MIXED GUEST CLATHRATES AND PLANETARY DYNAMICS: CONTINUOUS vs. EPISODIC EVENTS. J. P. Osegovic[1] and M. D. Max[2], [1]MDS Research, 1601 3rd St. S, St. Petersburg, FL 33705, josegovic@mdswater.com, [2] MDS Research, 1601 3rd St. S, St. Petersburg, FL 33705, mmax@mdswater.com.

Introduction: Clathrate hydrates may be a ubiquitous form of matter on temperate and cold planetary bodies. Clathrate hydrates are solids composed of a water host structure with caged ("en-clathrated") guests. The guests are typically small, inert gases, but other materials can also particpate [1, 2]. Hydrate has been hypothesized to exist on many planetary bodies including comets, Mars [3], Titan [4, 5], and Enceladus [6, 7].

Hydrate formation and dissociation is dependent on temperature, pressure, and composition. For hydrates that are composed of only one guest, such as biogenic methane hydrate found on Earth, the phase behavior is well described by a single-phase diagram. The behavior of these hydrates is simple to model. Mixed guest hydrates, such as thermogenic natural gas hydrate deposits, have a more complex phase relationship with several degrees of freedom. They are more complicated to model and difficult to interpret.

Hydrate kinetics are controlled by supersaturation and temperature. The higher the supersaturation and temperature, the faster the reaction progresses. Temperature cannot be raised arbitrarily and supersaturation is a function of temperature, amongst other parameters. At cryogenic temperatures, for example the surface of Titan, hydrate may form or dissociate very slowly. There is little experimental data on formation rates at low temperatures [8], but a greater body of work associated with dissociation (for example work see Stern *et al.* [9]). The bulk of these "low temperature" experiments were conducted at ~120 K or higher.

Hydrate was hypothesized to occur naturally on outer system bodies [10] before it was discovered on Earth. Terrestrial hydrate was initially detected by inference, with direct sampling becoming more common. Hydrate is now known to exist on Earth wherever the pressure, temperature, and reactants co-exist. Air, carbon dioxide, and natural gas hydrates occur naturally on Earth.

Hydrate Formation: Hydrate precipitation is a two step process requiring nucleation and growth phases. At low supersaturations, the guest + host phase is metastable and hydrate will not form for extended periods of time. As supersaturation increase, the metastable lifetime decreases. Once the metastable state is broken, nucleation and growth can occur. Nucleation is more sensitive to supersaturation than growth [11], and the initial reaction product is sensitive to the relationship between these two parameters.

Hydrate processes are controlled by heat and mass transfer limitation. In man-made settings, hydrate formation is usually episodic with a sudden pulse of formation that reduces local supersaturation followed by a longer phase where growth is controlled by heat flow. After the initial burst of formation associated with the high supersaturation to break metastablility, the rate of reaction decreases with time until heat transfer out of the formation region equals the rate of heat production by the reaction. Small deviations in heat flow are met with responses in reaction rate and the temperature of the system can be maintained for a considerable period of time.

If the heat flow out of the system exceeds the heat production (perhaps due to limittions of the mass transfer rate), then the system can cool down. The reaction rate will drop with temperature and metastablility may once again be obtained.

Mixed guest hydates add an additional variable. When hydrates form from multiple guest, certain preferred formers may be selectively enclathrated. The composition of the reactants change, which lowers supersaturation as the preferred materials are consumed. When the mixed guest hydrate undergoes dissociation stress, the preferred formers now become preferred dissociators. The resut is a change in the distribution of guests with simultaneous reduction in undersaturation.

Consequences of Episodic/Continuous Behavior: Hydrate formation and dissociation dynamics have different impacts depending on the stage of planetary formation.

Comets and other small bodies. For small bodies, episodic formation is strongly linked to thermal history. Hydrate formation on comets may occur very slowly at temperatures in deep space, but nucleation may be the limiting factor. If there is no initial heat impulse, for instance from internal heat, collision or transects nearer the sun, that will allow the first few crystals to form then growth cannot occur. Hydrate formation in the deep cold of small bodies in trans-Saturn space will be controlled by solid diffusion processes. Hydrate could provide a self-limiting source of gas, allowing comets to be productive for longer periods of time.

Enceladus. The plume from the south pole of Enceladus has been hypothesized to occur due to cyclic dissociation/cooling of clathrates [Kieffer]. The conditions of dissociation have been proposed to be linked

to hydrate → ice + gas reaction, with ice slowly sealing exposed clathrate beds.

