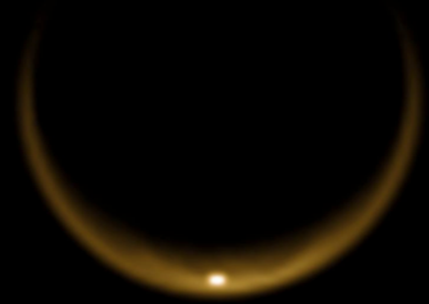


Dissolving Titan:

Dissolution geology on Saturn’s moon

Michael J. Malaska, PhD / NPP Senior Fellow
ORAU / Jet Propulsion Laboratory / California Institute of Technology

Funding from ORAU NPP Program / ASTID / OPR gratefully acknowledged

Dissolution geology on Earth

Cycling fluids + soluble materials → dissolution

Tsingy de Bamaraha, Madagascar (UNESCO World Heritage site)

Image source: Wikpedia

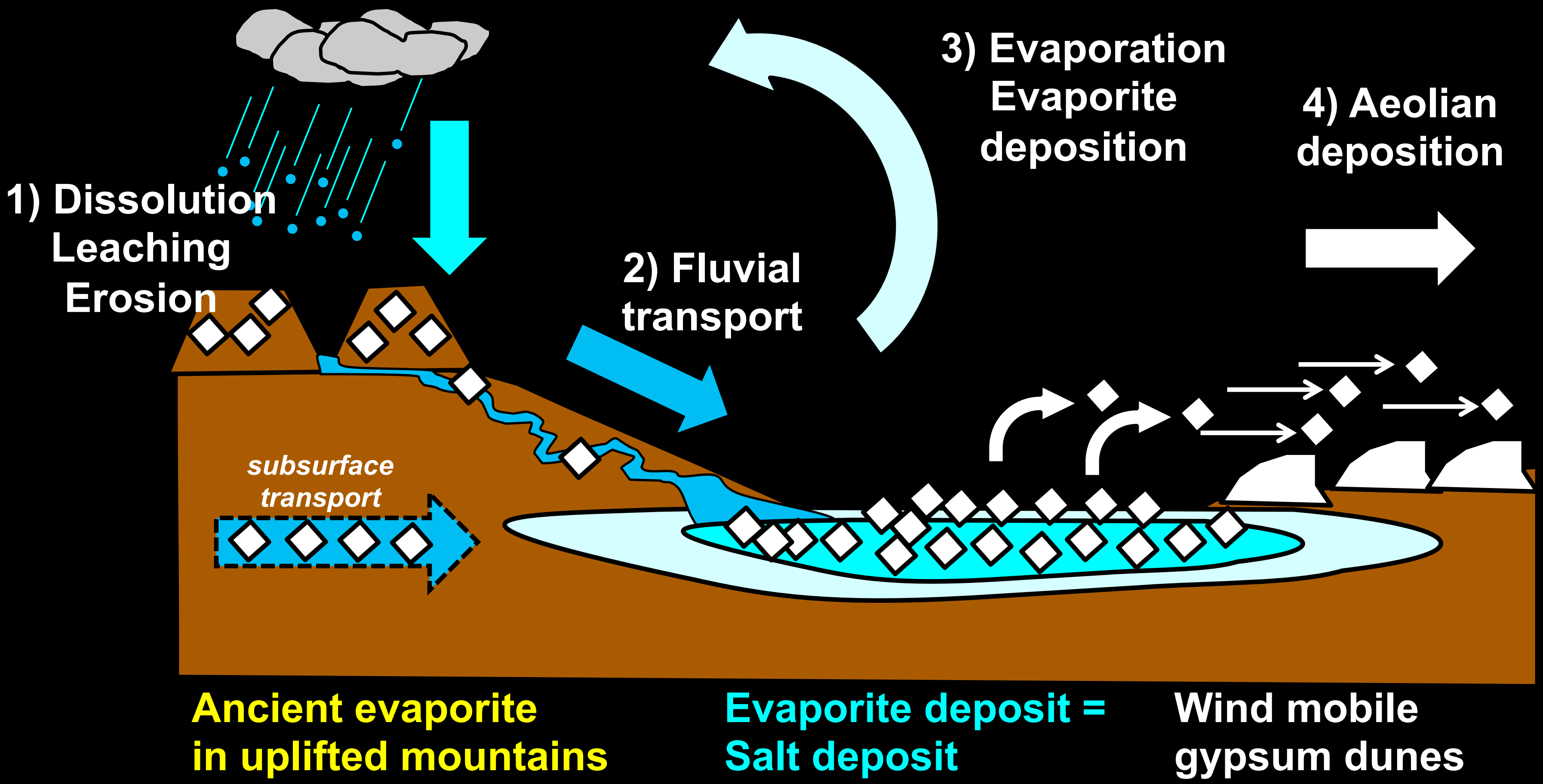
Lighthouse Reef Atoll Blue Hole, Belize.

Image credit USGS

Dissolution on Earth:
White Sands National Monument, NM

Image credit Mike Malaska October, 2011

White Sands National Monument: Dissolution of gypsum ($CaSO_4 \cdot 2H_2O$) in H_2O



Dissolution and evaporation of gypsum

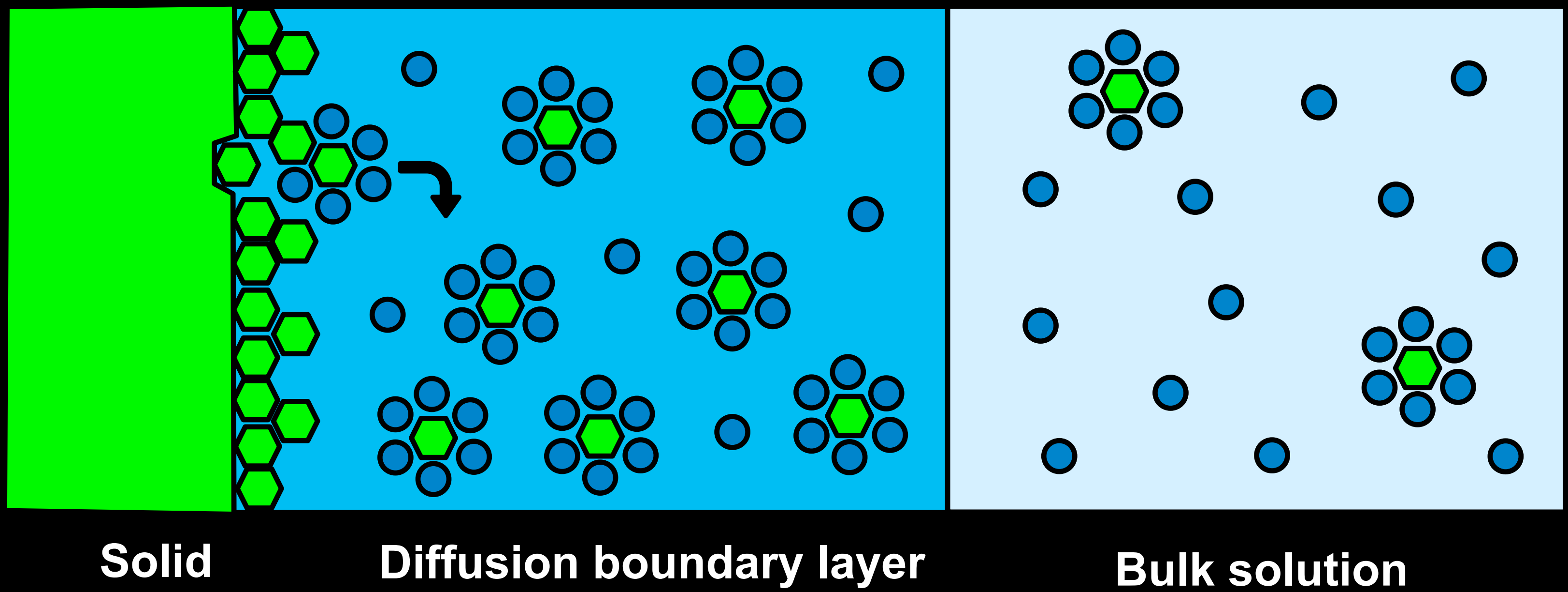
Karren features in gypsum rock
Bottomless Lake State Park, NM

Conduit in a gypsum cave
Carlsbad Caverns National Monument, NM

Unnamed playa in White Sands National Monument, NM

Image credits Mike Malaska

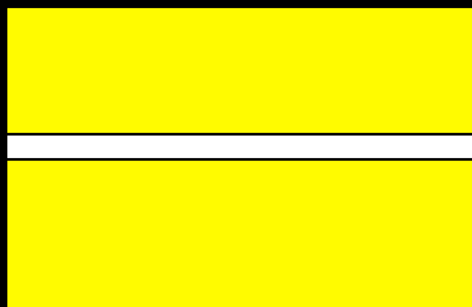
Dissolution as a molecular process



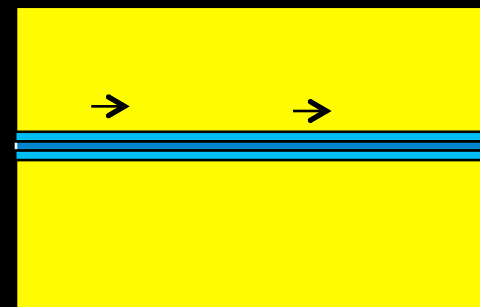
Solvent penetration
Dissolution
Weakening
Removal of insoluble materials

Fissure→Conduit

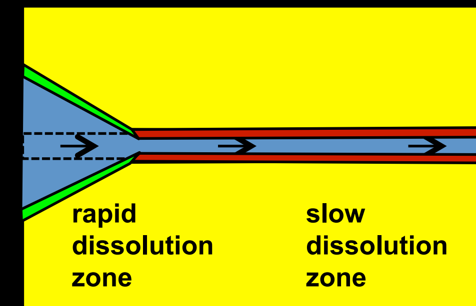
Deeper penetration and widening increases overall throughput



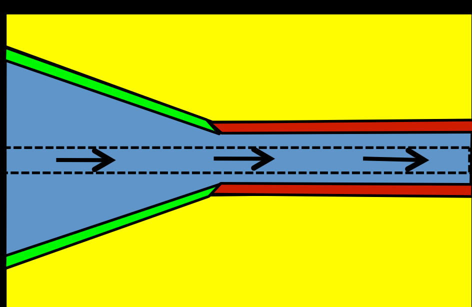
1) Initial fissure



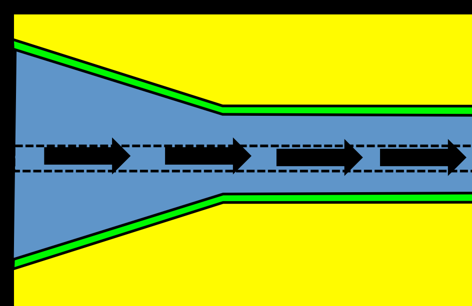
2) Fluid penetrates
Laminar flow regime



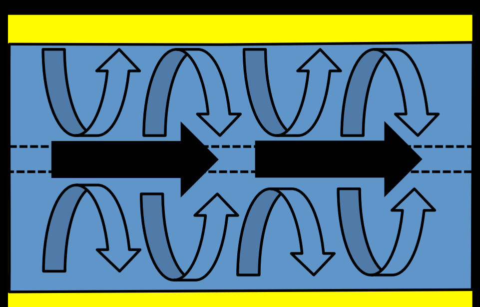
3) Material dissolves



4) Fissures widens



5) Breakthrough!
Flow increases
Laminar flow regime

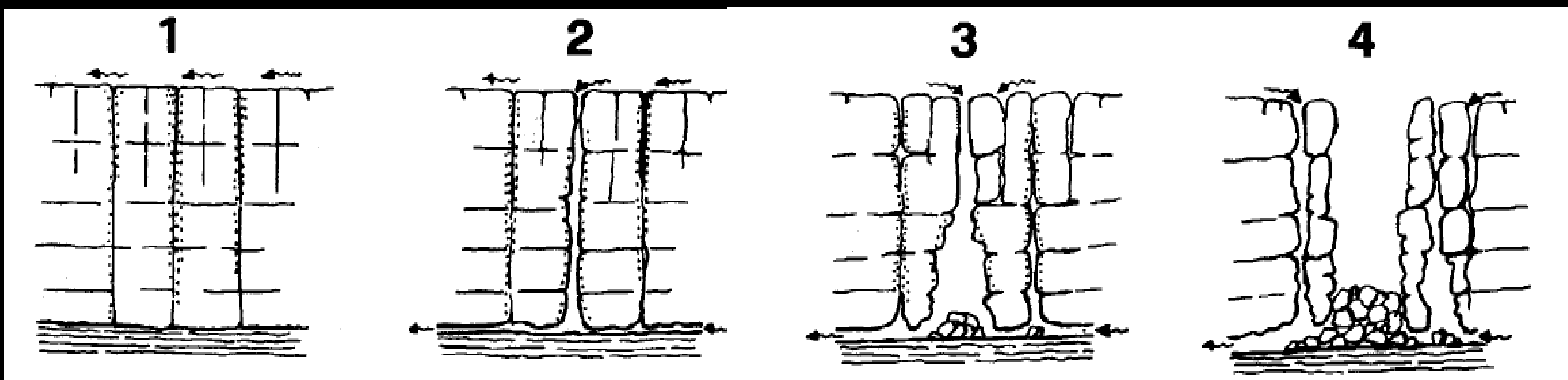


6) Turbulent flow
Increased dissolution

Reference: Clemens et al., Hard Rock Hydrosystems, IAHS Pub. No. 241 (1997) pp. 3-10.

