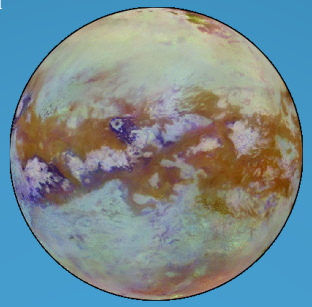
Effect of ammonia on the stability of tetrahydrofuran and cyclopentane clathrate hydrates

Claire PETUYA, *NASA Posdoctoral Program (NPP)*
Jet Propulsion Laboratory, California Institute of Technology

Titan



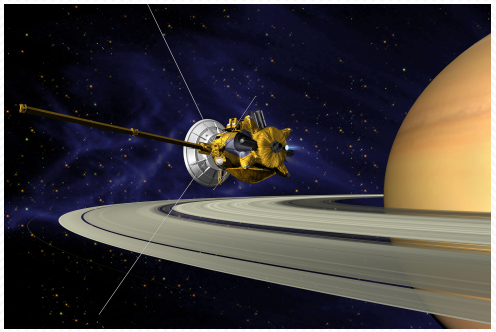
Visual and IR mapping spectrometer

Image credit: NASA/JPL/University of Arizona/University of Nantes

JPL advisor – *Mathieu Choukroun*
JPL coworkers – *Tuan Vu, Ashley Davies, Christophe Sotin*

Context

- ✓ Cassini/Huygens mission, 1997-2017 (NASA-ESA-ASI): to send a probe to study planet Saturn and its system (rings and natural satellites like Titan, Enceladus, Tethys…etc.).



Artist's concept of *Cassini*'s orbit insertion around Saturn

- ✓ The *Grand Finale* of Cassini mission on September 15th 2017 by destroying the spacecraft into Saturn's atmosphere to ensure and prevent biological contamination to any of the moons of Saturn, thought to offer potential habitability.

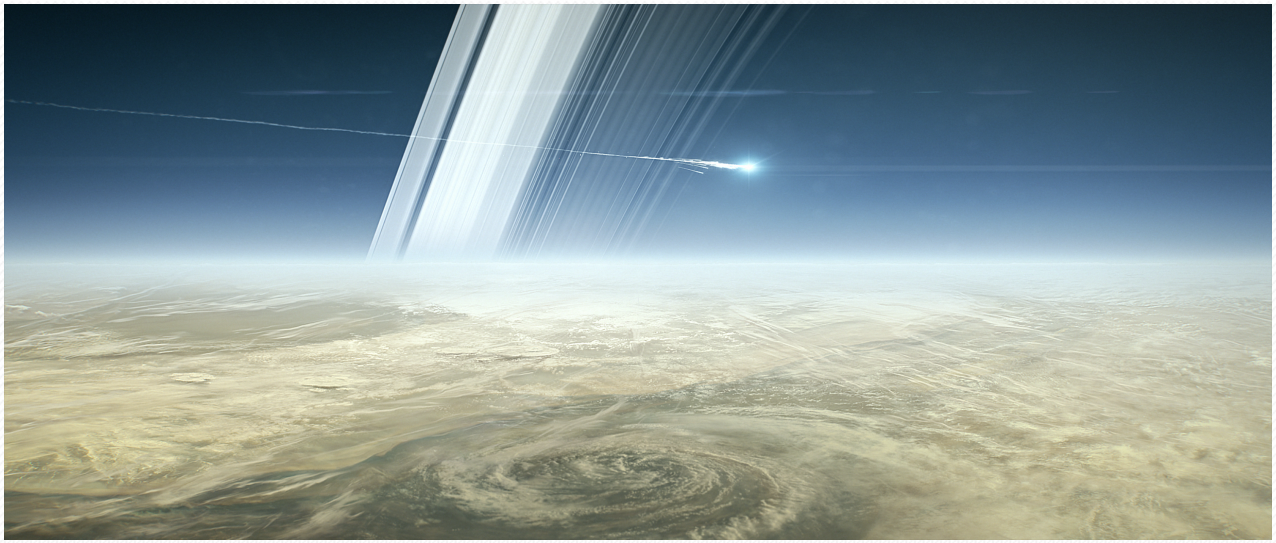


Image Credit: NASA/JPL-Caltech/Space Science Institute

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Members of the JPL Media Relations and Public Engagement offices, and leaders of the Cassini Mission received an Emmy for Outstanding Original Interactive Program for its presentation of the Cassini mission's Grand Finale at Saturn.

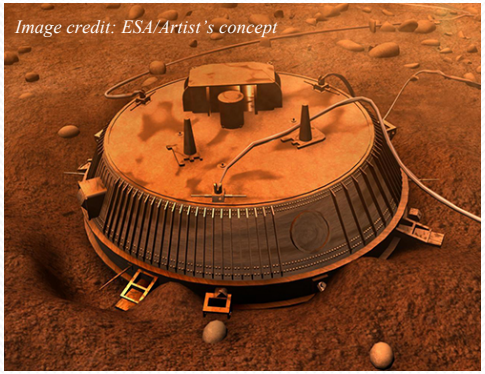
Image Credit: NASA/JPL-Caltech/Space Science Institute

Context

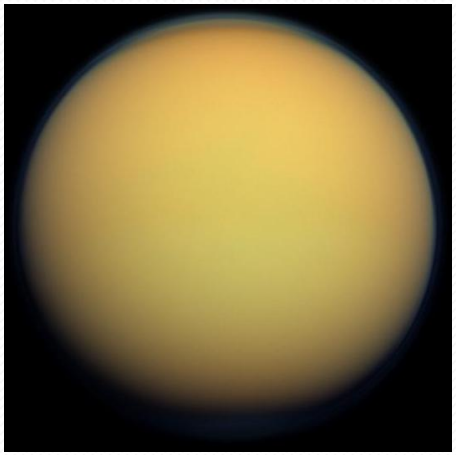
- ✓ ESA's Huygens lander landed on Titan in 2005 and helped better understand Titan's atmosphere and surface features.

- ✓ Titan is the largest moon of Saturn and the second-largest natural satellite in the Solar System. It is the only moon known to have a dense atmosphere

2.25 hour descent through the atmosphere of Titan



Transmit data for more than 1h on Titan's frigid surface



Titan in natural color. The thick atmosphere is orange due to a dense organonitrogen haze.

Images from ESA's Huygens probe descent imager/spectral radiometer side-looking imager and from the medium resolution imager, acquired after landing, were merged to produced this image.

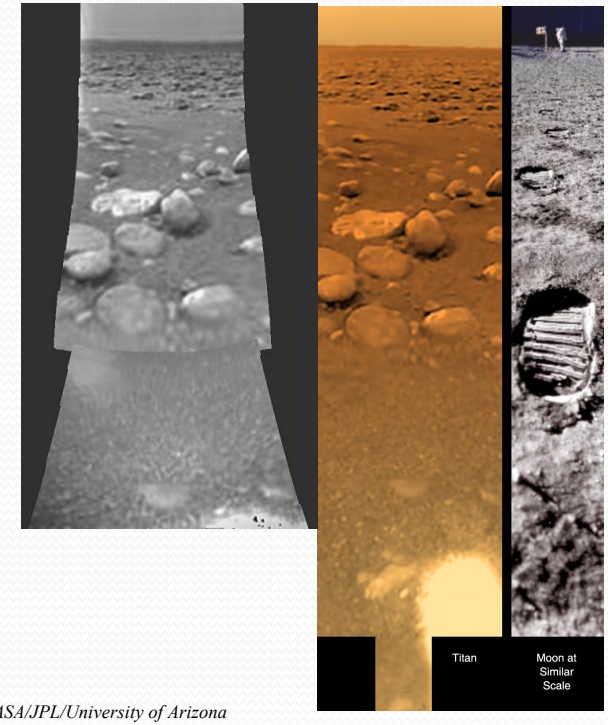


Image Credit: NASA/JPL-Caltech/Space Science Institute

Image Credit: ESA/NASA/JPL/University of Arizona

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- ✓ ESA's Huygens lander landed on Titan in 2005 (Saturn's largest moon) and helped better understand Titan's atmosphere and surface features.
- ✓ Discovery of **seas** and **lakes** of liquid methane and ethane on Titan's surface, near its pole, replenished by rain from hydrocarbon clouds (first observation of surface liquid on any other world than Earth).

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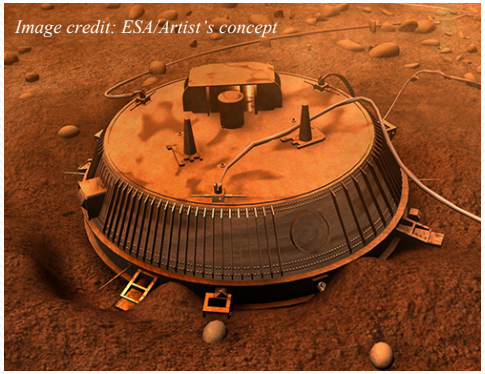

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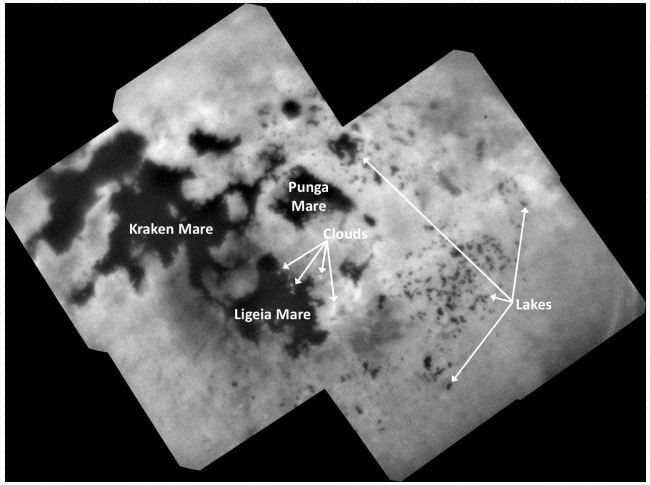

Titan Lakes by ISS – Narrow Angle instrument

Image Credit: NASA/JPL-Caltech/Space Science Institute

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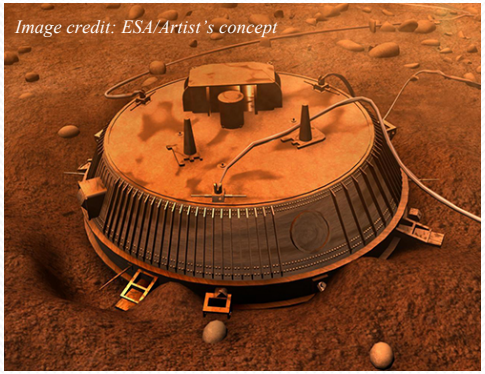

