Gas clathrate hydrate thermodynamics and kinetics: limits on near-surface volatile fluxes for cold terrestrial planet systems through deep time.

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Gas clathrate hydrates (a gas molecule such as CO_2, CH_4, H_2S, etc. trapped within a cage of water molecules) are thermodynamically stable at low-moderate temperatures and moderate-high pressures, conditions found near the surface of many terrestrial planetary bodies in our solar system, including Earth, Mars, Europa, Titan, Enceladus, and other icy moons. While gas hydrates are often thought of as ephemeral phases in Earth's ocean and permafrost sediments, they can serve as reservoirs for water, carbon, and other volatile phases over millions to billions of years. Hydrate stability zones (HSZ- the depth at which gas hydrates are thermodynamically stable given the P-T conditions) can extend to significant depths [1]. In addition, gas hydrate formation and dissociation rates below the freezing point of water are transport limited, relying on solid-state diffusion of gas to or from the ice-hydrate interface [2]. Slow gas diffusion rates through ice and hydrate at low temperatures result in geologically long-lived metastable gas hydrate reservoirs in the near subsurface.

Geologic models of gas hydrates in planetary systems must thefore consider both thermodynamic and kinetic constraints on clathrate reservoirs to better understand long-term volatile fluxes in the near subsurface. Gas diffusion as well as hydrate formation and dissociation rates are needed to effectively model these complext systems. Using gas hydrate formation and dissociation rates measured in our laboratory, we have developed a coupled thermodynamic and kinetic model of obliquity-driven changes in HSZs on Mars. Tthis model suggests that gas hydrates may provide a significant reservoir for carbon and water within the crust over 10s of km depth. In addition, these hydrate reservoirs may remain thermodynamically stable over geologic timescales, and even when preturbed, may persist as metastable bodies for thousands to millions of years, resulting in significant long-term volatile fluxes. Similar geologic models of gas hydrate reservoirs on Europa, Titan, and Enceladus are underway.

[1] Root and Elwood Madden (2012) *Icarus* doi:10.1016/j.icarus.2011.12.024
[2] Gainey and Elwood Madden (2012) *Icarus* doi:10.1016/j.icarus.2011.12.019