Fissure widening and collapse

Dissolution → weakening → erosion



Fissures **Widening** **Collapse** **Sinkhole**

Figure from: Piccini, L., 1995. International Journal of Speleology 24 (Phys.) 41-54. (Fig 6 in text)

Silica dissolution

Grand Sabana karst, Venezuela

Image Credit: Gerard Vigo

Dissolution landscape development

Pitting → Sinkholes → Polygonal karst →Tower or cone karst

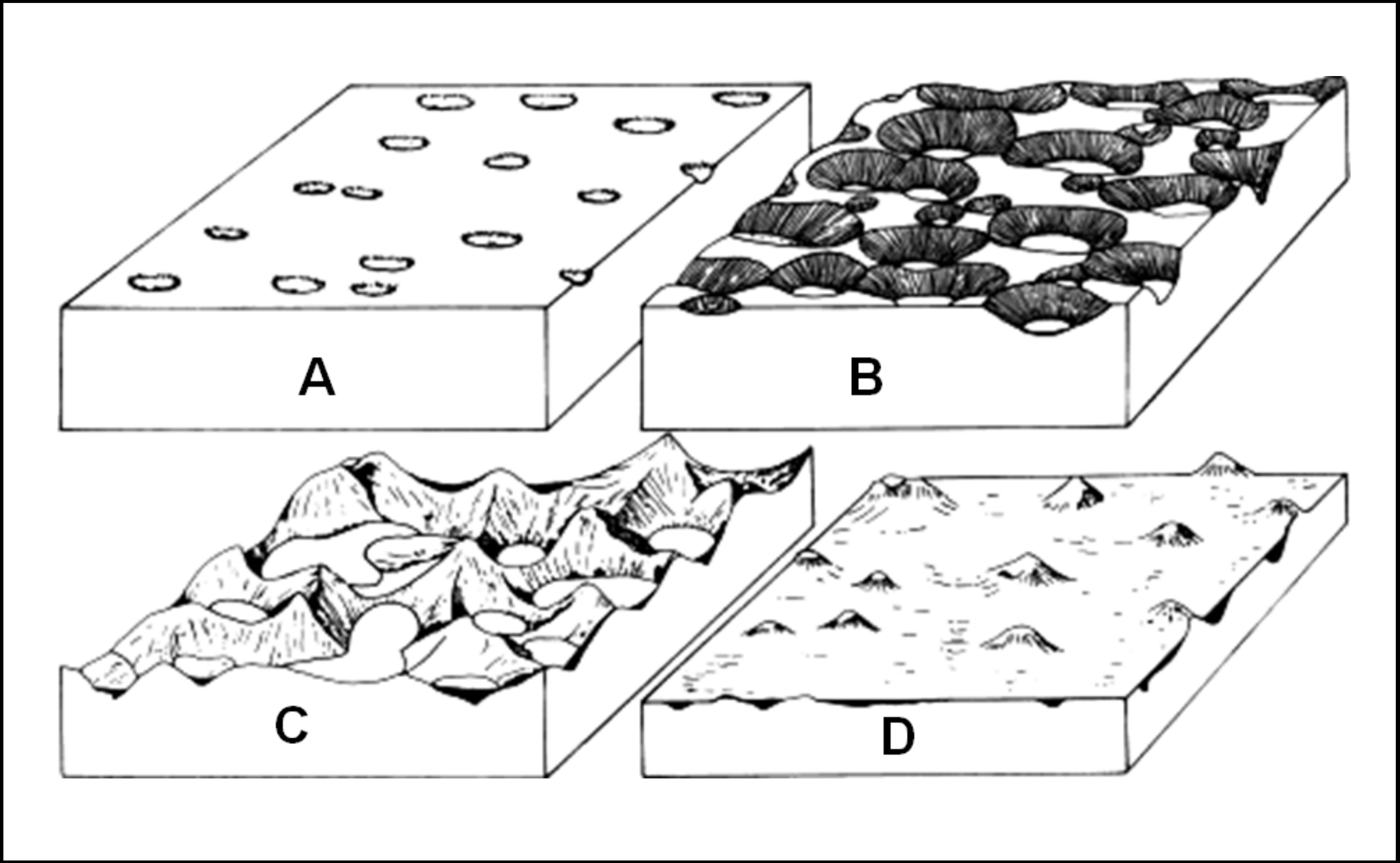


Figure from: Ford and Williams, Karst Hydrogeology and Geomorphology, 2007. Wiley. (Fig 9.63)

Quartzite Tower karst

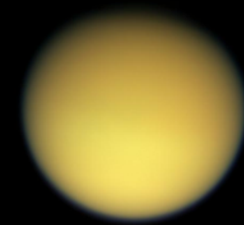
Purnululu National Park, Western Australia

Devonian quartz sandstone eroding out to a surrounding sand plain

***"the most outstanding example of cone karst in sandstones anywhere in the world"* - UNESCO**

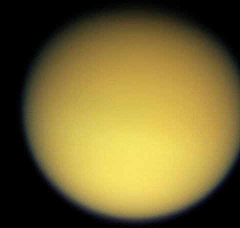
Image credit: Philip Griffin

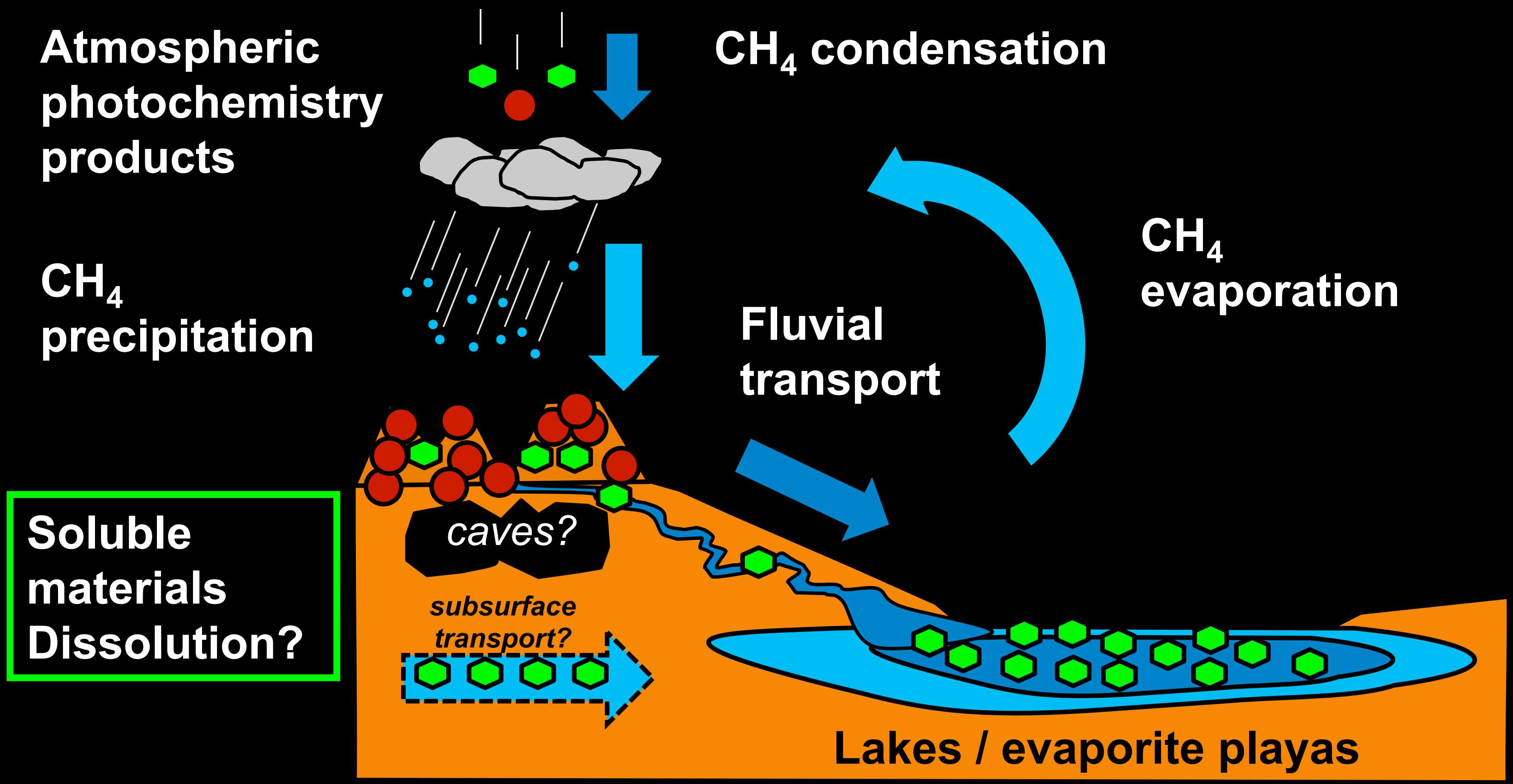
Fluids and materials



	Earth (298 K)	Titan (95 K)
Fluids	H_2O	Methane (CH_4) / N_2 Ethane (C_2H_6) Propane (C_3H_8)
Materials	Halite (NaCl) Gypsum ($CaSO_4 \cdot 2H_2O$) Limestone ($CaCO_3$) Dolomite ($CaMg(CO_3)_2$) Silica $(SiO_2)_x$	Acetylene (C_2H_2) Ethylene (C_2H_4) Hydrogen cyanide (HCN) Acetonitrile (CH_3CN) Acrylonitrile (CH_2CHCN) Benzene (C_6H_6) Cyanoacetylene (HCCCN)

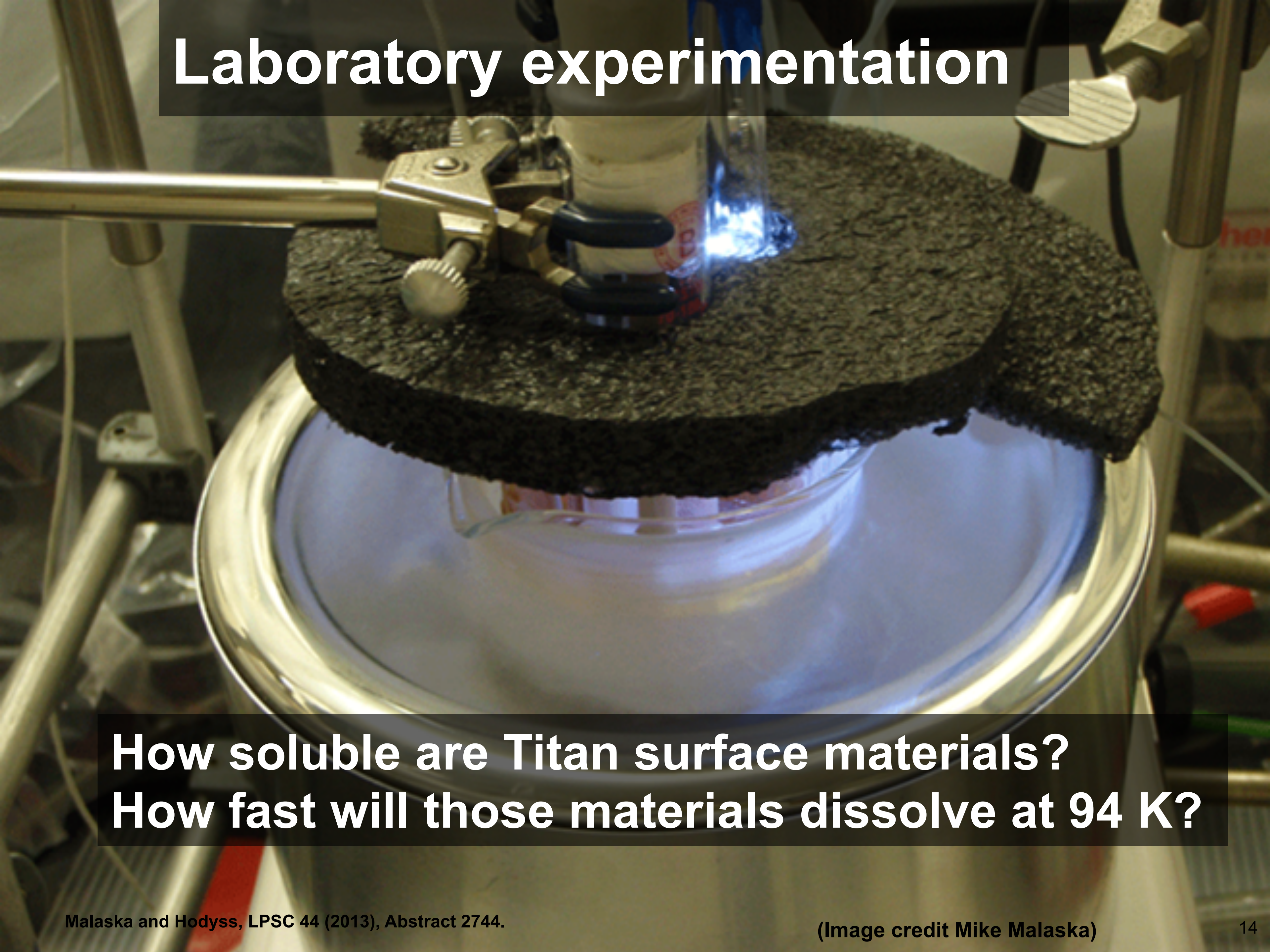
Titan Organic Cycle
Organics and CH_4





Malaska et al., Workshop on the Habitability of Icy Worlds (2014), Abstract 4020.

Laboratory experimentation



How soluble are Titan surface materials?
How fast will those materials dissolve at 94 K?

Malaska and Hodyss, LPSC 44 (2013), Abstract 2744.

(Image credit Mike Malaska)

Example: dissolution kinetics of iced coffee at 273 K is slow

How quickly will materials dissolve at 94 K?