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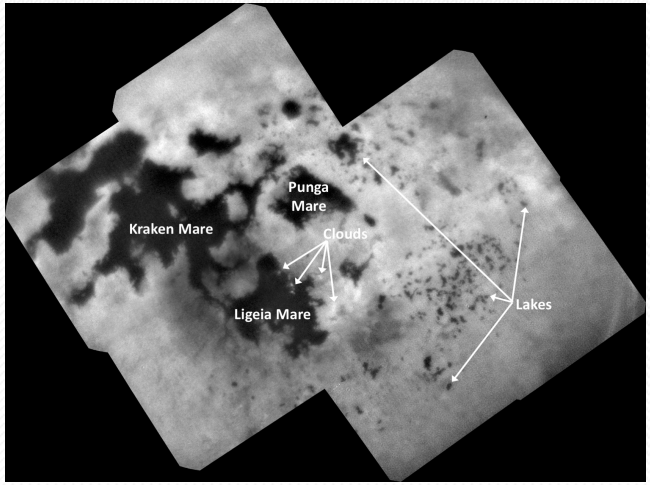

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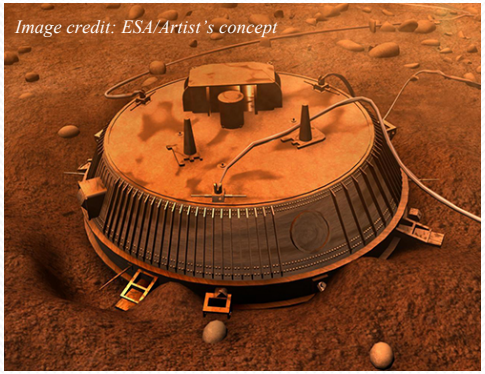

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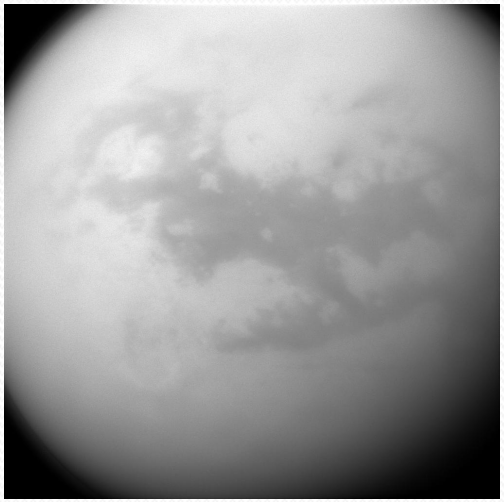

Dunelands by ISS – Narrow Angle instrument

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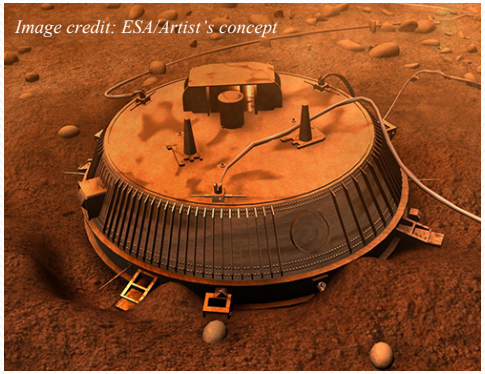
- ✓ Rippling **sand dunes** can be seen in the dark equatorial regions of Titan. Sand would be made of solid water ice coated with hydrocarbons that fall from the atmospehre
- ✓ Titan is the only other place in the solar system known to have an Earth-like **cycle of liquids** flowing across its surface as the planet cycles through its seasons
  - ✓ First high-resolution images and up-close scientific analysis.

2.25 hour descent through the atmosphere of Titan



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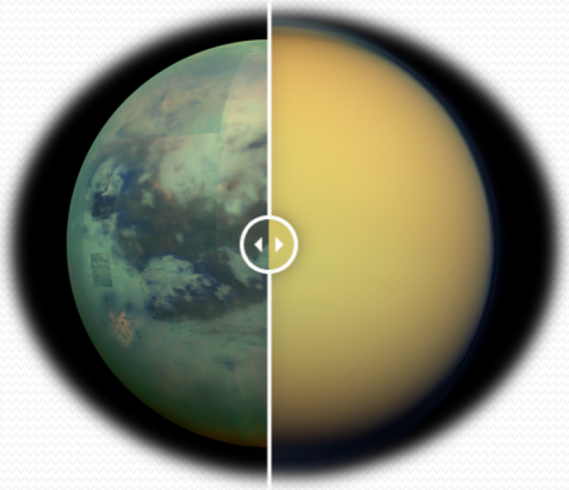


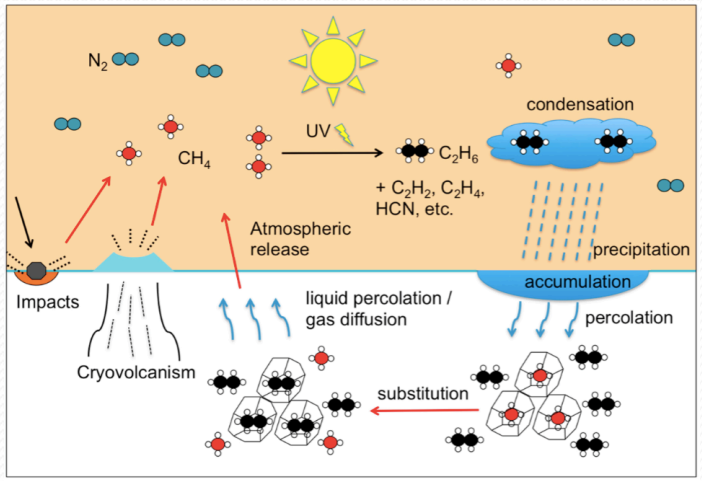
VIMS spectrometer allows to see the surface hidden beneath a thick atmosphere (organonitrogen haze).

Image Credit: NASA/JPL-Caltech/Space Science Institute/University of Arizona/University of Idaho

Context

Titan's features:

- ✓ Dense atmosphere: 94-98% N_2, 1.4-5% CH_4, 0.2% H_2, 1.5 bar (surface pressure)
- ✓ Cold temperatures: 94 K (surface temperature)
- ✓ Allow clathrate hydrates to be thermodynamically stable even on its surface
- ✓ Rich hydrocarbon cycle with surface lakes and seas of methane and ethane
- ✓ Complex atmospheric photochemistry

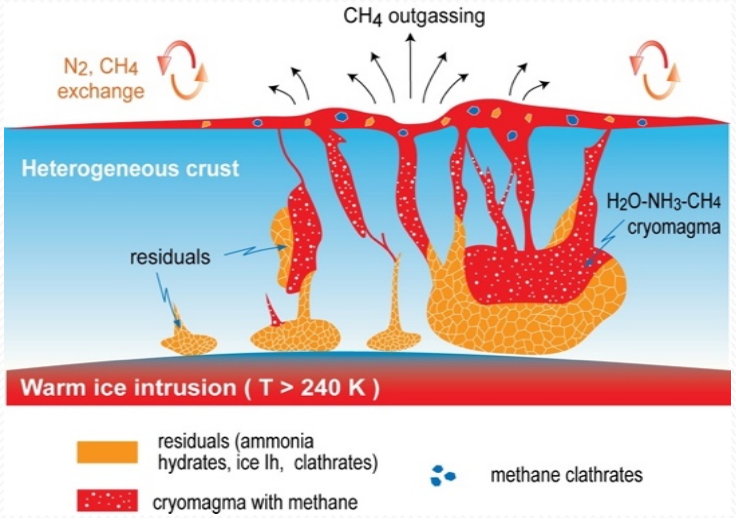


- ✓ Active photochemistry and solar winds should have make the current amounts of CH_4 disappear in 30-100 Myrs

➔ replenishment processes from the interior (cryovolcanism)

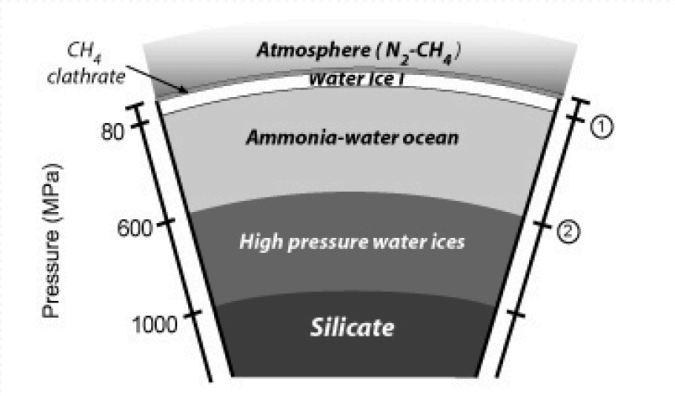
➔ Cryovolcanism is not enough to explain the amount of CH_4 released

- ✓ Methane clathrate hydrates likely coexist in Titan's icy shell with water ice Ih and ammonia hydrates

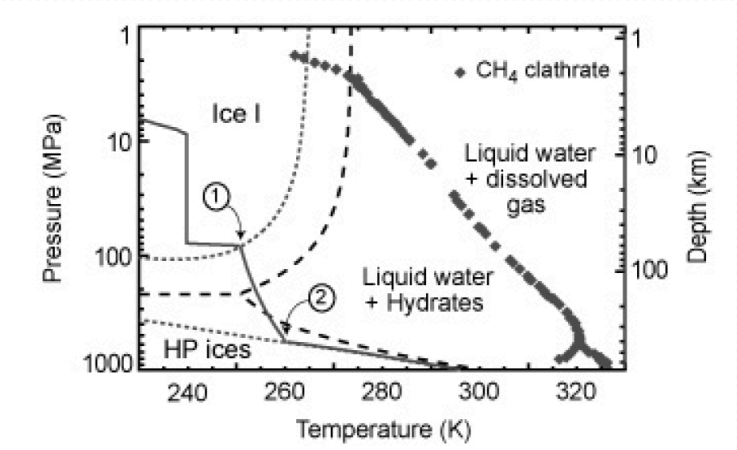


Context

- ✓ Huygens probe data provided the evidence that NH_3 is the primordial source of Titan's atmospheric N_2
- ✓ NH_3 is a strong antifreeze agent and induces incongruent melting point of water ices between the eutectic and the liquidus temperature
- ✓ This partial melting of ice have been suggested to promote cryovolcanism, possibly through the dissociation of surrounding clathrates, and expansion of methane gas released



