TIMING AND ABUNDANCE OF CLATHRATE FORMATION WITHIN OUTER SOLAR SYSTEM BODIES Samuel Courville[1,2*], Julie Castillo-Rogez[2], Mohit Melwani Daswani[2], Elodie Gloesener[2], Mathieu Choukroun[2], Joseph G. O'Rourke[1]. [1]Arizona State University, Tempe, AZ. *swcourvi@asu.edu. [2]Jet Propulsion Laboratory, California Institute of Technology.

Introduction: Clathrate is an ice-like solid material composed of water molecules that cage gas molecules, like methane or carbon dioxide [1]. Unlike ice, however, clathrate has a thermal conductivity up to an order of magnitude lower and a viscosity up to four orders of magnitude lower than ice, meaning that if clathrate is incorporated into the ice shell of an ocean world, then it may prevent convection and insulate the body's interior [e.g., 2-4]. Furthermore, clathrates sequester compounds that determine the redox conditions in oceans. The exact consequences of clathrate formation on the evolution of ocean worlds are a function of when, where, and how much clathrate forms. We model the timing and formation of clathrates in outer solar system objects, specifically using Pluto as an example.

Clathrates may represent a sizable fraction of material in the icy shells of icy moons and Kuiper belt objects. Clathrate layer thickness and formation location, e.g., at the top or base of the ocean, influences the geophysical evolution of the hydrosphere [3] and perhaps the ocean's survival [2]. We expand upon existing studies of clathrates in ocean worlds by tracking the abundance of clathrate-forming gasses (CH_4, CO_2, H_2S, CO, N_2, and H_2), including volatiles from accretion and from the metamorphic breakdown of carbonates and organics in a body's rocky core. Here, we focus on the fate of CH_4 and CO_2, the dominant clathrate species.

Modeling: Using Pluto as an example, we apply geochemical [i.e., 5, 6] and thermal modeling [i.e., 7] to predict the thickness of clathrates in three steps (Fig. 1). The steps account for two distinct clathrate production events: immediately after differentiation from accreted cometary ices (Fig. 2) and at a later stage from thermal metamorphism (Figs. 3 & 4). We assume accretion from material with a cometary composition [8, 9]. To model CH_4/CO_2-clathrate formation from accreted ices, we model water-rock reactions during differentiation (EQ3/6) and then model the freezing of the hydrosphere (FREZCHEM). To quantify clathrate production from thermal metamorphism, we model volatile release from heating Pluto's rocky core (Perple_X).

We assume that CH_4 and CO_2 from accreted ice become enclathrated before the two species can equilibrate with each other within the ocean. I.e., there is no catalyzing agent for the Fischer Tropsch mechanism to operate at low temperature within the ocean that would allow conversion of CO_2 to CH_4, or vice versa depending on the ocean's redox state [10].

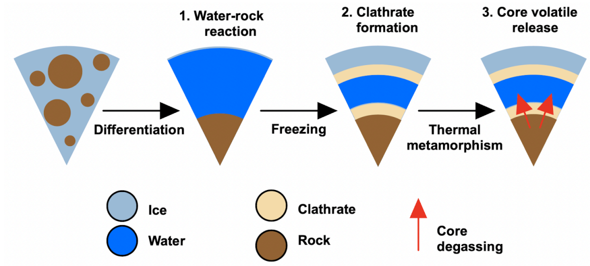

Figure 1. *We model the processes that determine clathrate formation in three steps: 1) water-rock reactions during differentiation, 2) clathrate formation during freezing, 3) metamorphic fluid production and late clathrate formation. CH_4 and CO_2 are the dominant clathrate species, and their relative abundance determines whether the clathrate forms at the top or base of the ocean.*

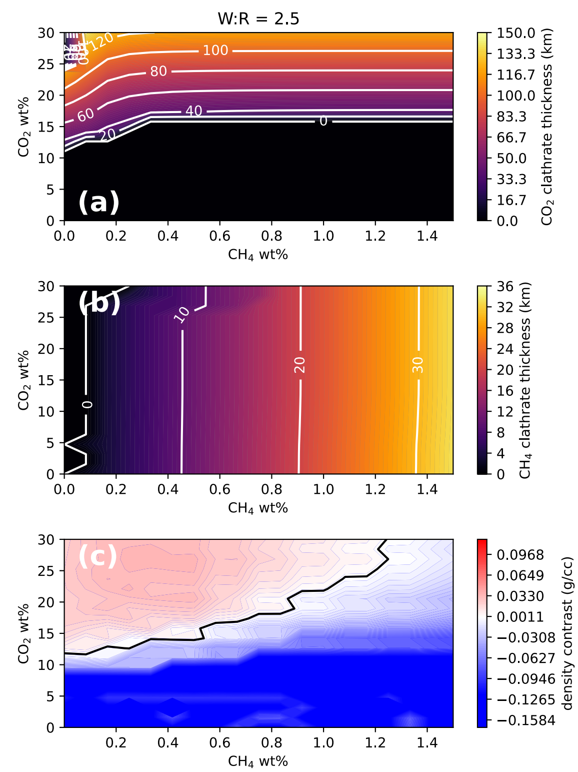

Figure 2. *Accreted ices may form thick clathrate layers at the base and/or top of Pluto's ocean. Assuming a 300-km thick ocean and an effective water-rock ratio of 2.5, (a) and (b) display the thickness of CH_4 and CO_2 clathrate, respectively, as a function of accreted CH_4 and CO_2 ice. If CO_2 and CH_4 form a mixed clathrate, (c) displays the difference in density of the mixed clathrate from the ocean, with blue indicating buoyancy.*