Instant coffee

Dissolves fast

Crystalline sugar

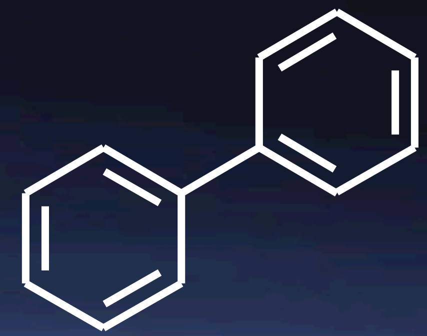
Dissolves slow

Image credit Mike Malaska

Example Titan organics

benzene

naphthalene



biphenyl

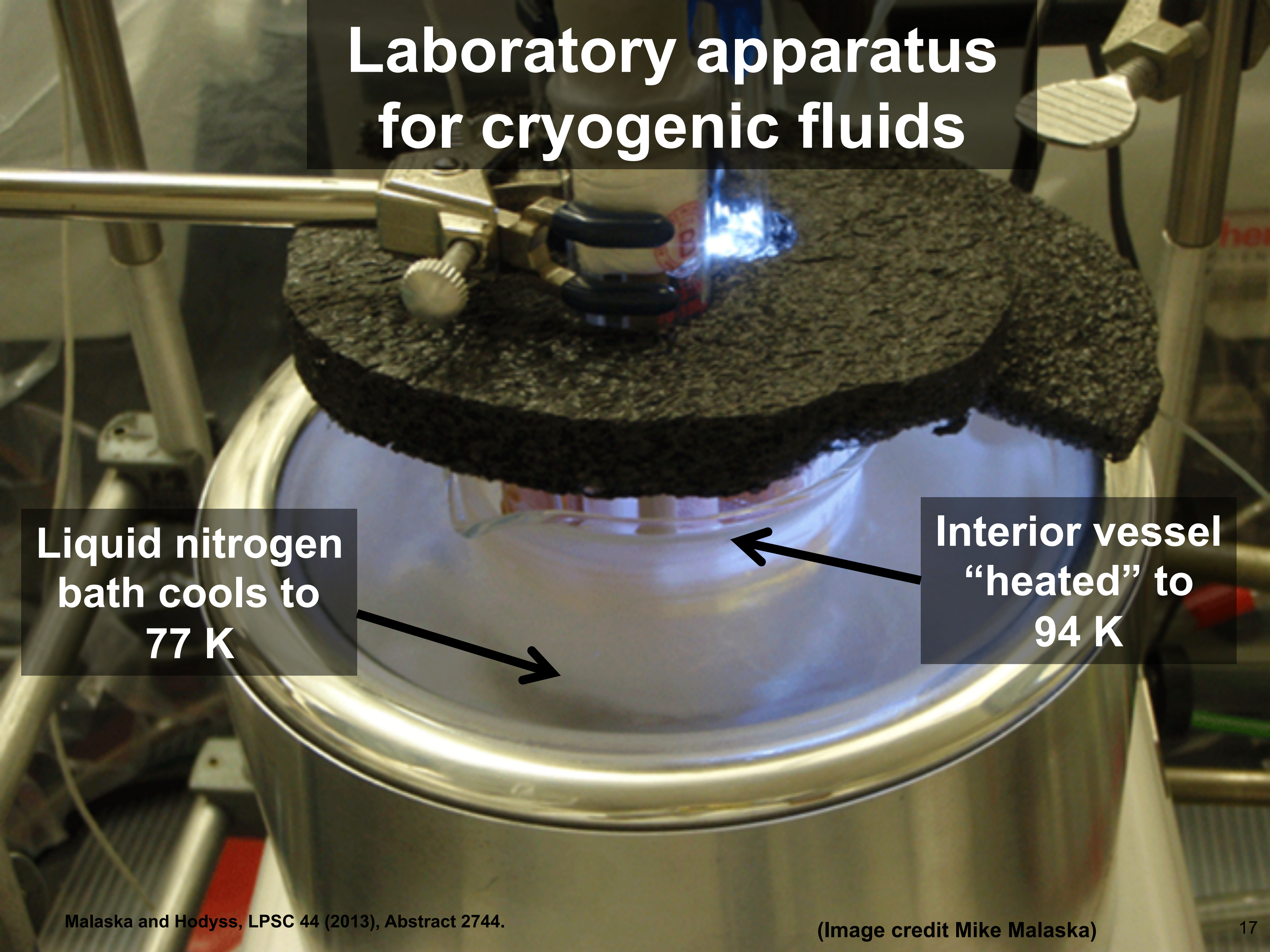
Benzene detected by INMS: Waite et al., 2007; Vuitton et al, 2008.
Benzene surface detection by VIMS: Clark et al., 2008
Tentative benzene detection by Huygens MS: Niemann et al., 2010.

Naphthalene atmospheric detection by CAPS: Waite et al., 2007.

Polyphenyls (biphenyl is simplest) atmospheric detection by CAPS: Delitsky and McKay, 2010.

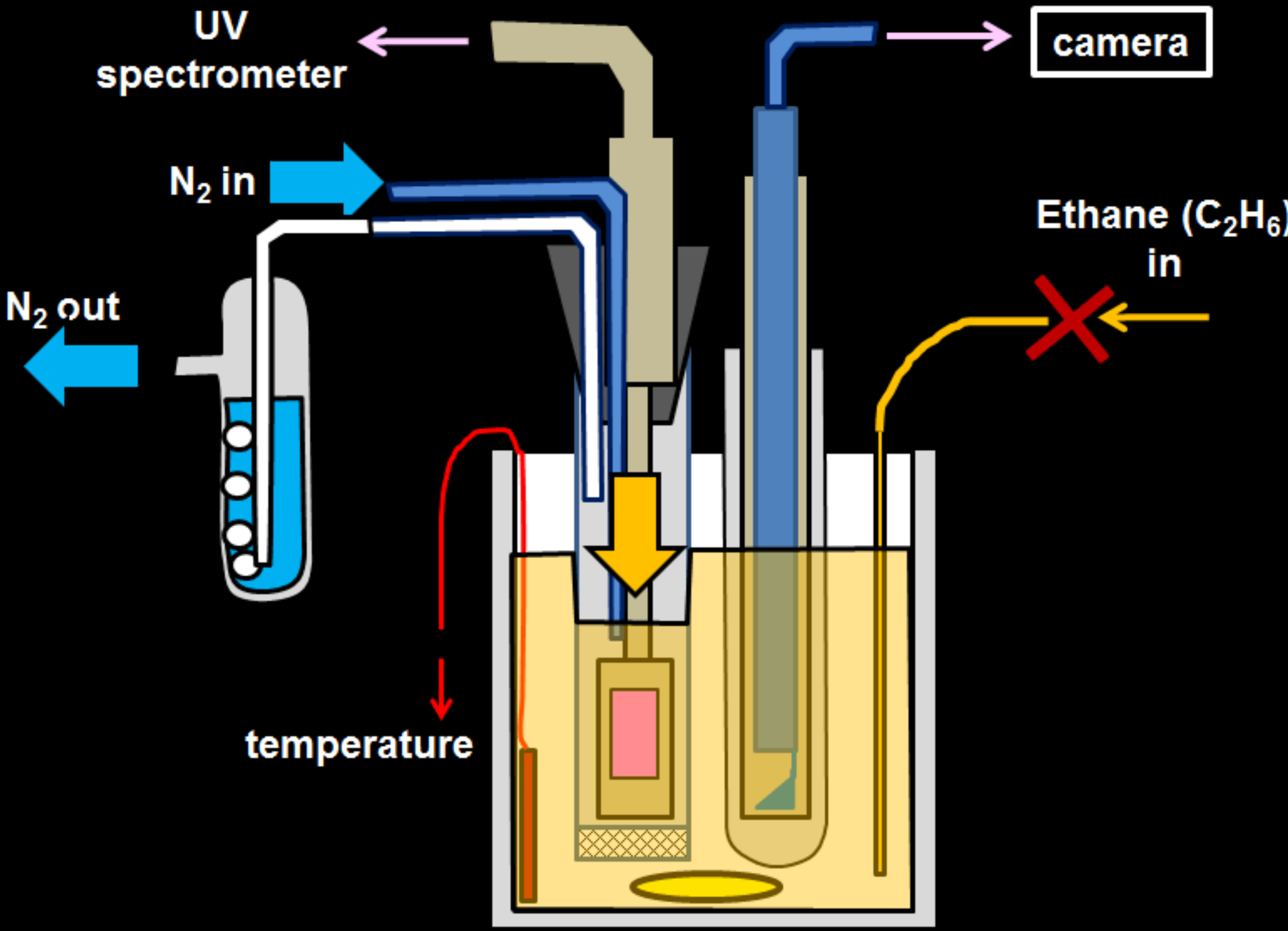
50 cm global layer benzene over 1 Gyr predicted by current Titan atmospheric photochemical models

Laboratory apparatus for cryogenic fluids



Malaska and Hodyss, LPSC 44 (2013), Abstract 2744.

(Image credit Mike Malaska)

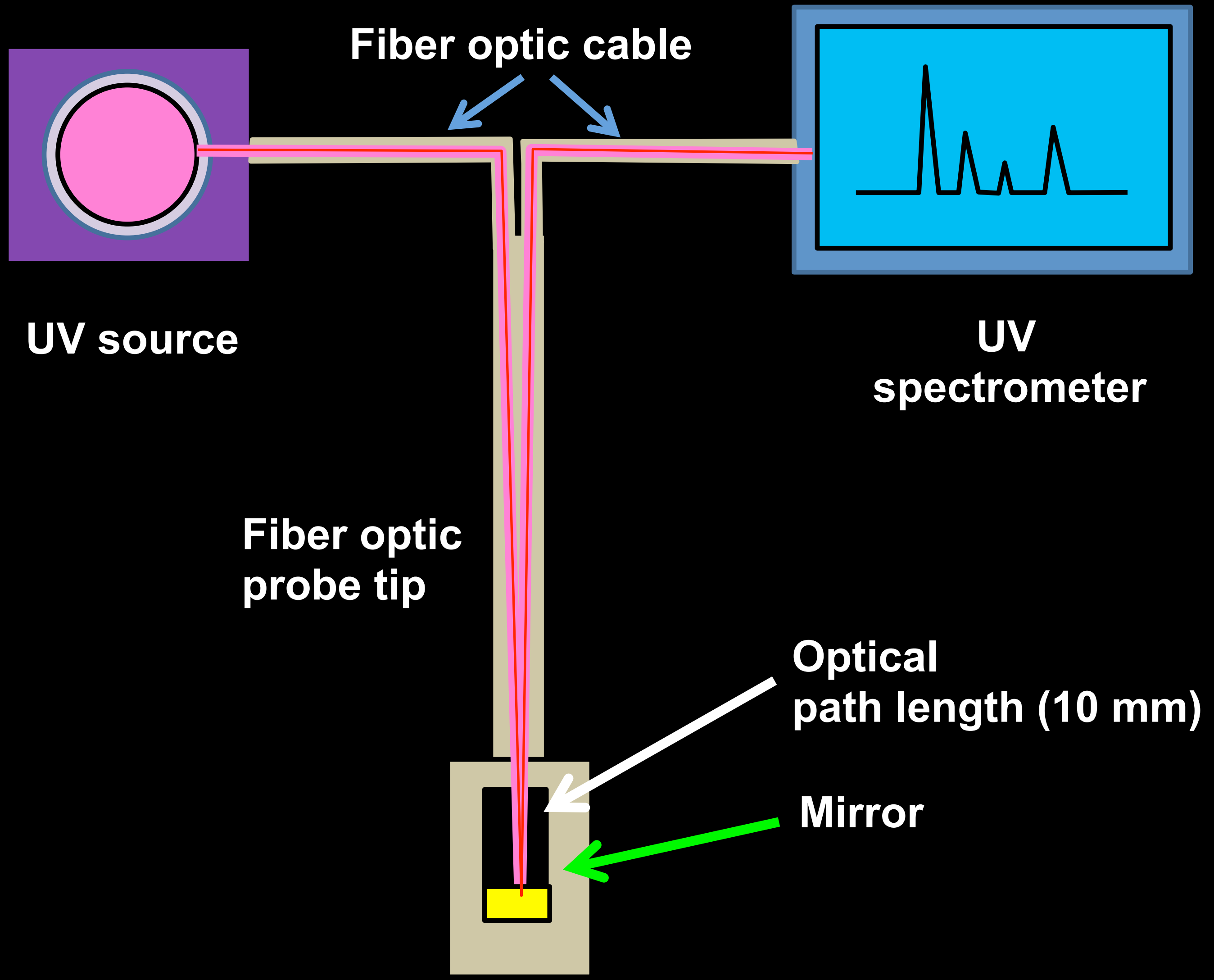


Flush and Fill

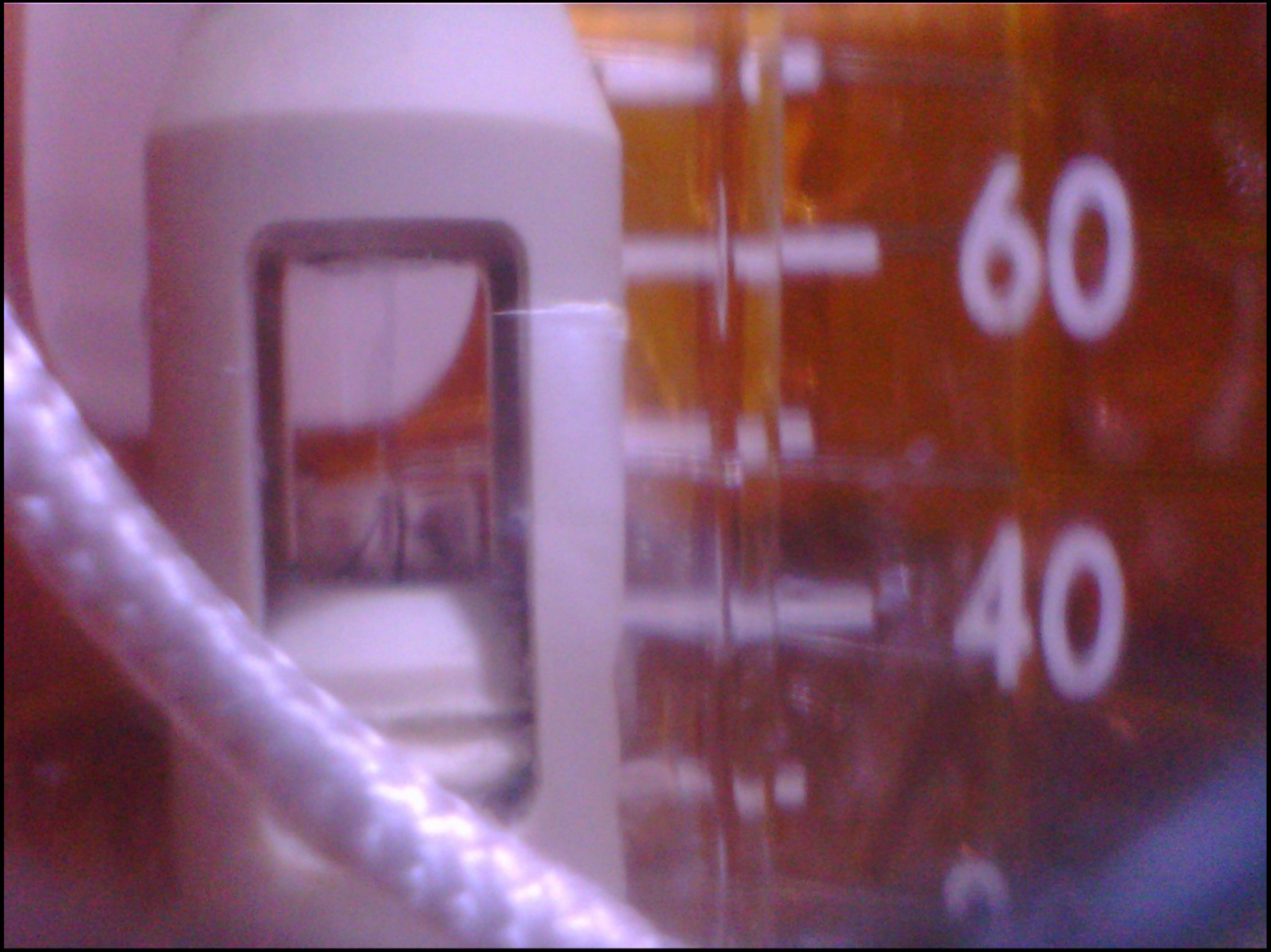
Filter tube
+ UV probe

Malaska and Hodyss, LPSC 44 (2013), Abstract 2744.