Schematic structure of Titan. The MH reservoir could be located either above or below the ice I crust
Tobie G. *et al.*, *Nature*, **2006**



Phase diagram of H_2O in the pure water case (dashed) and in presence of 5% of NH_3 (dotted); MH dissociation curve and Titan's internal profile.
Choukroun M. *et al.*, *ALPS Conference*, **2006**

- ✓ The interaction between ammonia and clathrate hydrates are poorly understood

THF-H_2O-NH_3

✓ THF clathrates have a partial dissociation in an aqueous ammonia solution like it is the case for water ice

Experimental Study on the Effect of Ammonia on the Phase Behavior of Tetrahydrofuran Clathrates

Tuan Hoang Vu,[†] Elodie Gloesener,[‡] Mathieu Choukroun,[*,†] Anaïs Ibourichene,[§] and Robert Hodyss[†]

[†]NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109, United States

[‡]Observatoire Royal de Belgique, Avenue Circulaire 3, 1180 Uccle, Belgium

[§]École Normale Supérieure, 45 Rue d'Ulm. 75005 Paris, France

dx.doi.org/10.1021/jp5042487 | *J. Phys. Chem. B* 2014, 118, 13371−13377

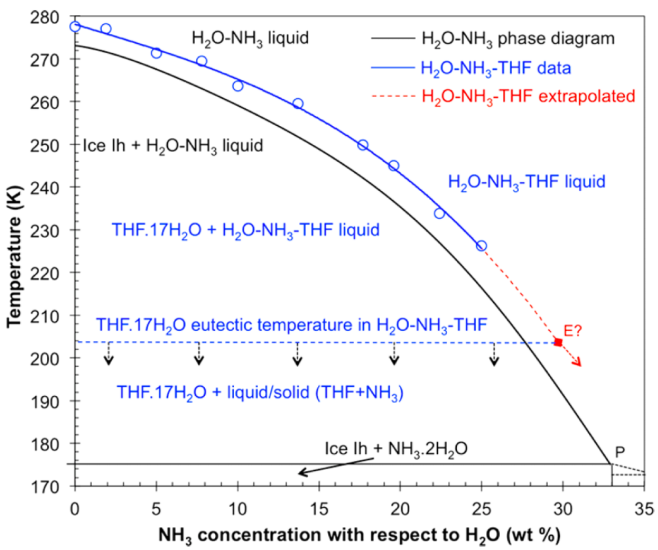
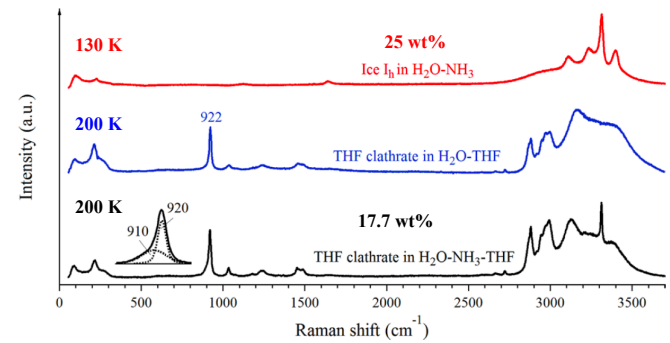


Figure 6. Phase diagrams for the H_2O−NH_3 and H_2O−NH_3−THF systems. THF is supersaturated with respect to the stoichiometry of THF clathrates. The data points are fitted with a third-order polynomial, where E represents the extrapolated eutectic point (arrows indicate potential overestimation of the eutectic temperature by the optical Raman method). P shows the peritectic point of the H_2O−NH_3 system at atmospheric pressure.



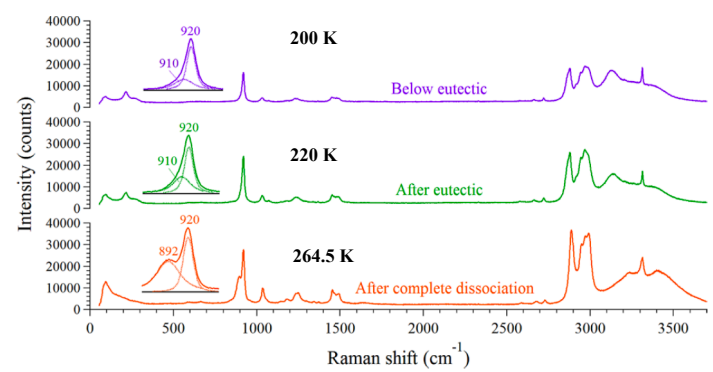


Figure 5. Raman spectra of the H_2O−NH_3−THF system at a concentration of 10 wt % NH_3 at 200 K (top), 220 K (center), and 264.5 K (bottom). Spectra are acquired at the same spot under the exact same experimental conditions, except for the temperature, and are plotted on the same vertical scale. Note the increase in the relative intensity of the C−H stretch region as THF is released from the dissociated clathrate. The inset shows peak deconvolution performed with Voigt profiles for the ring breathing mode of THF.

THF-H_2O-NH_3

Phase Diagram of the Ternary Water–Tetrahydrofuran–Ammonia System at Low Temperatures. Implications for Clathrate Hydrates and Outgassing on Titan

Victoria Muñoz-Iglesias, Mathieu Choukroun,* Tuan H. Vu, Robert Hodyss, Ahmed Mahjoub, William D. Smythe, and Christophe Sotin

Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109, United States

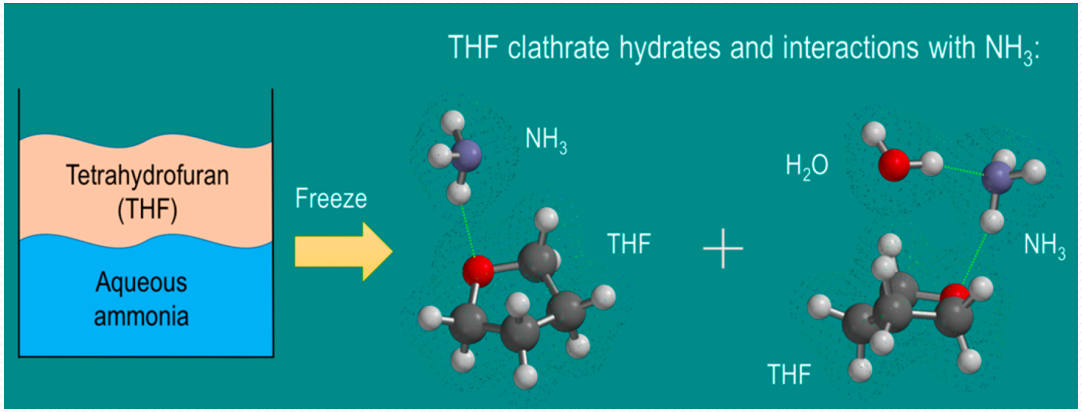
ACS Earth Space Chem. 2018, 2, 2, 135-146

- ✓ Study of the phase behavior of the H_2O-NH_3-THF ternary system

  P=1 bar; T=[77-280K]; [NH_3] up to 29.3wt%

  Different THF:H_2O (1:17) molar ratio ➔ Superstochiometric THF (THF in excess) or Understochiometric THF (H_2O in excess)

- ✓ Differential Scanning Calorimetry (**DSC**) ➔ to determine phase transitions as function of temperature and concentration
- ✓ **Raman** spectroscopy ➔ to identify the phases present and their evolution in aqueous ammonia solutions



- ✓ Ammonia promotes the start of a partial dissociation of THF-clathrates at temperatures far colder than the liquidus
- ✓ The H_2O-NH_3-THF ternary system exhibits a complex chemistry with multiple phases forming in thermodynamic equilibrium

THF-H_2O-NH_3

- ✓ Phases formed:
  - THF clathrates: **1** THF : **17** H_2O
  - Ammonia hydrates: H_2O-NH_3, $2H_2O$-NH_3
  - A new THF-NH_3 rich phase
  - Mixed THF-NH_3 clathrates (potentially)
  - Separation between THF-dominated liquid and H_2O-NH_3 dominated liquid phases

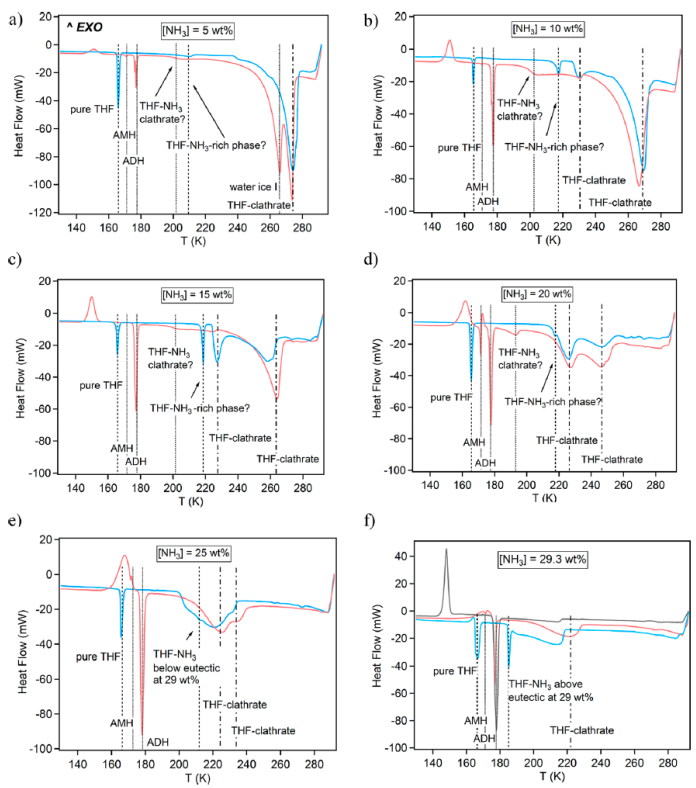
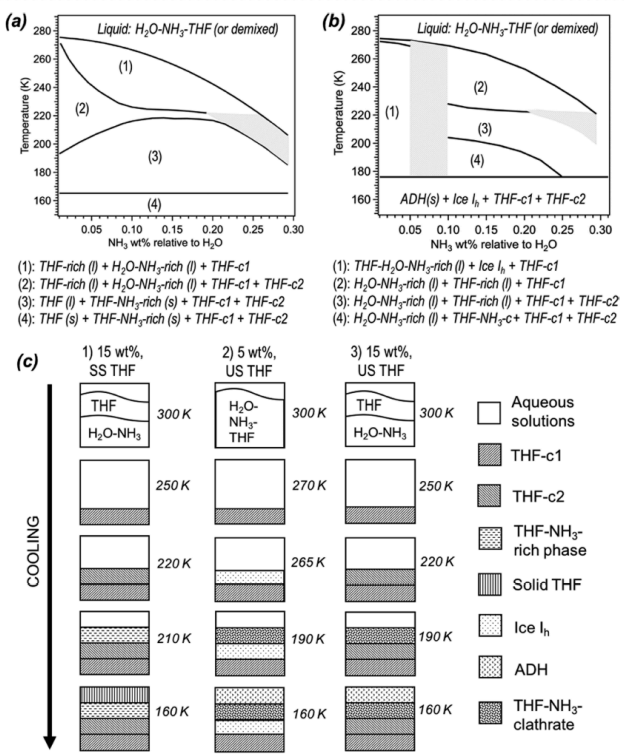


Figure 1. Thermograms of the ammonia aqueous solutions at 5 wt % (a), 10 wt % (b), 15 wt % (c), 20 wt % (d), 25 wt % (e), and 29.3 wt % (f) with understoichiometric THF (red) and superstoichiometric THF (blue). The corresponding thermogram of ammonia aqueous solution at 29.3 wt % (gray) is also shown in (f) for comparison. In the thermograms, positive heat flow values indicate exothermic processes (e.g., crystallization of a glassy phase), whereas negative values indicate endothermic reactions (such as melting or clathrate dissociation).



