

ON THE ORIGIN & THERMAL STABILITY OF ARROKOTH'S AND PLUTO'S ICES C.M. Lisse^a, L.A. Young^b, D.P. Cruikshank^c, S.A. Stern^b, J.T. Keane^d, O.M. Umurhan^c, G.R. Gladstone^c, J. W. Parker^b, R.P. Binzel^f, A.M. Earle^f, Y.J. Pendleton^c, S.A. Sandford^c, M. Horanyi^g, H.A. Weaver^a, A.F. Cheng^a, R.L. McNutt^a, M. El-Maarry^h, J.M. Moore^c, I. Linscottⁱ, B. Schmitt^j, J.J. Kavelaars^k, D.T. Britt^l, C.B. Olkin^b, ^mW.M. Grundy ^aJHU Applied Physics Laboratory, ^bSwRI Boulder, ^cNASA Ames Research Center, ^dCaltech, ^eSwRI San Antonio, ^fMIT, ^gLASP, ^hBirkbeck Univ. London, ⁱStanford, ^jUniversité Grenoble Alpes, ^kNRC Herzberg Inst, ^lUCF, ^mLowell Obs. *e-mail: carey.lisse@jhuapl.edu..

Introduction. Using the results of the 01 Jan 2019 New Horizons flyby of KBO MU69 [1], we have new constraints on the icy makeup of the small KBOs, which differ substantially from the icy makeup of comets in having abundant methanol ice phases, and from the largest KBOs in its lack of hypervolatile ($N_2/CO/CH_4$) ices [2]. Here we use this new information and new modeling of the thermodynamic properties of MU69's ices to argue that *only* the most refractory of ices, the hydrogen-bonded species H_2O , CH_3OH , and HCN , should be thermally stable in it over timespans longer than Myrs. This and the large amounts of N_2 , CO , and CH_4 seen on Pluto's surface [3] in turn implies that Pluto either formed very quickly, in the first few Myr of the solar system's existence, *or* that Pluto is completely differentiated throughout and its surface hypervolatiles were sourced from remnant $N_2/CO/CH_4$ trapped as impurities in the small KBOs amorphous refractory ice phases.

Evidence for Hypervolatile Ices on Large KBOs, But Not MU69 or Distant Centaurs. H_2O and CH_3OH and the hypervolatile ices (N_2 , CO , and CH_4), are known to be present on some of the largest KBOs like Pluto [5-6]. By contrast, MU69 & the Centaurs only show strong absorptions due to CH_3OH ice and tholins and continuum structure due to water ice [2, 5-7; Fig. 1]. Correlations of 23 Centaurs' activity with their perihelion distance led Jewitt [8] to conclude that the activity of the inner ($r_h < 10$ AU) Centaurs is driven not by CO or CO_2 ice sublimation, but instead by crystallization of amorphous water ice and the "squeezing out" of other icy molecules unable to fit into the lattice pores of the newly crystallized ice. SP comet surface spectra do not show any obvious absorption features due to ices [9-11]; however, their comae, produced most actively by water ice sublimation, show an abundant range of icy species [12-13], with most species on the order of 0.1–1.0 % of the H_2O gas abundance, with the exception of CO (0.5–25%), CO_2 (2–12%), and CH_3OH (0.5–5.0%). Cometary minor species abundances are consistent with their being sourced from crystalline water ice clathrate phases [14]. The important singular example Comet 20126/R2 has shown a direct example of what a hypervolatile rich small icy planetesimal appears like [2]. One final piece of important evidence is that on Pluto and Charon, we see only extensional surface features & spherical morphologies which argue against a smooth run of any homogenous bulk water ice phases from core to surface and for a highly differentiated interior due to internal processing and radioactive heating [15-16].