UV probe optical path



UV probe in liquid ethane at 94 K



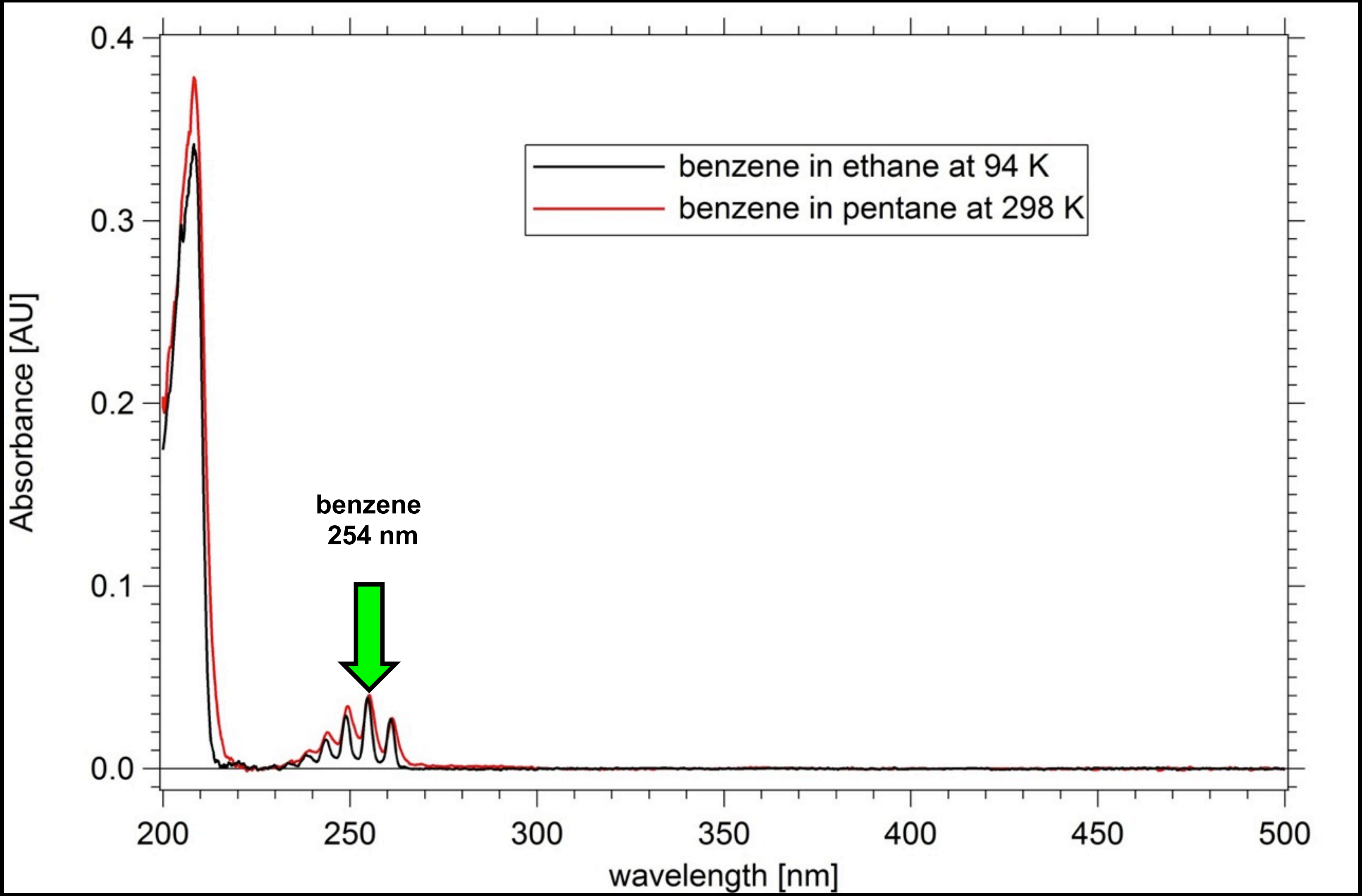
Malaska and Hodyss, LPSC 44 (2013), Abstract 2744.

Flush and Fill operation at 94 K

16x actual speed

Benzene UV absorbance at 94 K

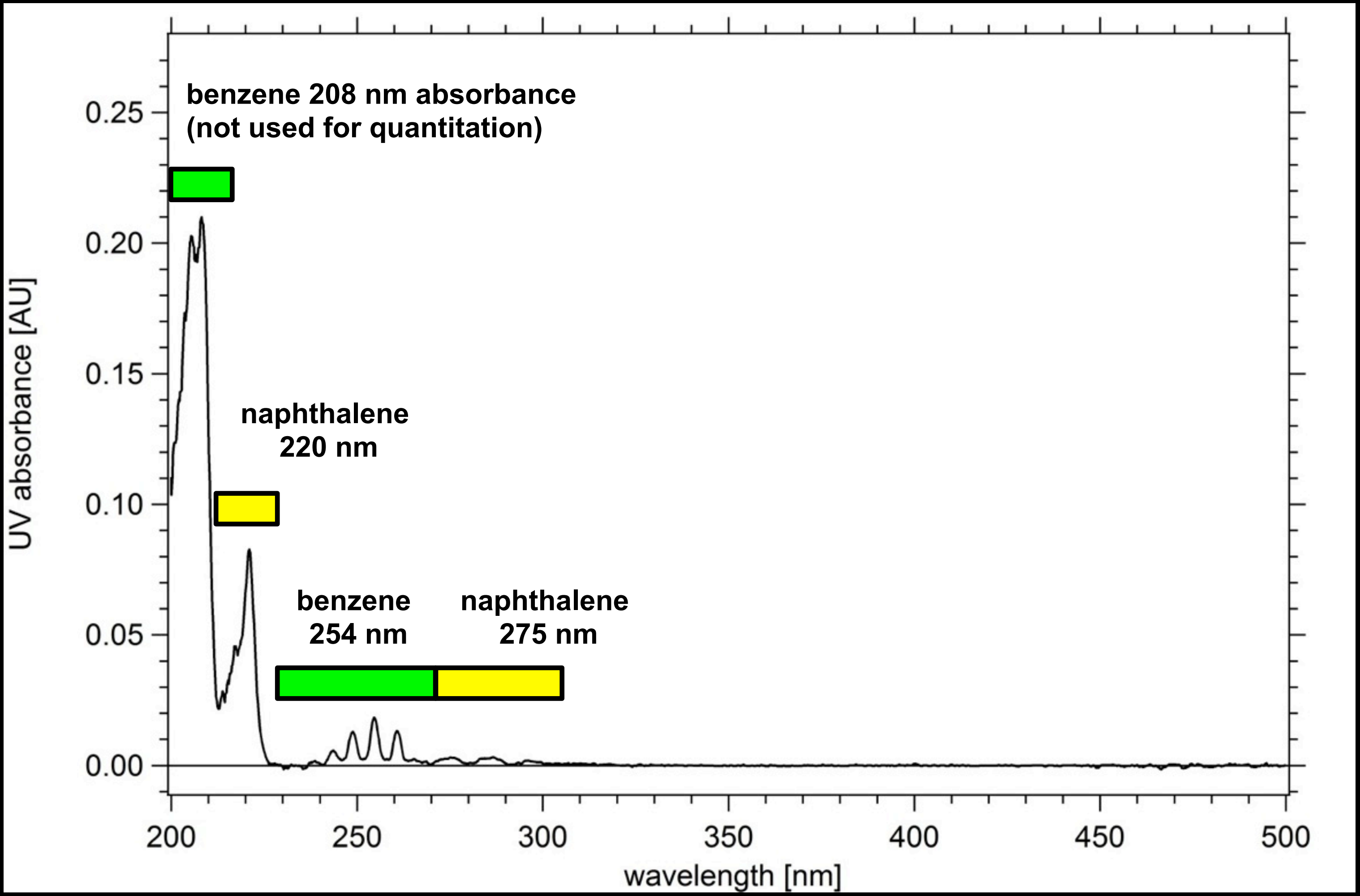
Comparison between ethane and pentane solutions at different temperatures
21-point calibration curve in pentane used for quantitation



Malaska and Hodyss, Icarus 242 (2014), 74-81.

Naphthalene and benzene

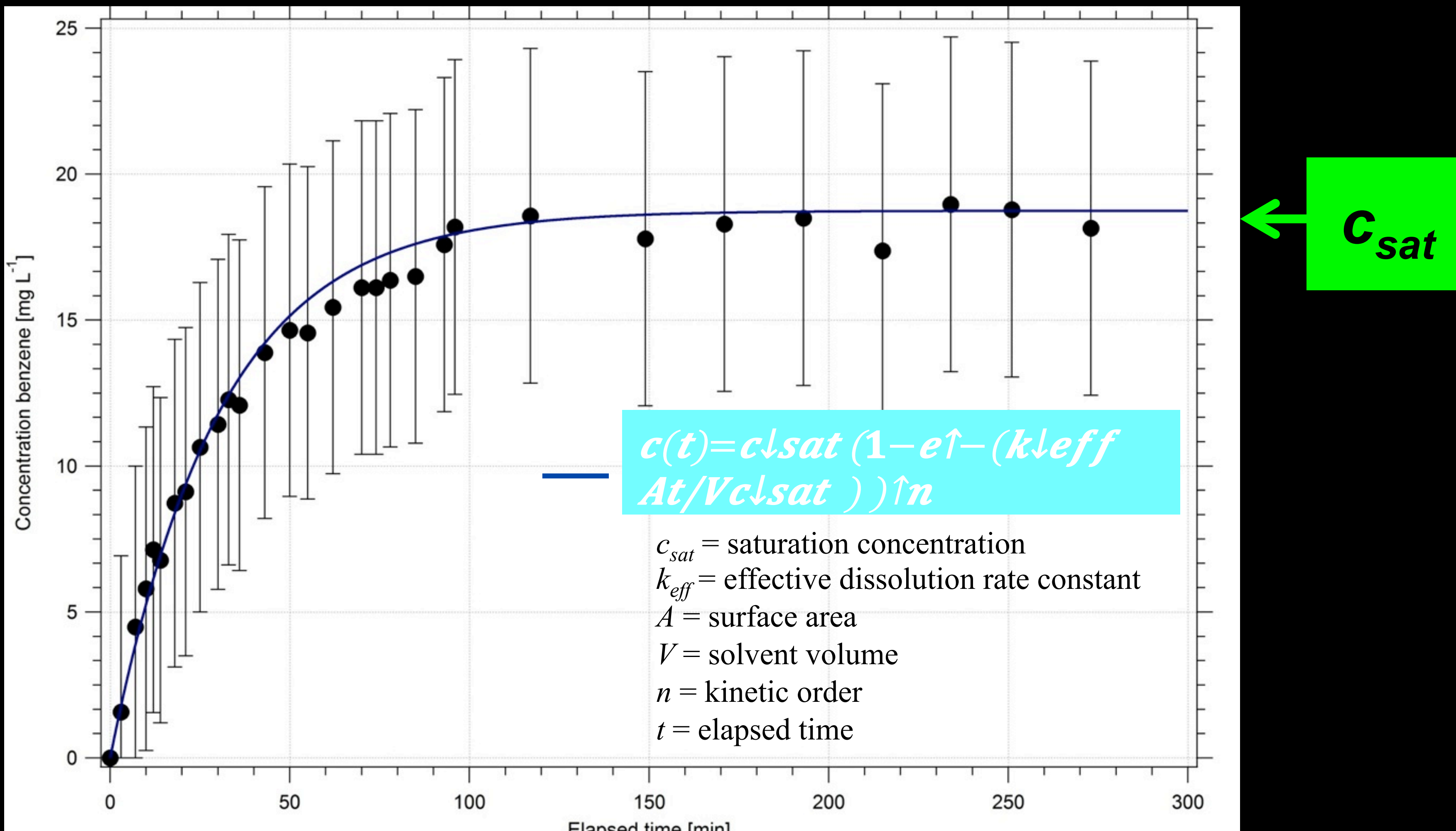
Detection of both aromatic molecules in ethane at 94 K



Malaska and Hodyss, LPSC 45 (2014), Abstract 1170.