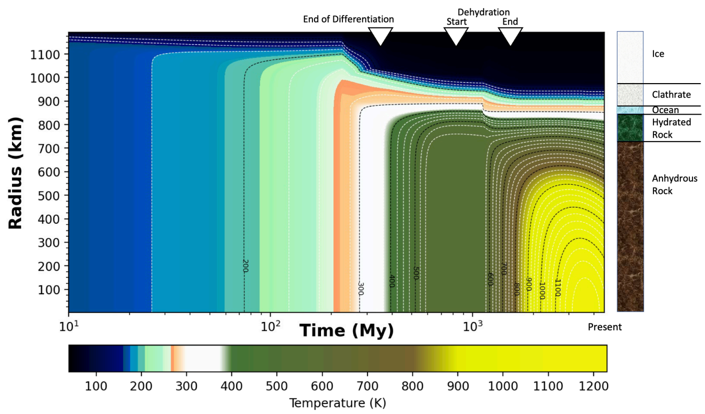

Figure 3. *Pluto's interior heats slowly from the decay of long-lived radioisotopes. When the interior reaches ~273 K, differentiation begins and water reacts with rock, leading to hydrated silicates that sediment into a core. This model assumes a 100 km thick clathrate layer accumulated early on below the ice shell. The rocky core initially heats faster due to greater concentration of radioisotopes per unit volume. Thermal metamorphism leads to the release of water from the silicates at temperatures beginning at ~600 K.*

Objects like Pluto accreted with a large fraction, ~40% by mass, of insoluble organic matter (IOM) [11]. However, our rocky core modeling does not yet include thermodynamic data for IOM, so we assume the carbon is largely in the form of graphite and is at equilibrium with the rest of the core mineral phase assemblage. Graphitization of IOM does not occur at low temperature, so IOM likely would have been gradually broken down over 100s of Mys as core temperature increased [10,11]. This breakdown would release additional CH_4 and CO_2. Future work will incorporate this aspect into thermodynamic evolution models. Hence, our preliminary results (Fig. 4) represent a low-bound for volatile release.

Results: We find that up to ~30 km of CH_4 clathrate and ~150 km of CO_2 clathrate could form from accreted volatiles in Pluto's early ocean (Fig. 2). The comparatively denser carbon dioxide clathrate may overwhelm the buoyant methane clathrate, confining clathrate formation to the base of the ocean if mixed clathrate forms. The fate of CO_2, dissolved or used in carbonates, is determined by the ocean's pH, which is largely controlled by the effective water-rock mass ratio [12]. Using a lower water:rock during Pluto's differentiation, ~<2, reduces the amount of dissolved CO_2 in the ocean, increasing the likelihood that Pluto forms buoyant clathrates. As a low-bound, we find 2 km and 10 km of CH_4 and CO_2 clathrate, respectively, may form from volatile release associated with mineral phase changes during core metamorphism (Figs 4). Clathrate formation may be limited if the ocean has mostly frozen leaving only a residual, concentrated brine against which clathrate stability must be assessed [1].

Conclusion: We find that if Pluto formed with an average cometary composition, then thick layers of mixed methane and carbon dioxide clathrates may form early in Pluto's history. If Pluto accreted rich in CO_2, then a dense clathrate layer would sediment on the ocean floor, representing a barrier to heat flowing from the core, and most of Pluto's water could be used in clathrate. Late clathrate formation from core volatile release may hinder the preservation of a thick plutonian ocean today. More broadly, our study provides methodology for predicting clathrate formation in other outer solar system bodies, which is necessary to predict ocean survival and ice shell structure.

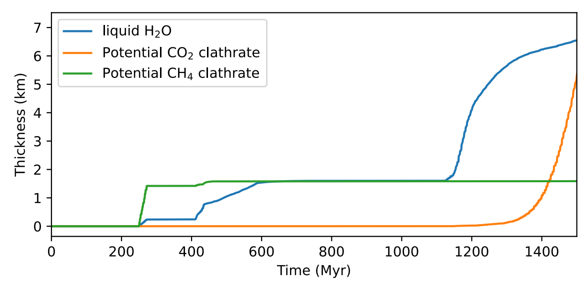

Figure 4. *Core metamorphism releases enough CH_4 and CO_2 for <10 km of clathrate production from mineral phase changes. Perple_X modeling yields a greenschist petrology for the early core with carbon largely in the form of graphite and carbonates. Releases of CH_4 and CO_2 are separated by several 100s My.*

References: [1] Sloan, E., & Koh, C. (2007). *CRC Press.* [2] Kamata, S., et al. (2019). *Nat. Geosci.*, 12(6), 407–410. [3] Carnahan, E., et al. (2022). *GRL,* 49(8). [4] Kalousová, K., & Sotin, C. (2020). *GRL,* 47(13). [5] Wolery, T. (1992). EQ3/6. doi:10.2172/138894 [6] Marion, G., et al. (2010). *Comps. & Geosci.,* 36(1), 10–15. [7] Melwani Daswani, M., & Castillo-Rogez, J. (2022). *PSJ,* 3(1), 21–21. [8] Mumma, M. & Charnley, S. (2011) *AREPS,* 49, 471–524 [9] Rubin, M., et al., (2019) *MNRAS.* 489, 594–607 [10] Sekine, Y., et al. (2005) *Icarus*, 178(1), 154-164 [11] McKinnon, W. et al., (2021). *UA Press*. 507-544. [12] Castillo-Rogez, J., et al. (2022) *GRL*, 49.

Acknowledgments: Part of this work was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (80NM0018D0004)