

SLOW HYDRATE DISSOCIATION MECHANISMS: EXAMINING THE NEGATIVE FEEDBACK EFFECTS M. E. Elwood Madden¹, S. M. Ulrich², T. J. Phelps². ¹School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd, Norman, OK 73019, melwood@ou.edu, ²Biosciences Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831, phelpstj@ornl.gov.

Introduction: Throughout the solar system, rapid and extensive gas hydrate dissociation has been suggested as a mechanism for cryovolcanism and erosional features [1,2]. Gas hydrate stability is determined by the temperature, pressure, concentration of the guest gas (usually CO₂ or methane), and activity of water in the system. An increase in temperature or decrease in pressure, concentration of the guest gas, or activity of water, destabilizes hydrate and results in dissociation. This releases the guest gas, resulting in a large volume change, while forming either liquid water or ice, depending on the temperature, pressure, and salinity of the system.

However, each of these triggers is self-limiting (has a negative feedback effect), limiting the extent of dissociation in a system near equilibrium. Therefore, in order to produce features associated with rapid, extensive hydrate dissociation, the system must be open, and the trigger must move the hydrate far from equilibrium conditions.

Negative feedbacks associated with hydrate dissociation: Dissociation of hydrate is an endothermic process. Therefore, as external temperatures rise, temperatures within the hydrate will be buffered by the dissociation process until all of the hydrate has been destroyed. In this case the rate of the reaction is limited by the availability of excess heat to the system, or the thermal conductivity of the material. Even if ambient temperatures are above the freezing point of water, local temperatures may be depressed due to the endothermic dissociation processes, causing water to freeze and form a coating of ice around the hydrate, further protecting it from dissociation.

Within a closed system, gas released during dissociation can produce enough pressure to stabilize the system and prevent further hydrate dissociation. In an open system, the rate of hydrate dissociation may be controlled by the rate of gas escape. Likewise, when concentrations of the guest gas decrease and hydrate dissociates, the concentration of the guest gas increases in the surrounding material and may buffer the system within the hydrate stability field.

The addition of salts to gas hydrates will also lead to dissociation as the activity of water decreases. This dissociation effect is directly comparable and correlated to the freezing point depression of salts observed in water ice [3]. As the hydrate dissociates to form liquid water and gas, the water released from the hydrate structure will be salt-free pure water, reducing

the overall salinity of the system. Therefore, more salt must be added to further the dissociation process.

Implications: These negative feedback effects associated with gas hydrate dissociation act as limiting agents, maintaining hydrate stability in systems which are near equilibrium. This allows hydrate to be stable over long periods of geologic time, acting as a long-term reservoir for both water and guest gases.

In systems far from equilibrium, these negative feedbacks may also impede the rate and extent of hydrate dissociation. This will allow a slow release of water and guest gas molecules over long periods of time, without the catastrophic effects predicted by some workers [4]. While gas hydrate dissociation can produce large volume changes, it is unlikely to occur over very short periods of time, unless conditions are very far from equilibrium, and gas, water, and heat may flow quickly into/out of the system.

In studies examining the feasibility of *in situ* gas production from natural gas hydrates in terrestrial permafrost and ocean sediments, depressurizing the system and/or addition of heat or salts dissociates hydrates locally, but the expansion of the dissociation front into surrounding areas may take several years [5]. On a planetary scale, this suggests that catastrophic triggers are likely needed to produce large scale dissociation of hydrate reservoirs and the accompanying surface features.

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