Benzene dissolution is fast at 94 K

Saturation concentration (c_{sat}) and dissolution rate constant (k_{eff}) determined from UV absorbance over time

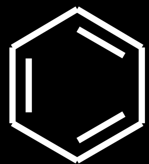
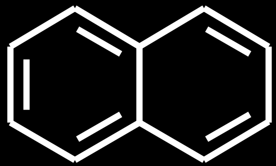
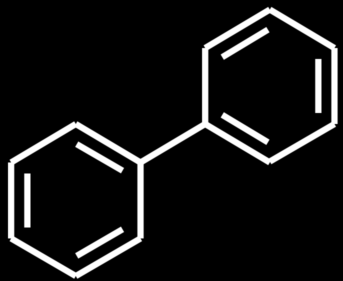


Malaska and Hodyss, Icarus 242 (2014), 74-81.

Lab results

How much dissolves? c_{sat}

How fast does it dissolve? k_{eff}

		saturation concentration c_{sat} [mg L^{-1}]	effective rate constant k_{eff} [mmol m^{-2} s^{-1}]
	benzene	18.5 (± 1.9)	3×10^{-6}
	naphthalene	0.159 (± 0.003)	4×10^{-8}
	biphenyl	0.039 (± 0.006)	4×10^{-9}

Malaska and Hodyss, Icarus 242 (2014), 74-81.

Experiment agrees with theoretical values

Material	chemical formula (structure)	estimated solubility in 77% CH4/23% N2 at 95 K [mg/L]	solubility in H2O at 298 K [mg/L]	estimated solubility in 97% C2H6/N2 at 95 K [mg/L]
Halite	NaCl		360,000	
ethylene	C2H4 (H2C=CH2)	2,810		25,000
hydrogen cyanide	HCN	1,080		17,000
Gypsum	CaSO4		2,400	
n-butane (C4H10)	C4H10 (CH3(CH2)2CH3)	580		4649
acetylene	C2H2 (HCCH)	1,300		2,600
Calcite	CaCO3		400	
Dolomite	CaMg(CO3)2		300	
propyne	CH3CCH	8		48
acrylonitrile	C2H3CN (H2C=CHCN)	3.2		42.4
carbon dioxide	CO2	44		22
acetonitrile	CH3CN	2.9		20.5
benzene (C6H6)	C6H6	0.78		16
Quartz	SiO2		12	
1,3-butadiene	C4H6 (H2C=C-C=CH2)	1.1		8.1
cyanogen	C2N2	0.2		6.2
cyanoacetylene	HC3N (HCCCN)	0.26		5.1
butadiyne	C4H2 (HCCCCH)	0.25		1.5
Gibbsite	Al(OH)3		0.001	
ice (meteor influx)	H2O	0.000000002		0.0000009
"tholin" polymer	R(CH2)n(HCN)m	0		0

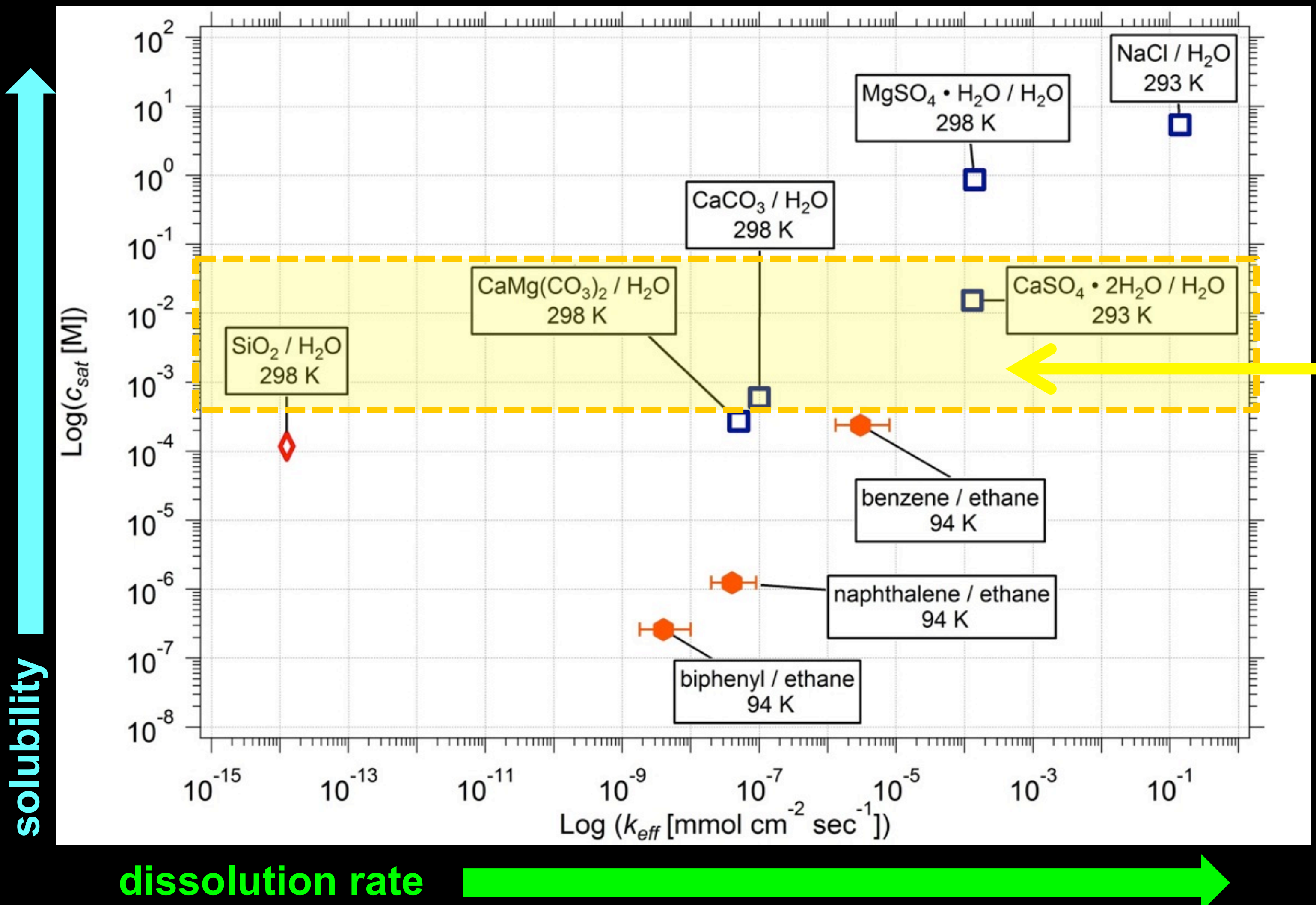
solubility

Measured value of benzene in ethane at 94 K [mg/L]: 18.5 mg/L

Predicted Titan solubility values from Raulin, 1987 and Cordier, 2009. (for HCN)

Titan materials geologically soluble

Titan molecules vs. terrestrial karst materials



Estimated ranges for ethylene, acetylene, HCN, *n*-butane, and ethylene in 77% CH_4/N_2

Malaska and Hodyss, Icarus 242 (2014), 74-81.

Lifetime of materials in a surface deposit Surface flux vs. predicted dissolution in CH_4/N_2

Short timeframe

Medium timeframe

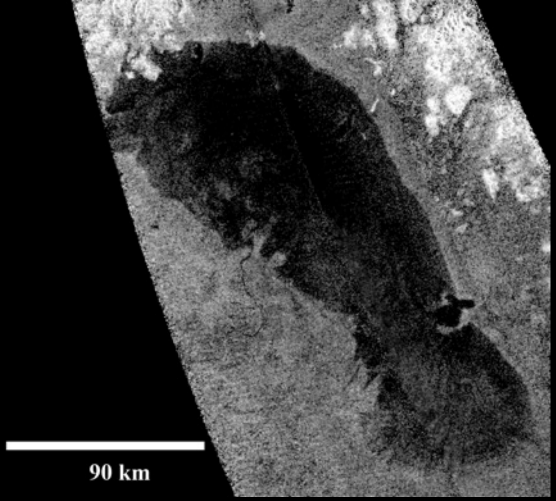
Long timeframe

	Surface flux high	Surface flux low
Solubility high	ethylene[1] acetylene HCN	*n*-butane, CO_2
Solubility low	acetonitrile acrylonitrile 1,3-butadiene cyanoacetylene	benzene cyanogen butadiyne propyne
	Polymer materials	H_2O

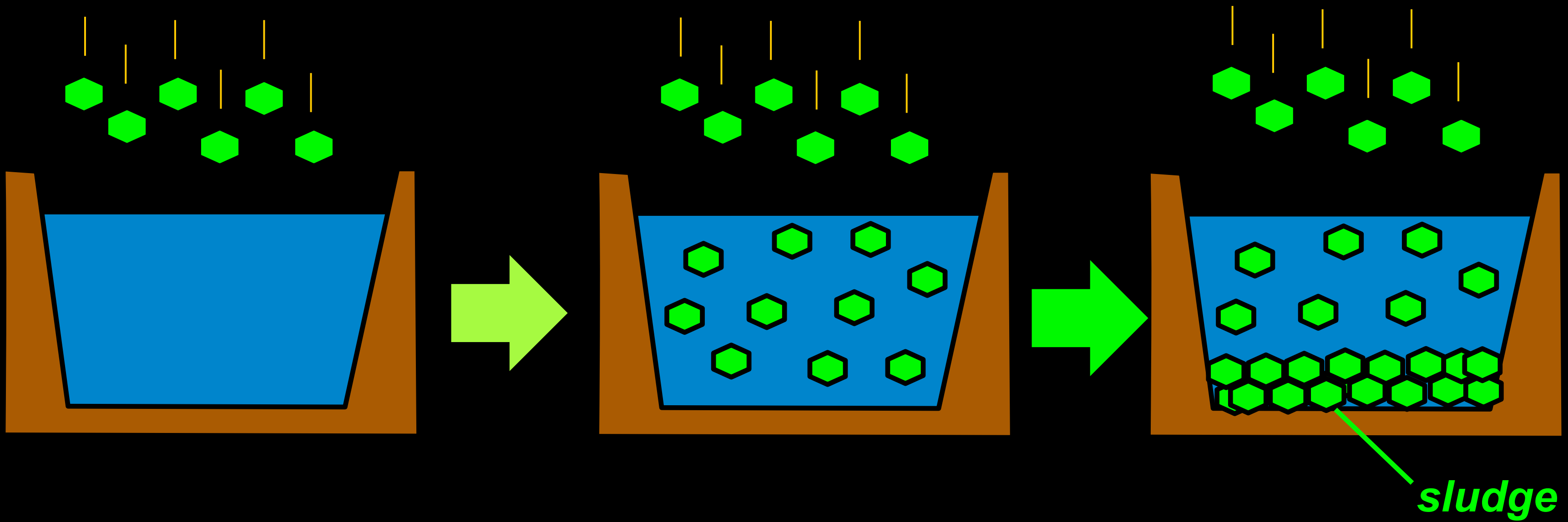
[1] not produced in Krasnopolsky, 2009 model

Other implications

Ontario Lacus will be saturated from benzene falling out of the atmosphere



Ontario Lacus surface: 1.5e4 km^2
Ontario Lacus depth: 10 m
Ontario Lacus volume: 1.5e2 km^3 (= 1.5e14 L)
Benzene atmospheric flux rate [1]: 1e6 molecules cm^{-2} s^{-1}

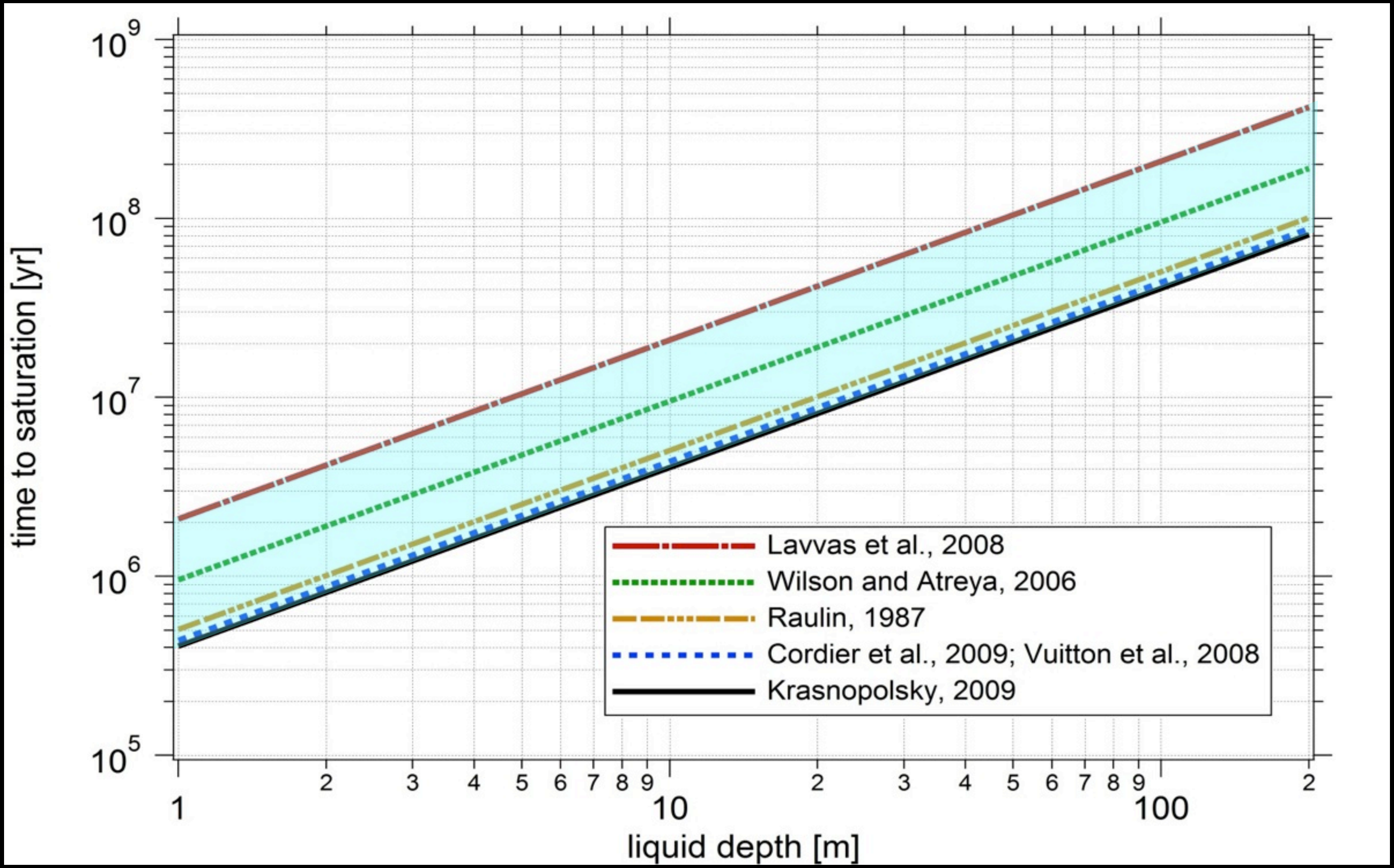


Benzene saturation at 18.5 mg L^{-1} reached in 4.5 Myr

[1] Cordier et al, Ap J 707, L128-L131.