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THF-H_2O-NH_3

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  - Ammonia hydrates: H_2O-NH_3, $2H_2O$-NH_3
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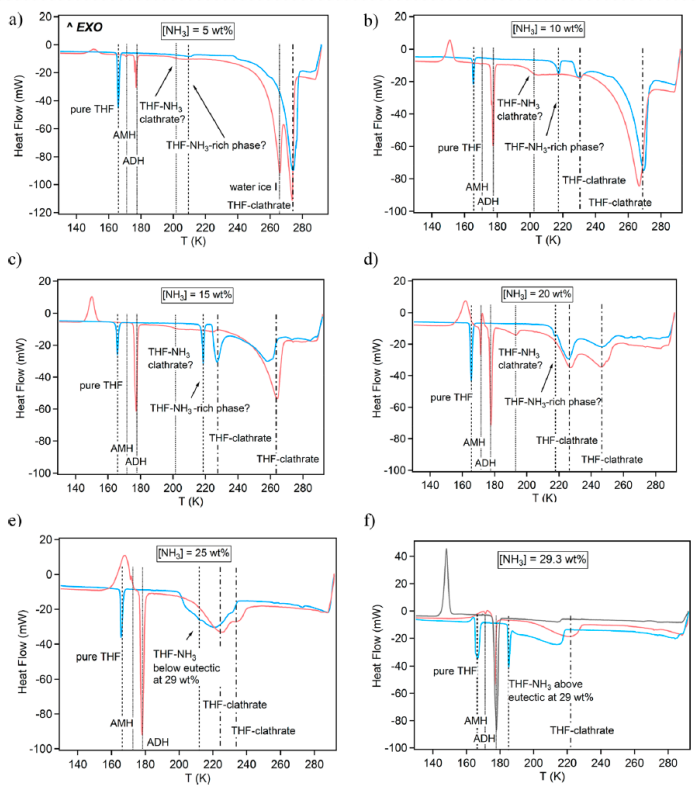

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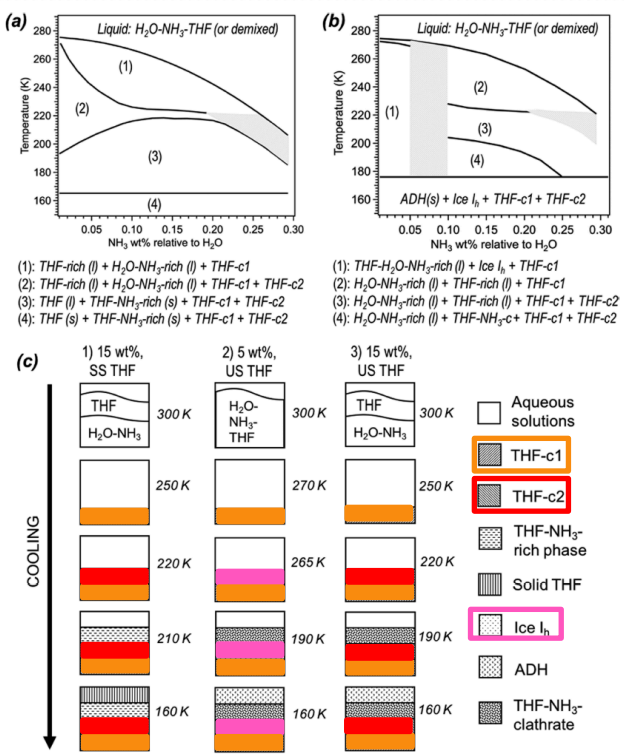

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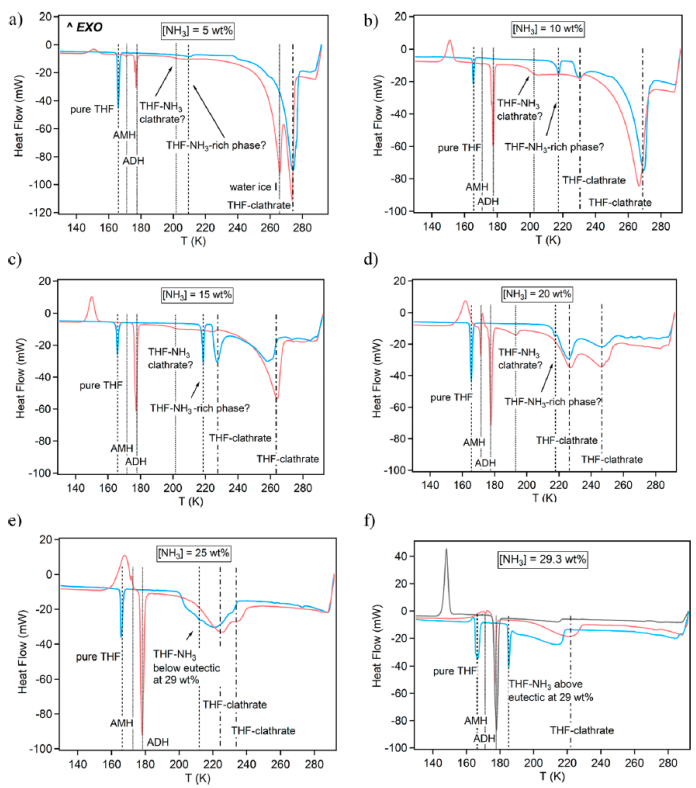

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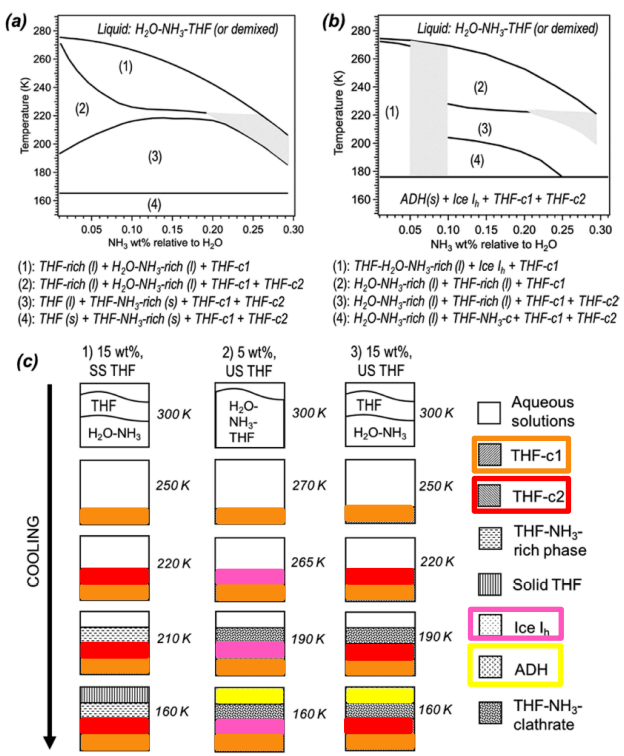

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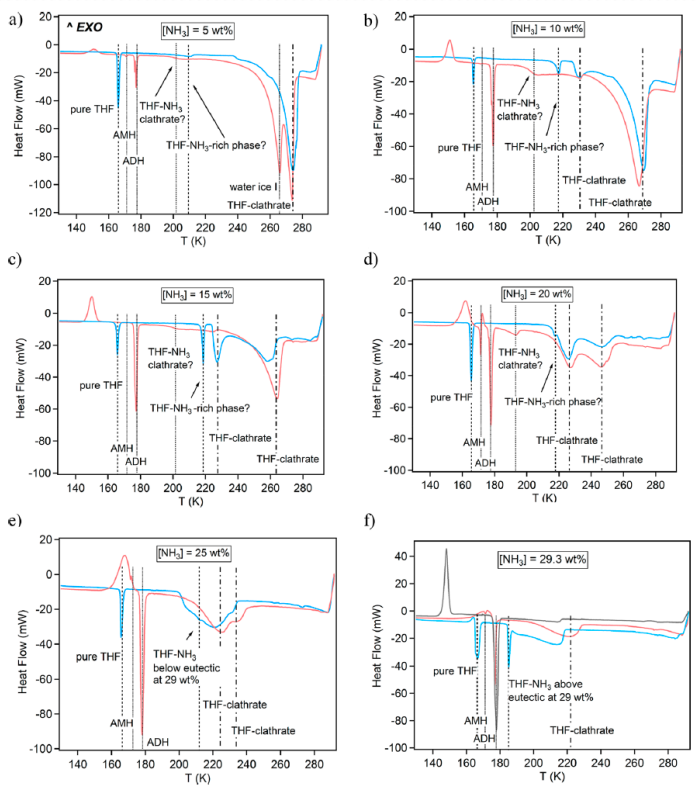

