Seepage and Leakage Next to Modern and Ancient Methane Clathrate Hydrate Accumulations: Comparative Sedimentology of the Pierre Shale Formation (Upper Cretaceous), Western Interior Foreland Basin of North America

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In deep water modern seafloors, methane clathrate hydrates are common materials, as hydrate evolution is pressure and temperature dependent. Accompanying hydrate accumulation sites are zones of active, methane rich fluid expulsion that contain micro particles and dissolved solids. Organisms capable of exploiting methane and hydrogen sulfide from bacterial and inorganic anaerobic methane oxidation (AMO) thrive in these depositional environments. As a consequence of AMO, synsedimentary seafloor diagenesis results in the precipitation of ^{13}C depleted carbonate minerals and the induration of the sediment with high and low magnesium calcite, ferroan calcite, aragonite, siderite and/or dolomite.

In the Pierre Shale Formation of South Central Colorado, limestones with vast numbers of coquinoid nymphalucinid bivalves, abundant pellet grainstones, packstones and wackestones, and variably sized, mm to cm large, irregularly nodular, sparry masses occur in the Teepee Buttes. Significantly, the nymphalucinid bivalves belong to an extremely successful group of organisms that in modern settings exploits zones of AMO. Furthermore, nodular spar masses are displacive and consist of three phases of primary calcite cements: in order of precipitation these are high magnesium botryoidal fibrous, ferroan “dendrolublinite”, and ferroan blocky. High magnesium botryoidal cements line the periphery of nodular spar masses and have $\delta^{13}C_{PDB}$ ratios ranging from -44.8 to -46.3 , reflecting a methanogenic source. Ferroan calcites display ‰ $^{13}C_{PDB}$ ratios with greater separation, ranging from -12.6 to -44.5 ‰, and are also found with cm to dm long tubules lined with ferroan calcite cemented terrigenous mudstone. Blocky ferroan spar with meniscate outlines seals the tubules. These combined features indicate that, during sedimentation of the Pierre Shale Formation, nodular methane hydrates precipitated in the sediment below the seafloor. In addition, nodular openings created following hydrate dissociation were stabilized with methanogenic carbonate mineral phases, and iron rich methanic fluids with micro particulates were expulsed into overlying waters.