Saturation time of Titan ethane lakes from direct benzene airfall

A 100 m deep ethane lake will saturate in benzene in 100's of Myr

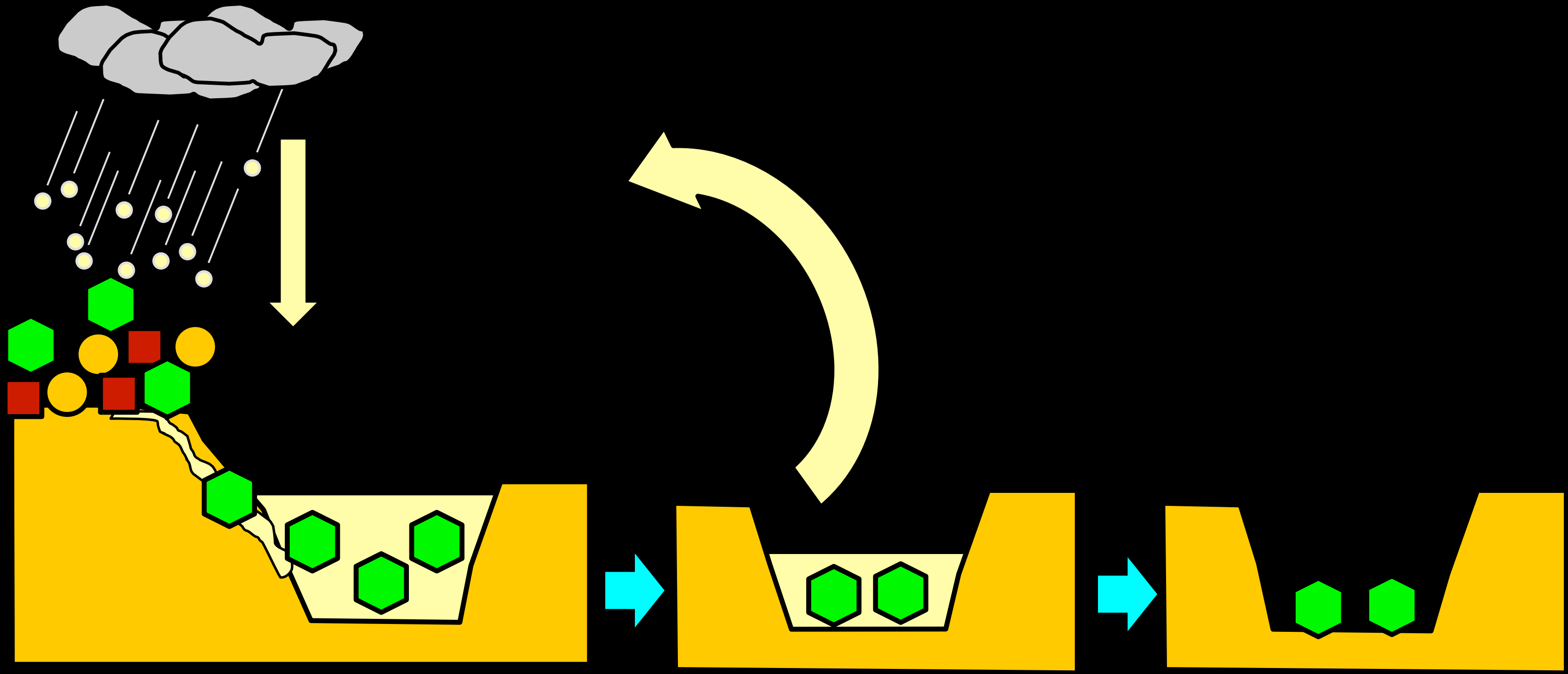


Malaska and Hodyss, Icarus 242 (2014), 74-81.

Evaporites on Titan

Transport and concentration of dissolved organic compounds

Terrestrial playa



1) Initial atmospheric chemistry products

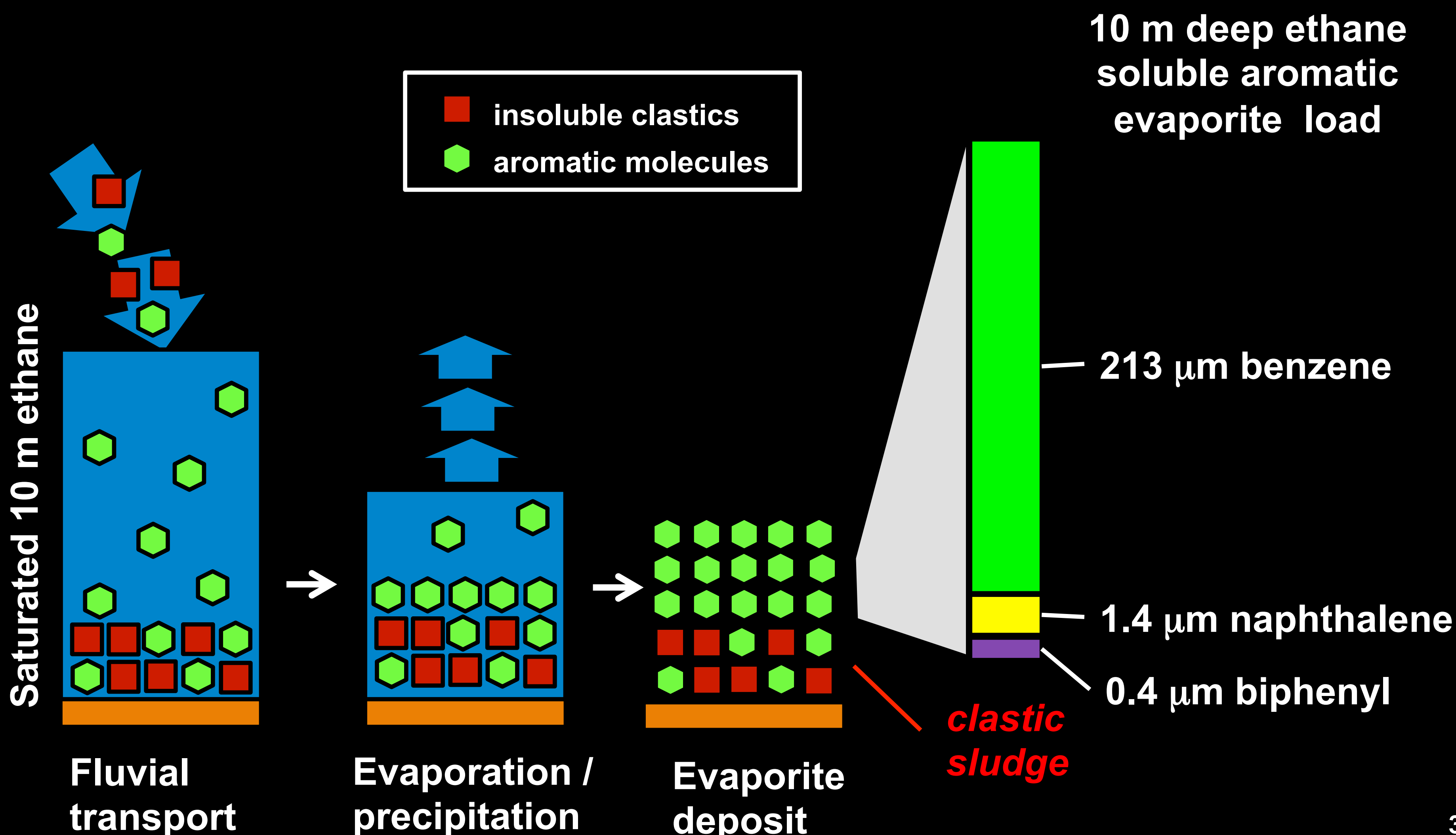
2) Dissolution/transport

3) Soluble organics

4) Lakes dry out

5) Materials precipitate

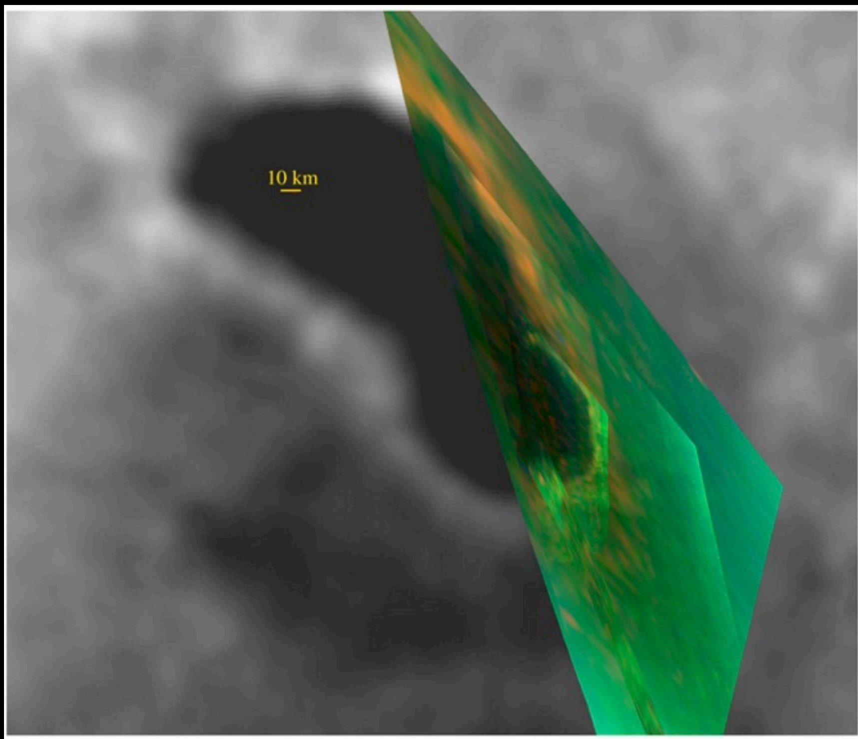
Evaporation of a 10 m deep saturated aromatic-rich ethane → playa deposit

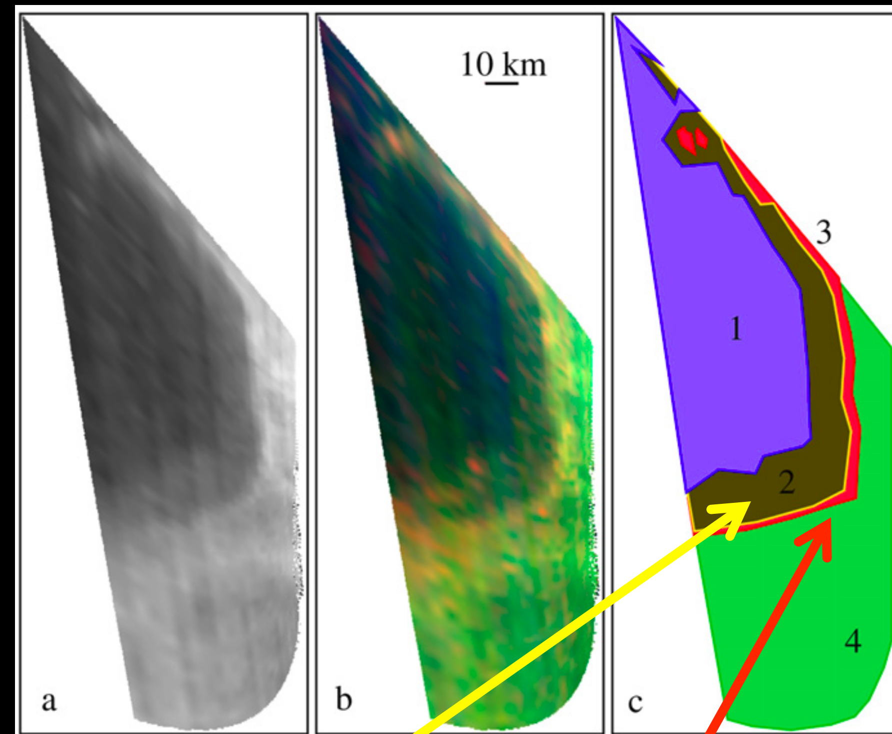


Malaska et al., Workshop on the Habitability of Icy Worlds (2014), Abstract 4020.