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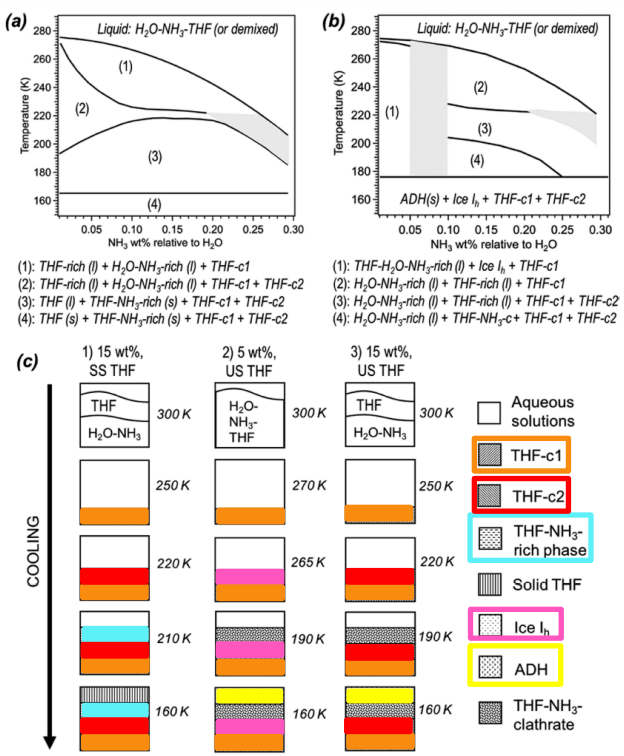
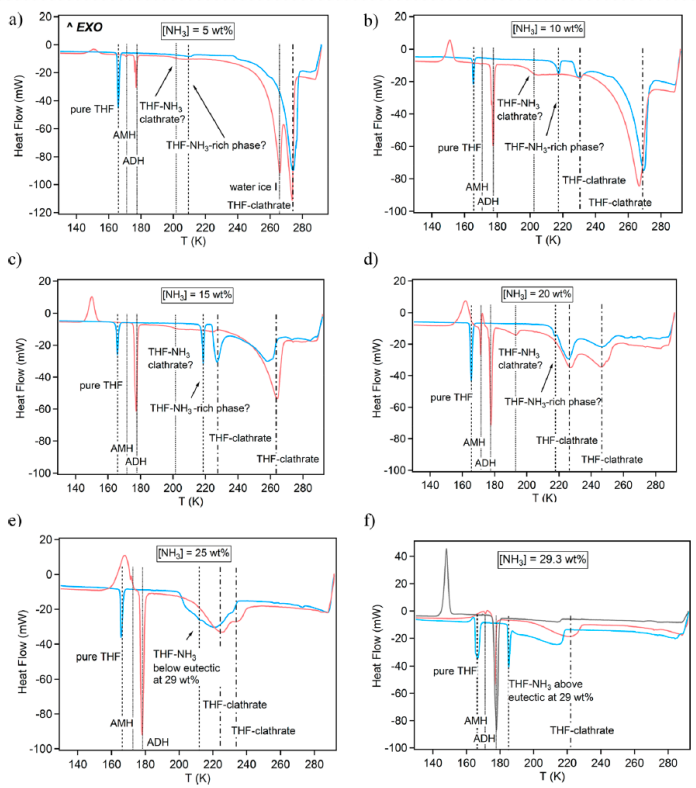


Figure 5. Top: Interpreted phase diagrams of the H_2O–NH_3–THF system at ammonia concentrations up to 29.3 wt % and superstoichiometric THF (panel a) and understoichiometric THF (panel b) conditions. Shaded areas indicate portions of the phase diagrams where transitions between fields are observed but their exact temperature location remains uncertain. Bottom (panel c): Conceptual crystallization sequences for three different cases: (1) superstoichiometric THF conditions, (2) understoichiometric THF conditions and NH_3 concentrations <10 wt %, and (3) understoichiometric THF conditions and NH_3 concentrations >10 wt %. The boxes are solely for graphical representation and their size does not reflect the proportions of each compound formed.

THF-H_2O-NH_3

- ✓ Phases formed:
  - THF clathrates: **1** THF : **17** H_2O
  - Ammonia hydrates: H_2O-NH_3, $2H_2O$-NH_3
  - A new THF-NH_3 rich phase
  - Mixed THF-NH_3 clathrates (potentially)
  - Separation between THF-dominated liquid and H_2O-NH_3 dominated liquid phases



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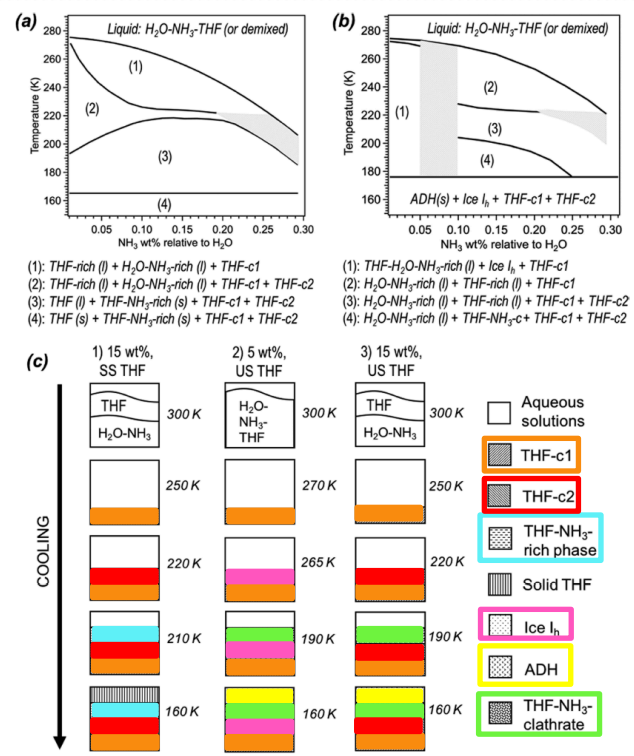

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THF-H_2O-NH_3

To sum up

- ✓ The presence of aqueous NH_3 promotes partial dissociation of THF clathrates between 200 K and 280 K.
- ✓ The effect of NH_3 on THF clathrates is the same as on water ice, suggesting it is the formation of hydrogen bonds with the H_2O skeleton that is responsible for these effects.
- ✓ This process is anticipated to occur in a similar fashion with all species forming clathrates on Titan.

- ✓ They suggest that the partial dissociation of CH_4 clathrate hydrates could result in a slow but steady release of CH_4 to the atmosphere of Titan.
- ✓ 10% of partial dissociation of the predicted CH_4 clathrate reservoir would released enough CH_4 to sustain the hydrocarbon cycle for 650 Myrs.
- ✓ This process may not necessarily be associated with specific surface features on Titan.

Aim of my project

- Study the effect of ammonia on CP clathrate hydrates stability
  - Clathrate stable at atmospheric pressure
  - Cyclopentane has a bad solubility in water (unlike the THF)

- Study the effect of ammonia on CH_4 clathrate hydrates stability
  - Dissociation curves (DSC and XRD)
  - Storage capacity or even kinetic of the cage filling (Raman)

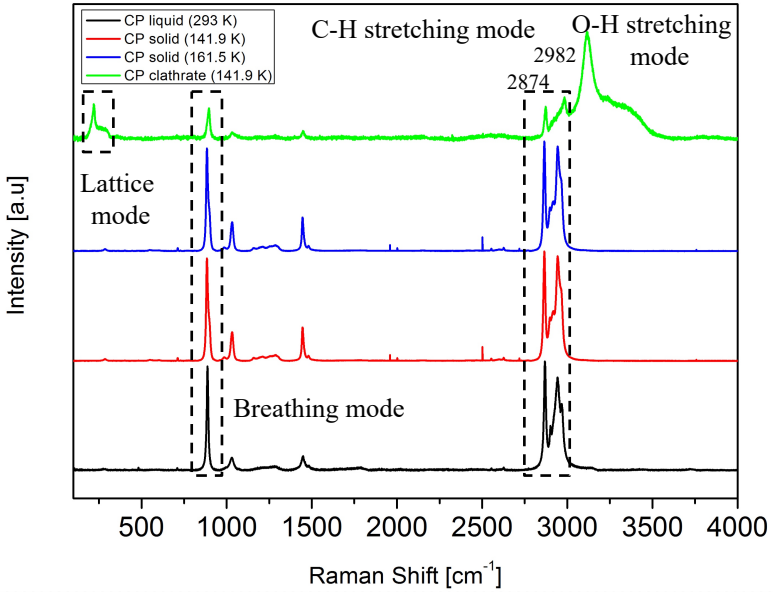
- Geophysical modeling
  - Calculations of thermal profiles
  - Determine extent of partial dissociation for sets of conditions
  - Calculate corresponding methane release

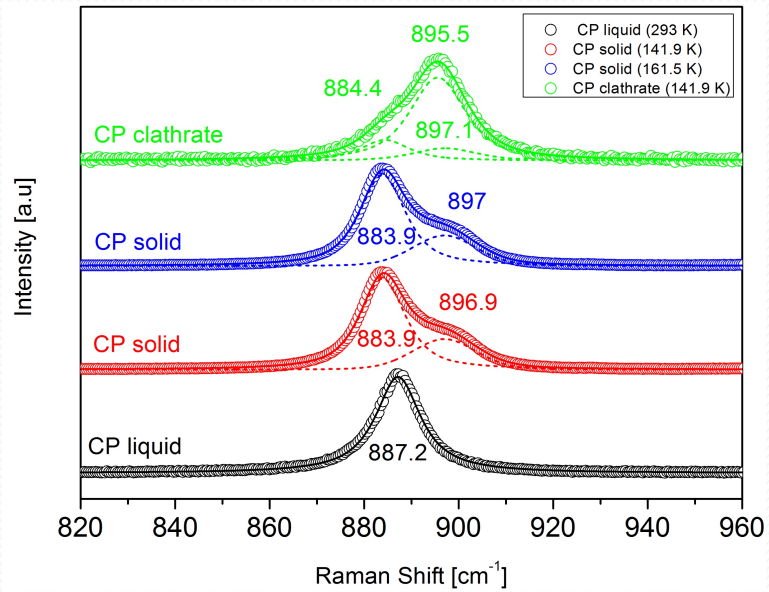
CP-H_2O

- Raman spectroscopy
  - Sample formed in a glovebox to allow the growth of the clathrate hydrate during a day
    - Mixture of 1ml of CP and 3 ml of H_2O
    - T=271K ± 1 K, P=1 bar
  - Raman features: 532 nm, 50x, 1800 gr/mm (spectral resolution=1.5 cm^{-1}), [100-4000cm^{-1}]