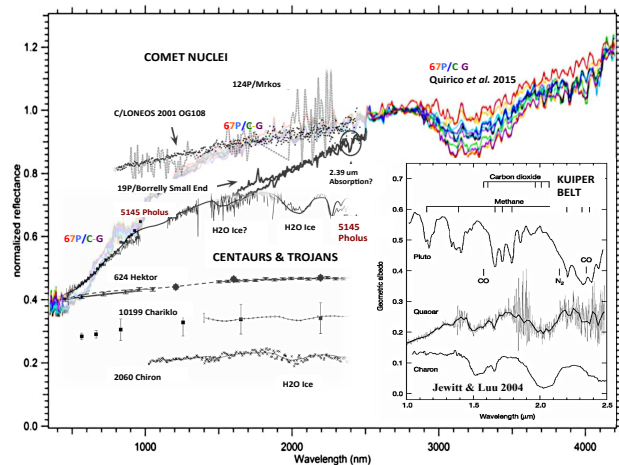


Figure 1: Compendium of NIR reflectance spectra for Solar System comets, Centaurs, and Trojan small bodies, as published in [4]. **Centaaur Pholus**, which is relatively good match for MU69 spectrally, is commonly known as the 'reddest object in the solar system', but in reality is only very red from 0.4 - 1.5 μm . Longwards of 1.5 μm H_2O ice absorption on its surface takes over and the reflectance becomes flat to slightly blue with increasing wavelength. (*Inset*) Typical KBO NIR reflectance spectra, dominated by hypervolatile surface ice absorptions, are grey to slightly blue in the NIR.

Possible Solutions to the Problem. Here we discuss three plausible physical scenarios for the formation of a hypervolatile rich Pluto. **(1)** Since pure hypervolatile ices should be exhausted on small proto-KBOs within the first 10^5 - 10^6 yrs of their formation and warming by internal radioactivity and external sunlight (Fig. 2), one simple solution to the presence of N_2 and CH_4 is to **form Pluto and the other large KBOs very quickly, within 1 Myr of the proto-planetary disk (PPD) midplane clearing, while the hypervolatiles are still contained in any source pebbles and small KBOs.** The ices seen on Pluto's surface in this scenario would be extracted from source KBOs by differentiation and concentrated on the surface. This scenario, while possible, is in some tension with the long dynamical timescales found in the large heliocentric distance, low total PPD mass Kuiper Belt. It would also require that the heating effects of short lived radionuclides be minimal.

(2) Another physical possibility that explains the hypervolatile ice presence is **the formation of Pluto early on, but while there is still appreciable nebular gas in the KB region containing the hypervolatiles.** This can include the time in the first 10^6 yrs when the small KBOs are outgassing their hypervolatiles and then act as local secondary gas sources. The large KBOs act as large gravitational 'cold' traps for the residual disk gas.

The hypervolatile ices seen on Pluto's surface in this scenario are a "late patina" that is accreted on top of a

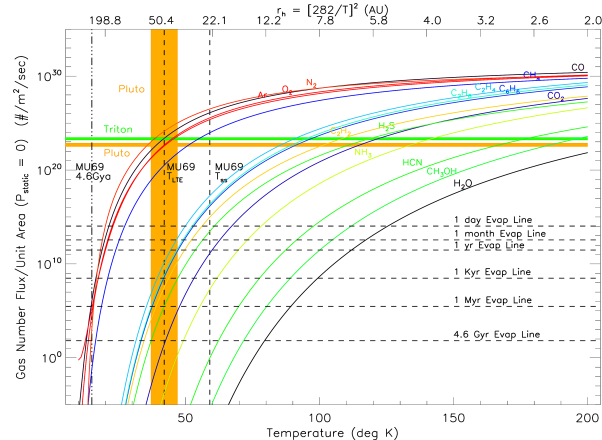


Figure 2 – Production rate of gas molecules, Q_{gas} , for a pure ice species vs ambient temperature, after [3]. The curves are controlled by the Vapor Pressure vs Temperature behavior for an ice. The dashed horizontal lines show the maximal Q_{gas} for which any appreciable solid ice will remain in a zero Pa environment. Above these lines, $Q_{\text{gas}} \cdot \Delta(\text{Time}) >$ the molar surface density of an ice, $\sim 10^{19}/\text{m}^2$. The MU69 flyby showed no evidence for pure hypervolatile ices in abundance today on the surface of MU69, consistent with the very short predicted residence times for pure hypervolatile ices (red curves) at current KB temperatures. By contrast, at the ~ 10 ubar surface of Pluto, the recondensation rate for hypervolatile ice (yellow horizontal line) can match its sublimation rate, and solid ice can coexist with atmospheric gas.

nearly fully developed Pluto, differentiated or not. The timescale for this scenario is relatively quick, limited by the **5-10 Myr PPD disk gas clearing lifetime** measured for nearby Milky Way stars in the latest surveys [18].

(3) Extraction of hypervolatile ices from amorphous & crystalline water ice phases in a differentiated Pluto. In this scenario, discussed in detail in [17], the ices we see on the surface of Pluto are endogenous, with the least dense and most volatile species dominating its surface. They are analogous to the $\sim 10^{-4}$ fraction (by mass) of the Earth of water that covers $\sim 70\%$ of its surface. Whether one has to use a “strict comet crystalline water ice abundance recipe” + total complete Plutonian differentiation (in order to get enough hypervolatiles on the surface), or the higher abundances of hypervolatiles available in amorphous water ice phases of the small KBOs [3] + partial internal differentiation is a matter of debate. McKinnon+ 2017 [19] argued from impact modeling of the Pluto-Charon system that full differentiation is unlikely for these bodies.