Observed Ontario Lacus evaporite deposits

Hyperspectral imaging shows "Bathtub ring"





Ontario Lacus VIMS cubes from T38

Unit 2 is dark organic mudflat

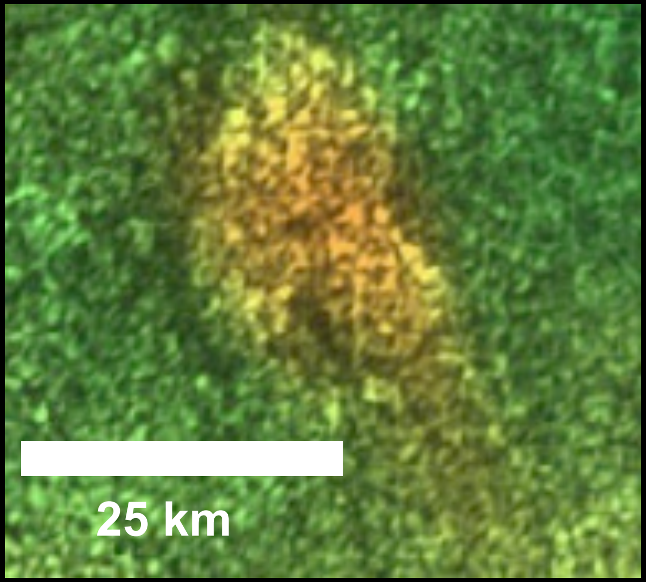
Unit 3 is 5 micron bright organic evaporite deposit

Reference:
Barnes et al., Icarus 201 (2009) 217-225. "Shoreline features of Titan's Ontario Lacus from *Cassini/VIMS* observations." (Fig. 4 and 6)
doi:10.1016/j.icarus.2008.12.028

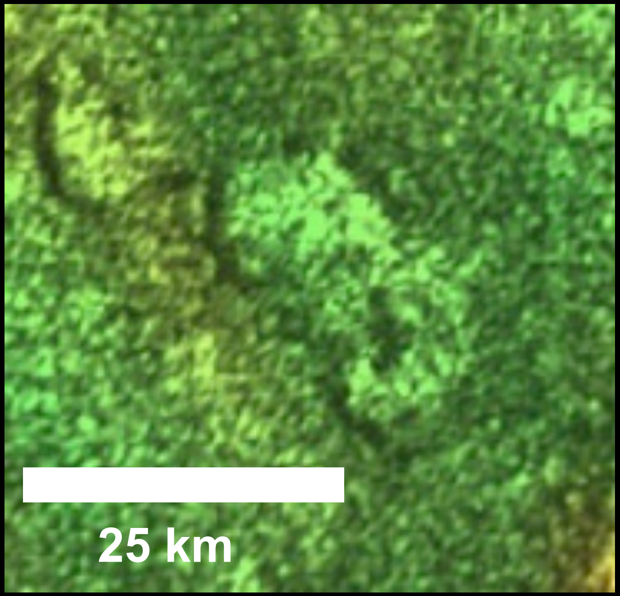
Some Titan dry lakebeds have 5 μm bright evaporite, some don't

SAR radar image + hyperspectral imaging of Titan northern lakes

Cassini SAR RADAR + VIMS RGB[5 μm, 2 μm, 1.28 μm]



Dry lake
+ evaporite

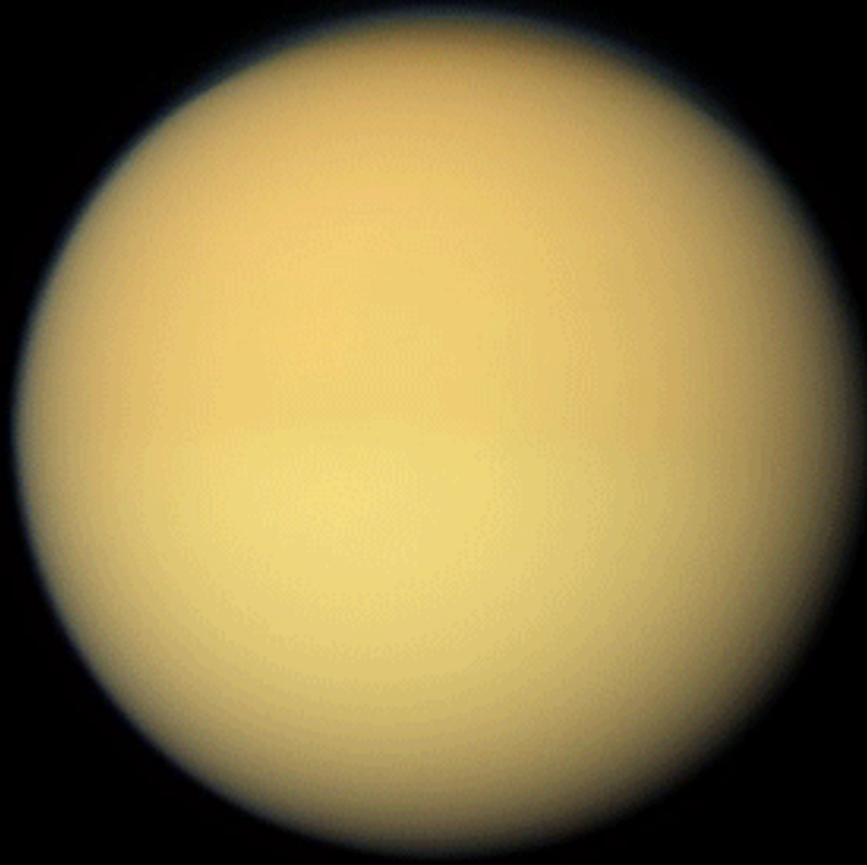


Dry lake only

Closed drainage vs. open drainage?

Barnes et al., Icarus 216 (2011) 136-140. (Figure 2 in text)

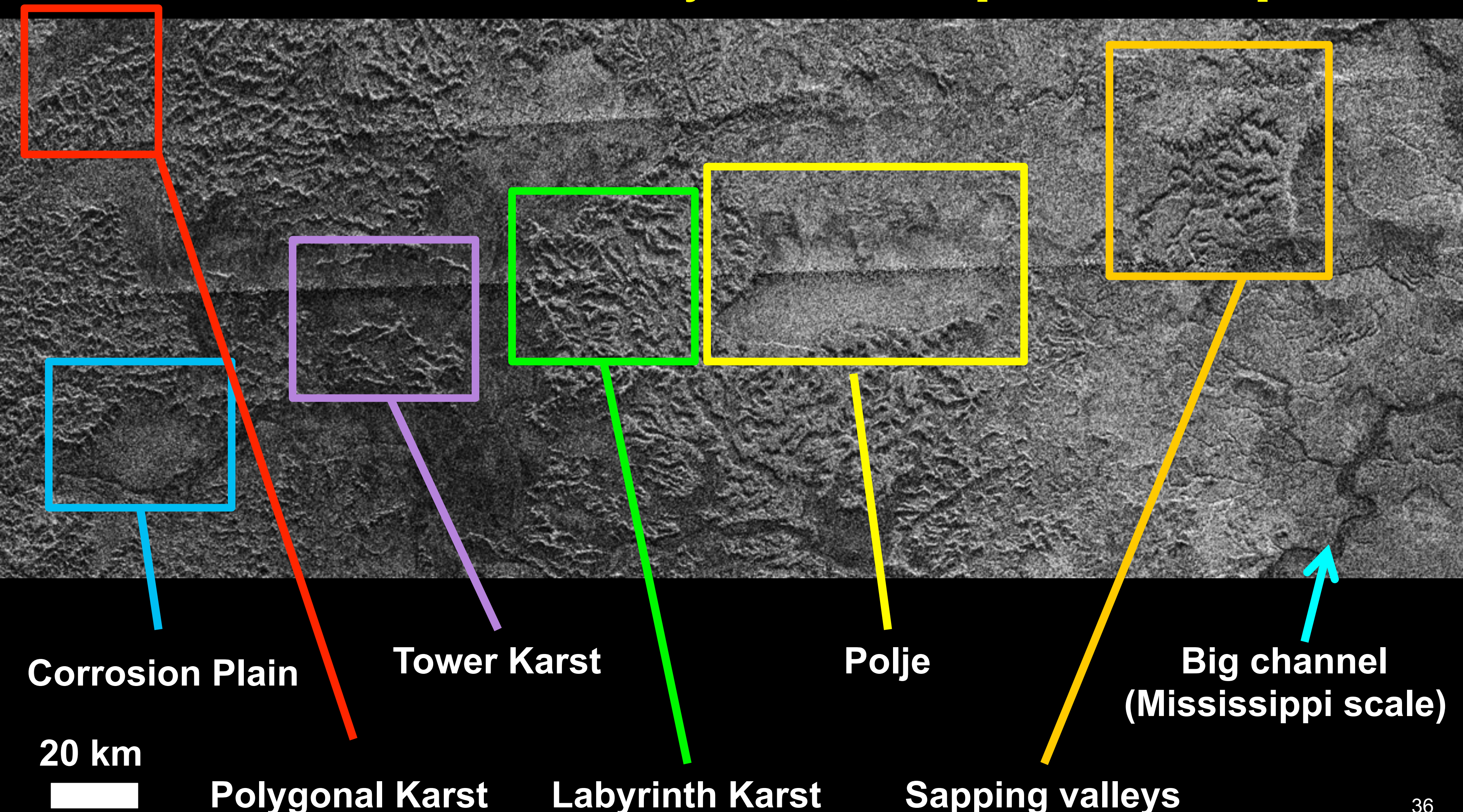
Titan observations



Evidence for dissolution geology from Cassini RADAR

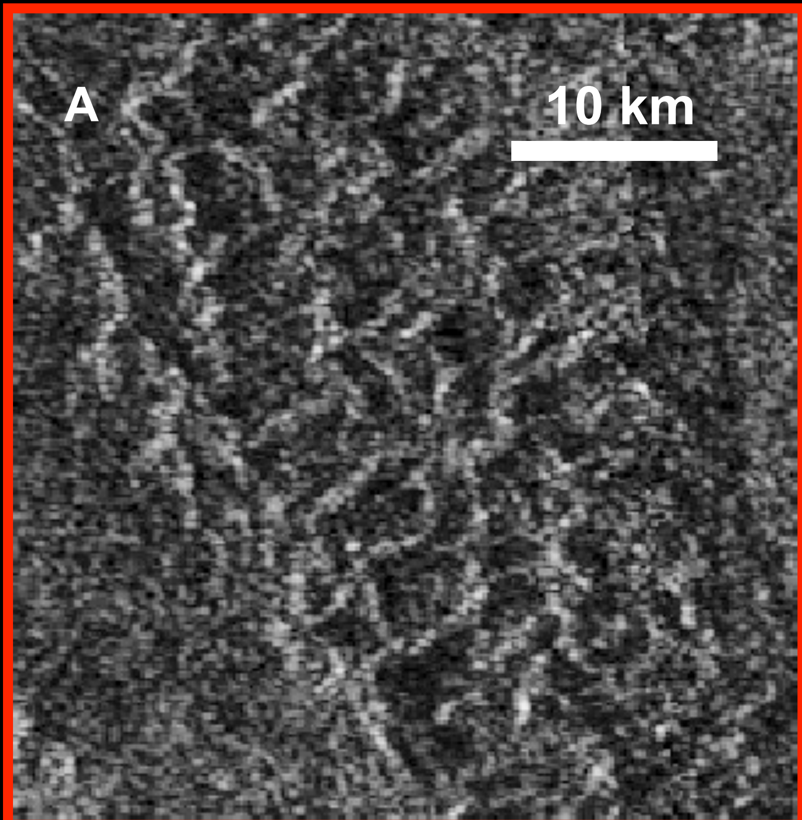
Geomorphological evidence for dissolution geology on Titan

Karst-like features near Sikun Labyrinthus, Titan [77.9 S, 29.8 W]

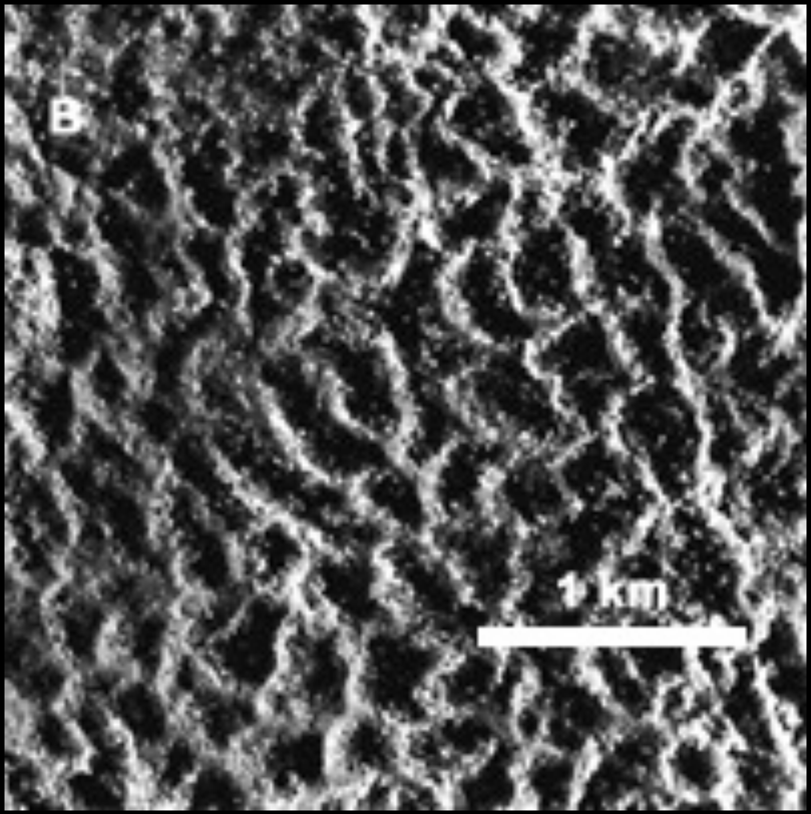


Polygonal Karst-like terrain on Titan

Closed valleys
Structural control of valleys



Polygonal Karst-like terrain,
Ecaz Labyrinth,
Titan [83°S, 38°W]