CP phases comparison: T_{melt} (CP) = 179 K

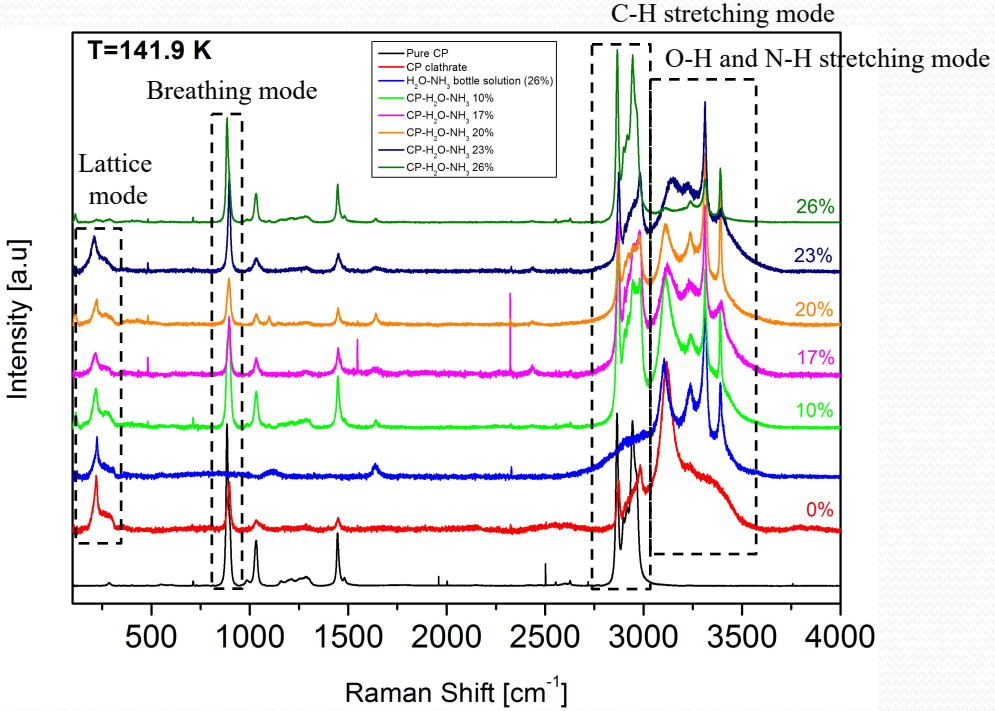
The ring breathing mode





CP-H_2O-NH_3

- Raman spectroscopy
  - Sample formed in a freezer to allow the growth of the clathrate hydrate during a night
    - Mixture of 1ml of CP and 3 ml of H_2O-NH_3
    - NH_3 concentration: 10wt%, 17wt%, 20wt%, 23wt%, 26wt%
    - T=243 K, 228 K, 223 K, 203 K, 198 K (respectively with the NH_3 concentration), P=1 bar
  - Raman features: 532 nm, 50x, 1800 gr/mm (spectral resolution=1.5 cm^{-1}), [100-4000cm^{-1}]



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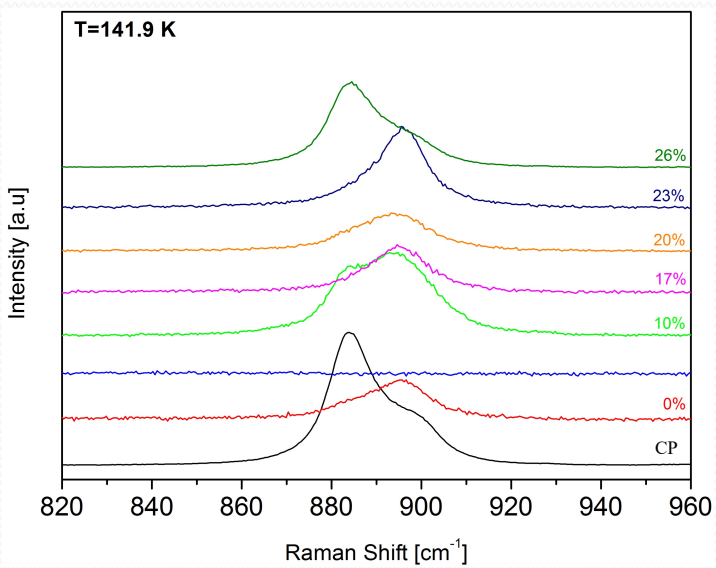
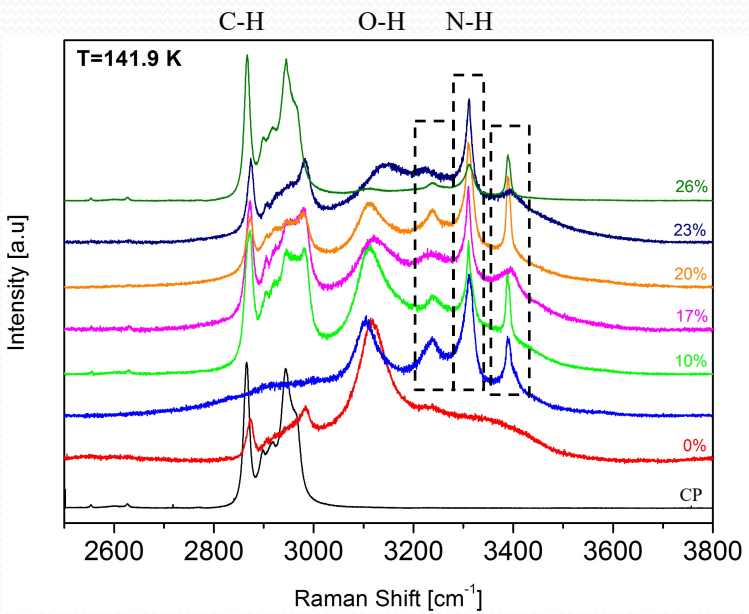
Breathing mode



Stretching mode



CP-H_2O-NH_3

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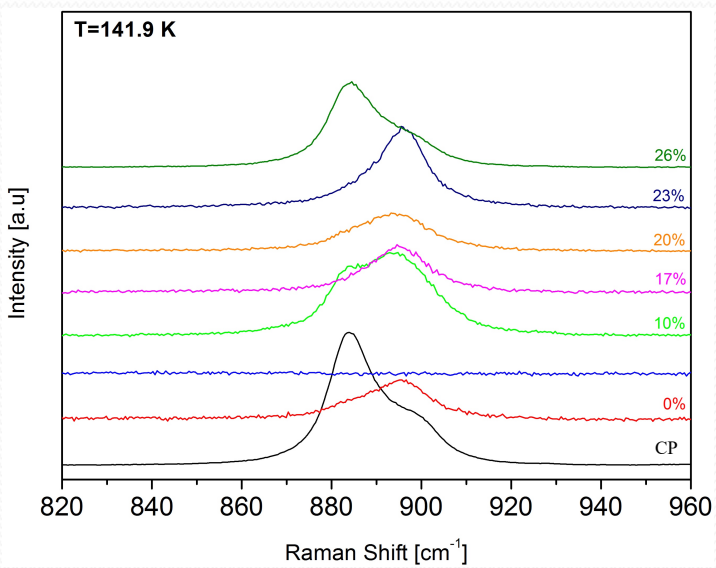
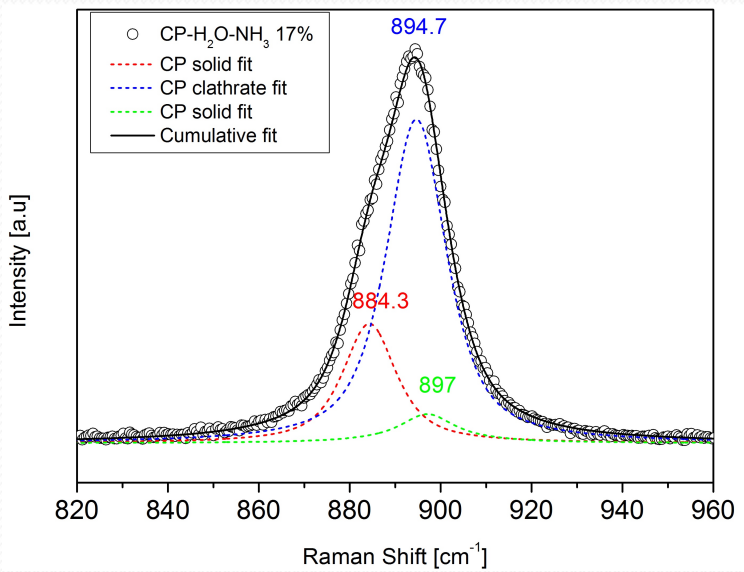
Breathing mode



17wt% of NH_3



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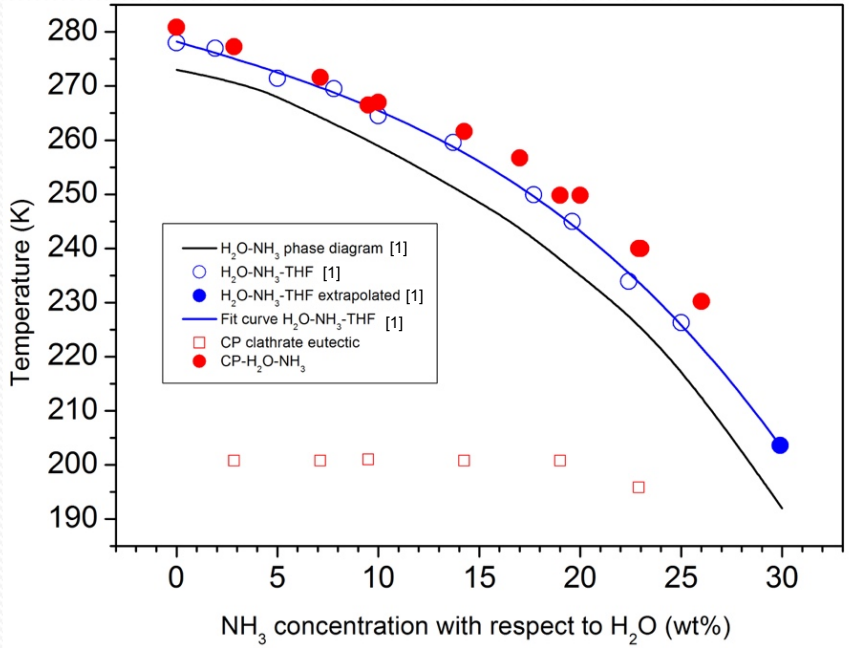
✓ Equilibrium curve of CP clathrate close to the equilibrium curve of THF clathrate

