seawater/drilling mud by the coring of tight gas hydrate layers or the intrusion of these fluids into the loosen sediment due to gas hydrate dissociation or gas expansion. After the correction of contamination with seawater/drilling mud, pore waters collected from gas hydrate-free sediment layers between dense massive/granular/platy gas hydrate accumulation zones are strongly enriched in chloride compared to the seawater value of 560 mM, reaching up to ~1200 mM at 15 to 25 mbsf, and the in-situ chloride concentration (Cl-baseline) shifts to ~600 mM to the bottom of gas hydrate stability at both sites. This is because the rate of gas hydrate formation and chloride exclusion from the crystal exceeds the diffusion of pore water. The most rapid and active formation of gas hydrate occurs as shallow as 15 to 25 mbsf in the research area, the formation of dense gas hydrates at these depths responsible for the topographic change like mound overlying gas chimney. The high Cl-baseline below this interval indicates active gas hydrate formation as well, the in-situ pore water geochemistry is essentially characterized by the rapid formation and distribution of massive gas hydrates within the gas chimney.

The concentrations of chloride from gas hydrate-bearing sediment and sometimes from normal sediment decrease by ~200 mM from the Cl-baseline value. The former results from the dissociation of gas hydrate during the core recovery, and the latter indicates that the invisibly small gas hydrates existed in the sediments and dissociated. The chloride concentration also decrease to ~400 mM below the gas hydrate stability, indicating the dissociation of all of the gas hydrates in sediments after the burial and subsequent diffusion of gas hydrate-derived fresh water into sediments.

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