With mixed guest hydrates in an open system, the formation composition does not always match the dissociation composition. The formation guest compositions can be calculated based on the measured vapor composition proposed to be produced by hydrates and an assumption of dissociation conditions (Fig. 1) .

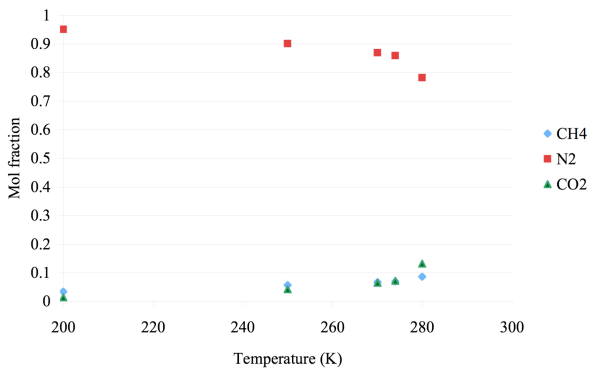

Figure 1. Using the plume gas compstion for Enceladus, the gas composition that formed the potential hydrate deposits can be calculated based on several formation scenarios.

Titan. The surface of Titan is at suitable conditions of pressure, temperature, and composition to form hydrate at high supersaturation [4], but at low absolute temperatures. Hydrate nucleation may be a very strong limiting factor for in-place formation, and may not be directly achievable without introduction of nuclei. The nuclei could be created during an exceptional event, like an impact where heat allows hydrate formation to occur rapidly for a short period of time, or by introduction of nuclei to the surface by cryovulcanism. Hydrate could also be a relict mineral, having been created by conditions in the past and then left in place or transported to the survace actively.

Hydrate produced in an atmosphere by combination of products from the photochemical destruction of organic molecules is technically possible, but likely just a curiosity as, even if enough oxygen is present to produce significant concentrations of water, there is no evidence that the hydrate phase prevents further photochemical degredation.

Conclusions: Hydrate formed from multiple guests must be considered in respect to local environment as a function of history. The thermal history of hydrates may be of primary importance in understanding the role they play in planetary bodies. The rate of hydrate formation is sensitive to heat and mass flows. Certain periods of an object's history may be particularly preferential for formation, which can have long term impacts on the evolution of associated gases. Certain periods of planetary formation may be dominated by heat flows due to hydrate formation or dissociation and hydrate may be a dominate actor in icy body geochemistry.

References: [1] Max, M.D, Johnson, A.H., Dillon, W. P. "Economic Geology of Natural Gas Hydrates", Springer, Dordrecht, 2006.

[2] Sloan, E. D., Koh, C. A. "Clathrate Hydrates of the Natural Gases 3rd Ed." C.R.C. Press, Boca Raton, 2008.

[3] Max, M. D., Clifford, S. M. "The State, Potential Distribution, and Biological Implicatins of Methane in the Martian Crust" *Journal of Geophysical Research* **105(E2)**, 4165-4171 (2000).

[4] Osegovic, J. P., Max. M. D. "Compound Clathrate Hydrates on Titan's Surface" *JGR: Planets* **100**, E08004, doi:10.1029/2005JE002435 (2005).

[5] Thomas, C., Mousis, O., Ballenegger, V. Picaud, S. "Clathrate Hydrates as a Sink of Nobel Gasses in Titan's Atmosphere" *Astronomy and Astrohysics* **474**, L17-L20 (2007).

[6] Kieffer, S.W. *et al.* "A Clathrate Reservoir Hypothesis for Enceladus' South Polar Plume" *Science*, **1764**, 314 (2008).

[7] Fortes, A. D. (2007)"Metasomatic clathrate xenoliths as a possible source for the south polar plumes of Enceladus" *Icarus* **ASAP**, doi:10.1016/j.icarus.2007.06.013.

[8] Hallbrucker, A., Mayer, E. "Unexpectedly Stable Clathrate Hydrates Formed From Microporous Vapor-Deposited Amorphous Solid Water At Low "External" Guest Pressures And Their Astrophysical Implications" *Icarus* **90**, 176-180 (1991).

[9] Stern, L. A., Circone, S., Kirby, S. H., Durham, W. B. (2003) *Can. J. Phys.* **81**, 271–283.

[10] Miller, S. L. (1961) "The Occurrence of Gas Hydrates in the Solar System" *Proc. N. A. S.* **47**, 1798-1808.

[11] Osegovic, J. P., Tatro, S. R., Holman, S. A., Ames, A. L., Max, M. D. (2007) "Growth kinetics of ethane hydrate from a seawater solution at an ethane gas interface" *Journal of Petroleum Science and Engineering* **56**(1-3), 42-46.