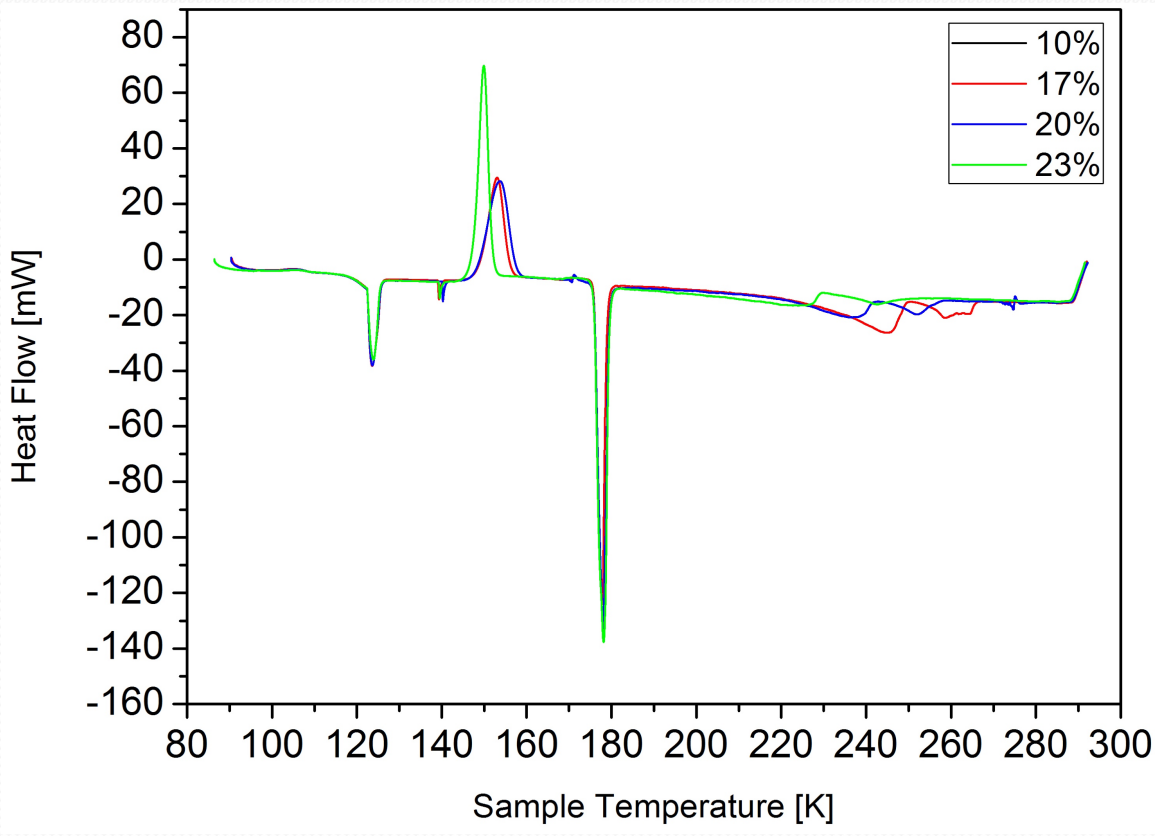
✓ CP clathrate eutectic, determined with optical imaging (Tuan's work), need to be confirm with DSC and XRD



[1] Vu, T.H. *et al.*, *JPCB*, **2014**, *118*, 13371-13377

CP-H_2O-NH_3

- Differential Scanning Calorimetry (DSC)
  - Run: cool from 298 K to 223 K//stay at 223 K during 24h//cool to 83 K//stabilize half a day//increase at 0.1K/min



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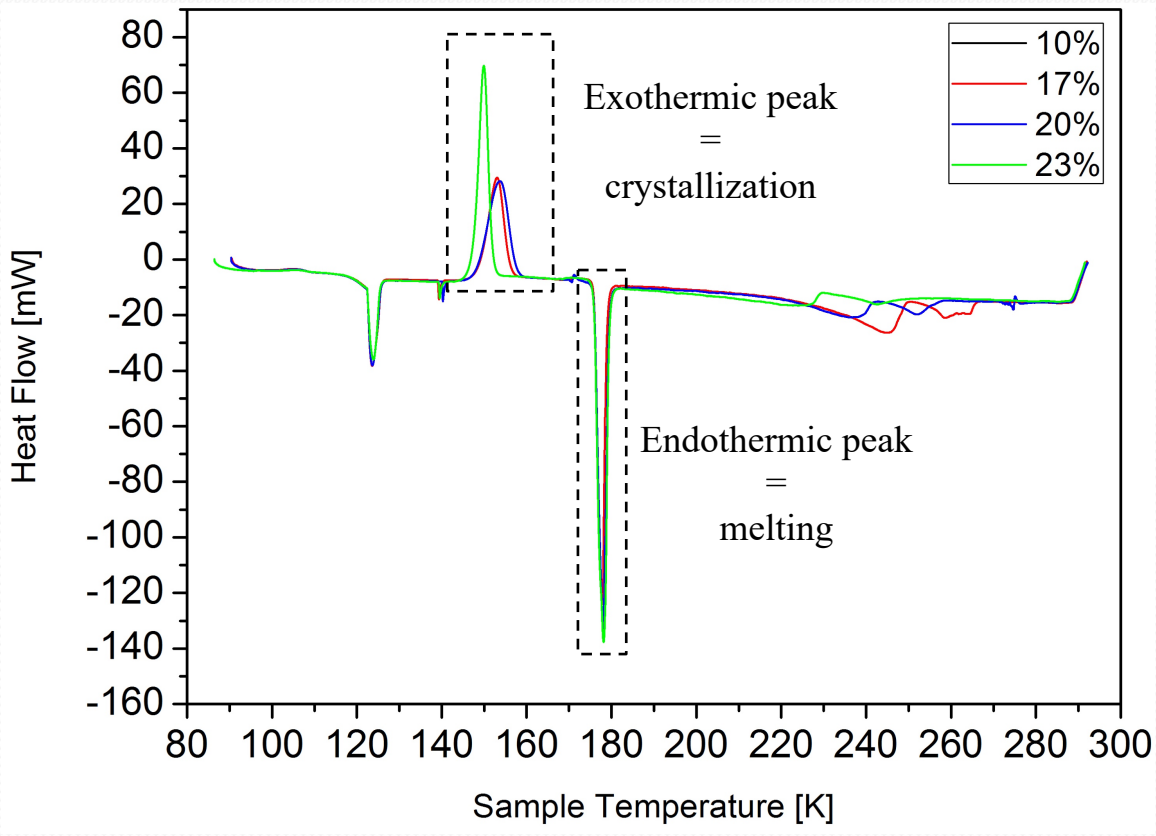

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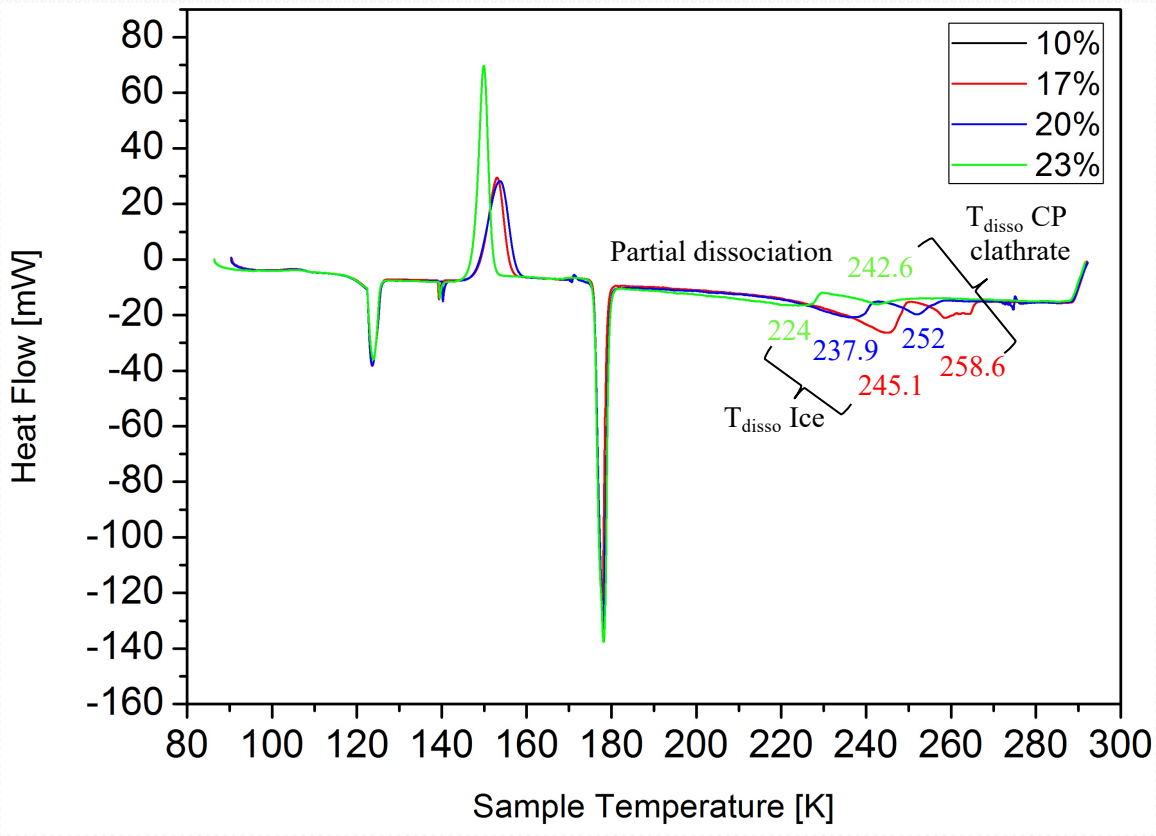