New evidence from the NH MU69 flyby for the “hyper-abundance” of surface methanol ice, the strong similarity in the NIR surface spectra of MU69 and distant Centaur Pholus, and the outgassing activity patterns of the Centaurs [8] all argue for the presence of abundant amorphous water ice phases and refractory hydrogen-bonded non-water ice phases (CH_3OH , HCN , etc.) in the

small KBOs [3]. The carrying capacity for hypervolatile species in amorphous ice is, in general, much higher than that of clathrated material in the crystalline water ice phases [20] existing in the inner system comets. Amorphous-water-ice-rich small KBOs could easily carry a few % of N_2 vs H_2O (by number), an order of magnitude higher than the $\sim 0.2\%$ found vs water in comets [9, 21].

Since Glein & Waite [22] have calculated that Pluto can be made from fully differentiated comet stuff with the lightest phases on the surface, an object made from small KBO stuff that contains more hypervolatiles in cold amorphous water ice, rather than annealed inner system crystalline water ice, could even more easily produce Pluto's surface N_2 and CH_4 , and without requiring complete internal differentiation of the body. It could also produce the surface hypervolatiles seen today in spite of earlier higher atmospheric loss rates due to an early warm Pluto, the Charon-forming impact, passing O/B stars and nearby supernovae, or periodic “super seasons” [23, 24].

References: [1] Stern, S.A. + 2019, *Science* **364**, 9771; Grundy+ 2020, *Science* **367**, aay3705 [2] Lisse+ 2021, *Icarus* (in press, doi:10.1016/j.icarus.2020.114072) [3] Stern, S.A.+ 2015, *Science* **350**, 1815; Protopapa, S.+ 2017, *Icarus* **287**, 218 [4] Lisse+ 2017, *AJ* **154**, 182 [5] Barucci, M.A.+ 2008, in “*The Solar System Beyond Neptune*”, 143–160; Barucci M.A.+ 2011, *Icarus* **214**, 297 [6] Brown, M.E. 2012, *Ann Rev Earth & Planet Sci* **40**, 467 [7] Cruikshank, D.P. 2005, *SSRV* **116**, 421–439 [8] Jewitt, D.C. 2009, *AJ* **137**, 4296; Li+ 2020, *Astron J* **159**, 209 [9] Abell, P.A.+ 2005, *Icarus* **179**, 174 [10] Soderblom, L.A.+ 2004, *Icarus* **167**, 100 [11] Quirico, E.+ 2016, *Icarus* **272**, 32 [12] Bockelée-Morvan+ 2004, “The Composition of Cometary Volatiles”, in *Comets II*, 391–423 [13] Mumma, M.J. & Charnley, S.B. *ARAA* **49**, 471–524 [14] Mousis, O.+ 2018, *ApJ* **757**, 146 [15] Moore, J.M.+ 2016, *Science* **351**, 1284 [16] Nimmo, F.+ 2016, *Nature* **540**, 94; Nimmo, F.+ 2017, *Icarus* **287**, 12 [17] Singer, K.N. & Stern, S.A. 2015, *ApJ Lett* **808**, L50; Singer, K.N.+ 2019 *Science* **363**, 955 [18] Richert, A. J. W. 2018, *MNRAS* **477**, 5191 [19] McKinnon+ 2017, *Icarus* **287**, 2 [20] Bar-Nun, A.+ 1988, *PhysRev B* **38**, 7749; Devlin, J.P. 2001, *JGR* **106**, 33,333; Bar-Nun A., & Laufer, D. 2003, *Icarus* **161**, 157; Zhao, W.-H.+ 2014, *Acc. Chem. Res.* **47**, 2505 [21] Cochran, A.L.+ 2000, *Icarus* **146**, 583 [22] Glein, C.R. & Waite, J.H. 2018, *Icarus* **313**, 79 [23] Stern, S.A. 2003, *Nature* **424**, 639 [24] Stern, S.A.+ 2017, *Icarus* **287**, 47

Acknowledgments: This work was supported by NASA's *New Horizons* project. We are grateful to the entire flight team of managers, operators, schedulers, & scientists who made the historic flybys of Pluto in July 2015 and MU69 in January 2019 possible.