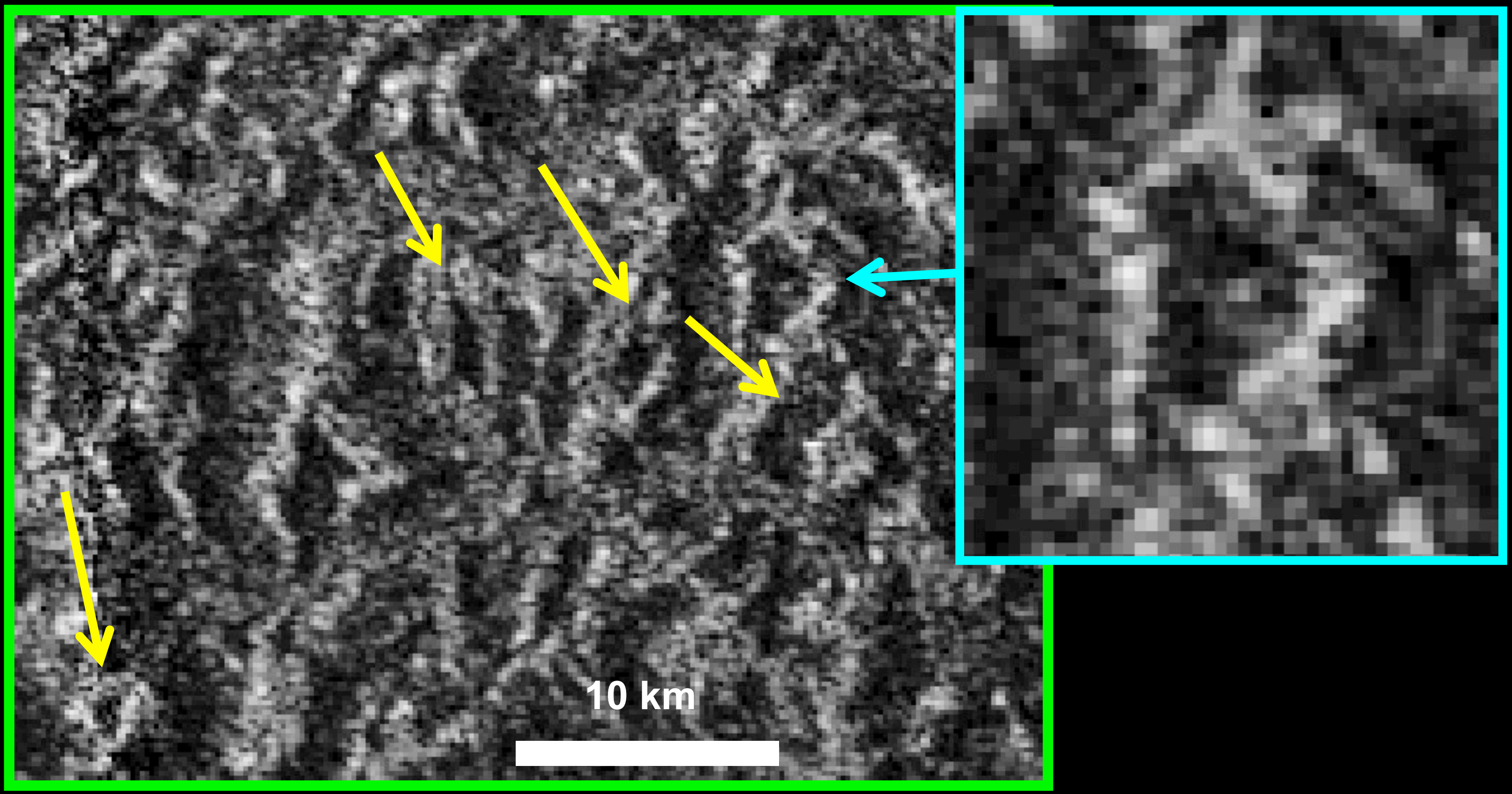


Polygonal Karst,
Darai Hills, Papua New Guinea,
Earth [6.8°S, 143.3°E]
(figure reproduced from [1])

[1] Williams, GSA Bulletin 82 (1972) 761-796.

Closed valleys diagnostic for karst

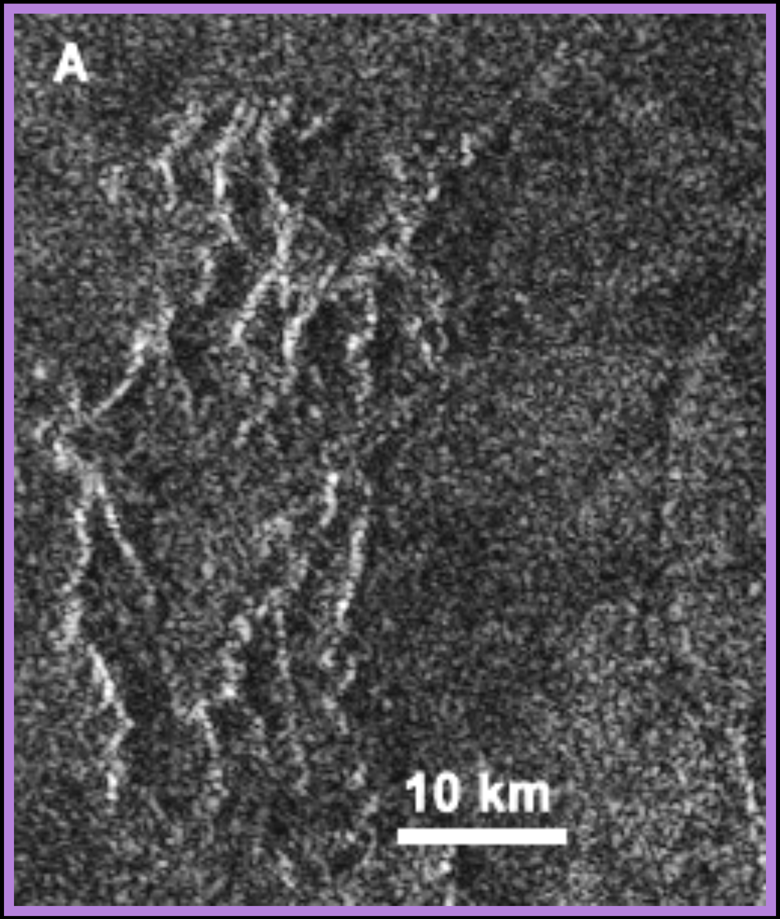
Sikun Labyrinth, Titan



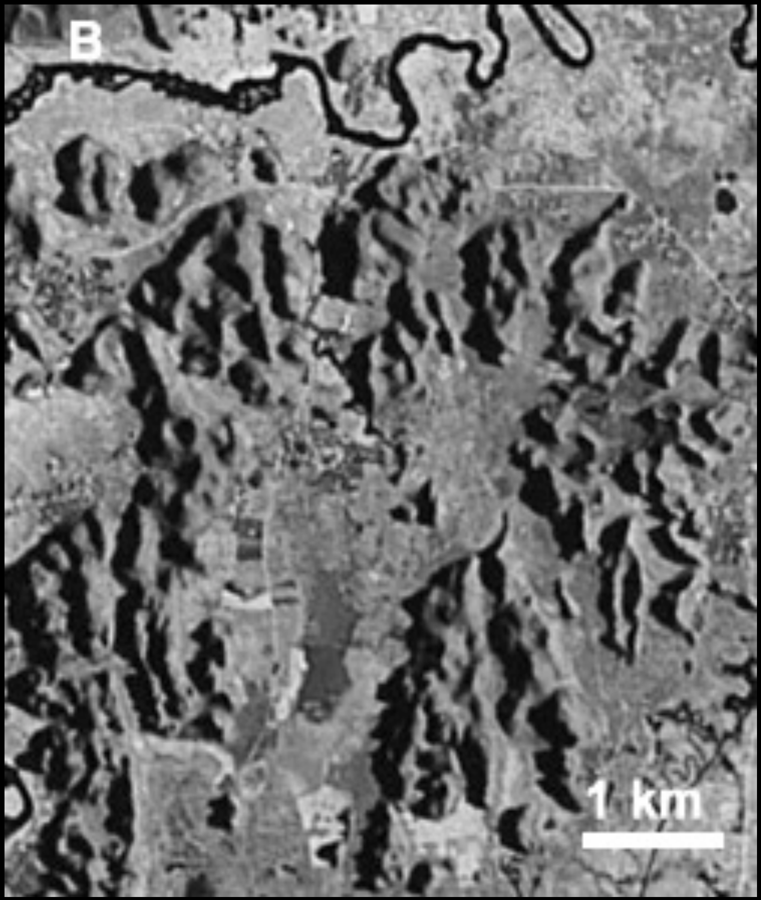
"Karst is always developed when dolines are found and so they can be considered index landforms of karst…" [1]

[1] Ford, D. and Williams, P. "Karst Hydrology and Geomorphology" (2007), Wiley, Chichester, Great Britain.

Tower Karst[1]-like terrain on Titan



Tower Karst-like terrain,
Sikun Labyrinth region,
Titan [80°S, 32.3°W]



Tower Karst, Tanpaixiang,
Guangxi Province, China
Earth [23.4°N, 108.8°E]
(Google Earth image)

[1] U.S. EPA. "A Lexicon of Cave and Karst Terminology with Special Reference to Environmental Karst Hydrology" (2002 Edition). U.S. EPA/600/R-02/003, 2002.

Titan Labyrinth Terrain analog?

Purnululu National Park, Western Australia
Devonian quartz sandstone eroding out to a surrounding sand plain

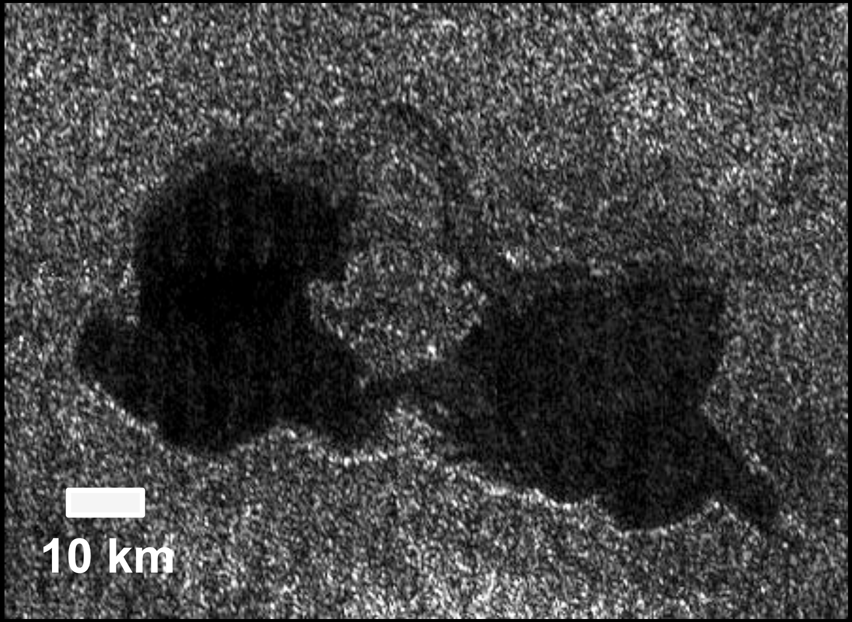
"the most outstanding example of cone karst in sandstones anywhere in the world" **UNESCO**

Image credit: Philip Griffin

Titan similarities to Earth sinkhole lakes

SAR RADAR image of hydrocarbon karst-like lake on Titan

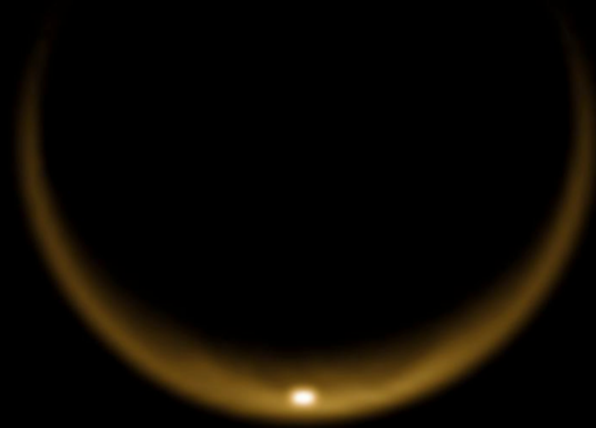
Titan



Abaya Lacus
"Kissing Lakes" T16 SAR
Titan [73°N, 47°W]

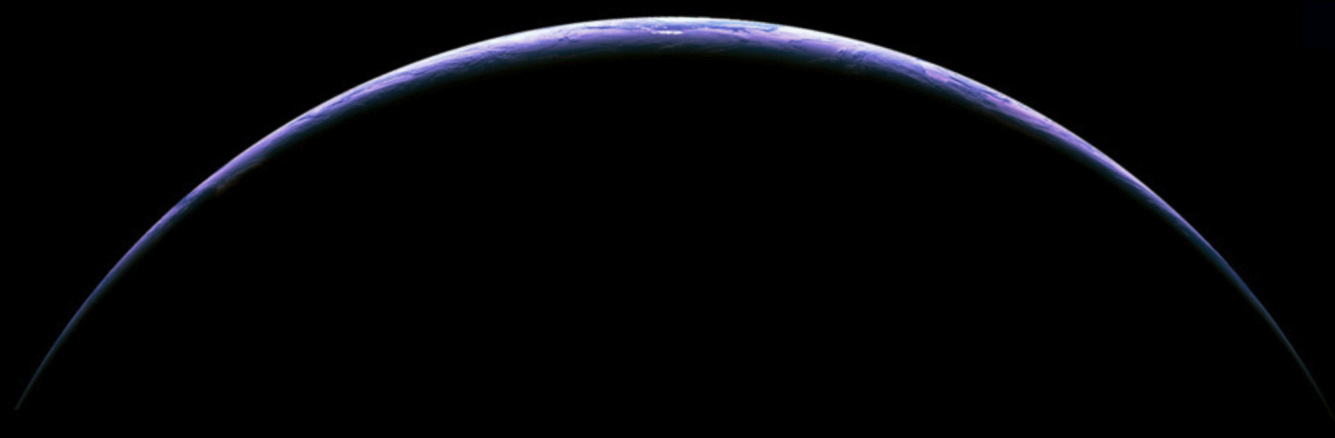
Earth

Lazy Lagoon in a gypsum plain,
Bottomless Lakes State Park, NM
Earth [33.3°N, 104.3°W]
(Google Earth image)



Dissolution geology on Titan

Theoretical calculations?	Yes
Laboratory simulation?	Yes
Observed evaporite deposits?	Yes
Geomorphological evidence?	Yes



Planetary dissolution geology – a general process?

Circulating fluids [Example: H_2O – hydrocarbons]
Soluble matrix [Example: salts – organic molecules]
Solvent exposure [fluid flux X duration]

Outtake

What happens when apparatus heater connections fail?
→ Ethane freezes around 90 K

16x actual speed

(Fiber-optic ATR probe)

Ethane freezes from the bottom, like a normal material.
Dissolved N_2 exsolvates and bubbles out.