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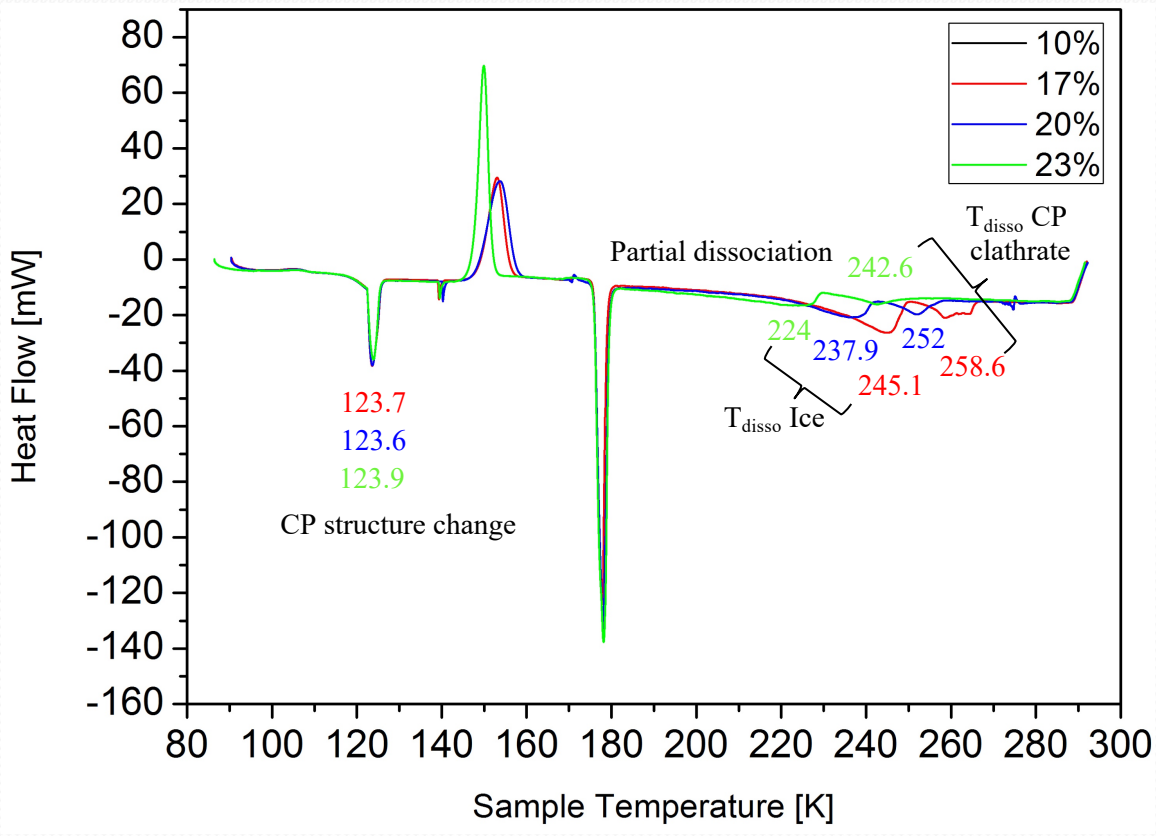
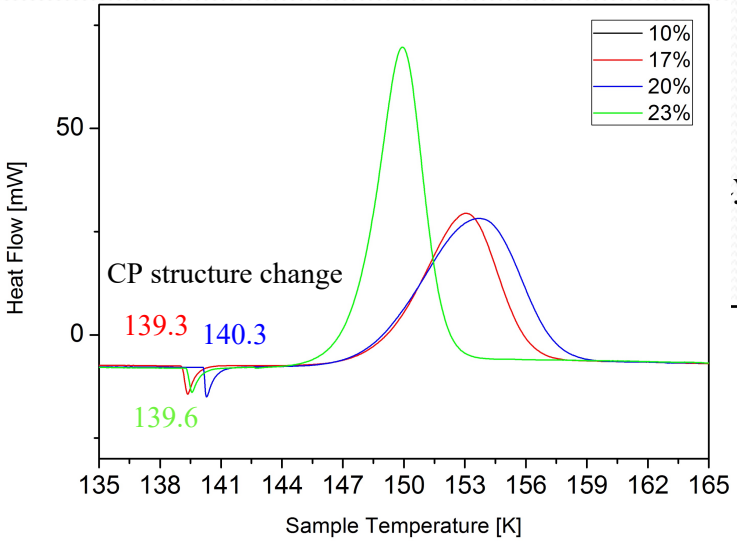
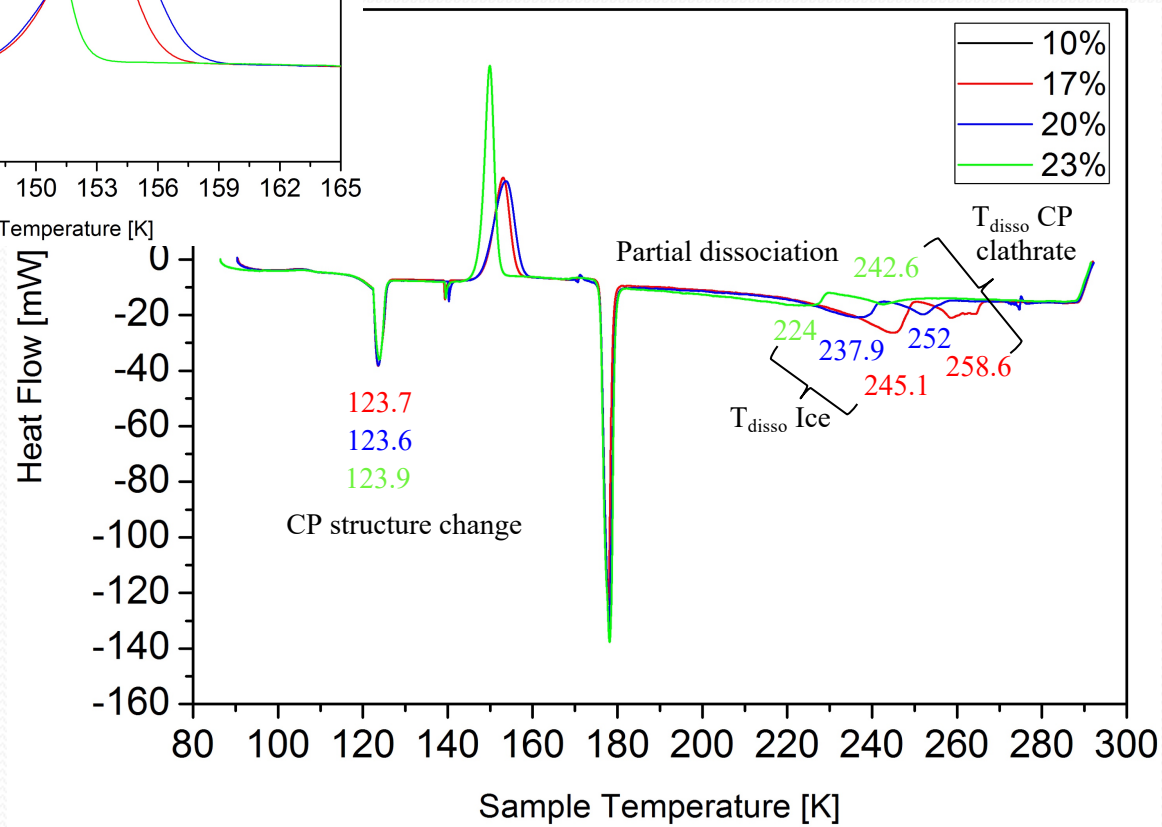


CP-H_2O-NH_3

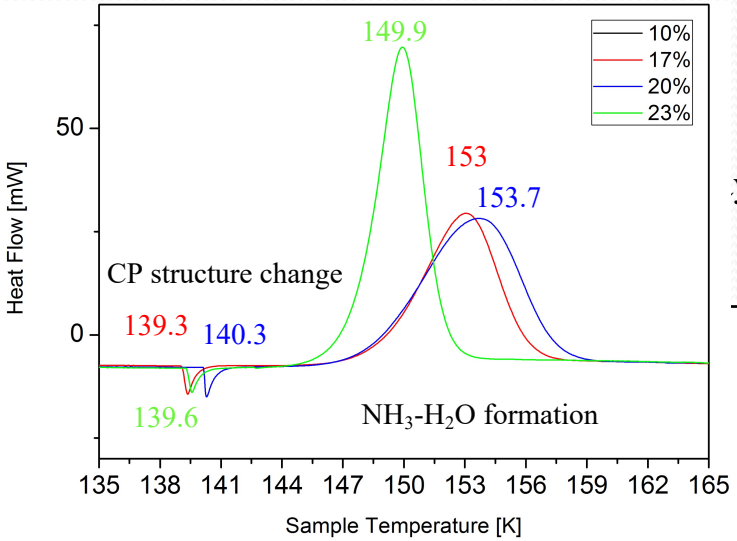


Calorimetry (DSC)

y at 223 K during 24h//cool to 83 K//stabilize half a day//increase at



CP-H_2O-NH_3



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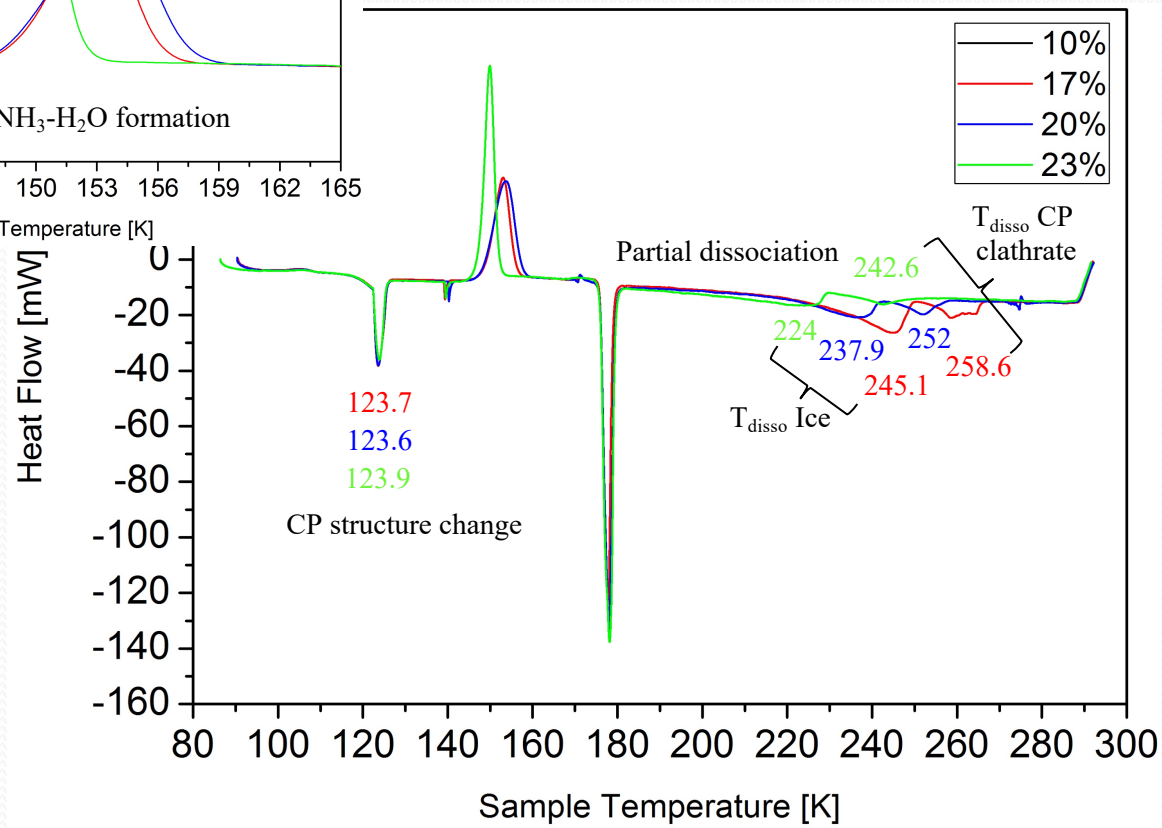
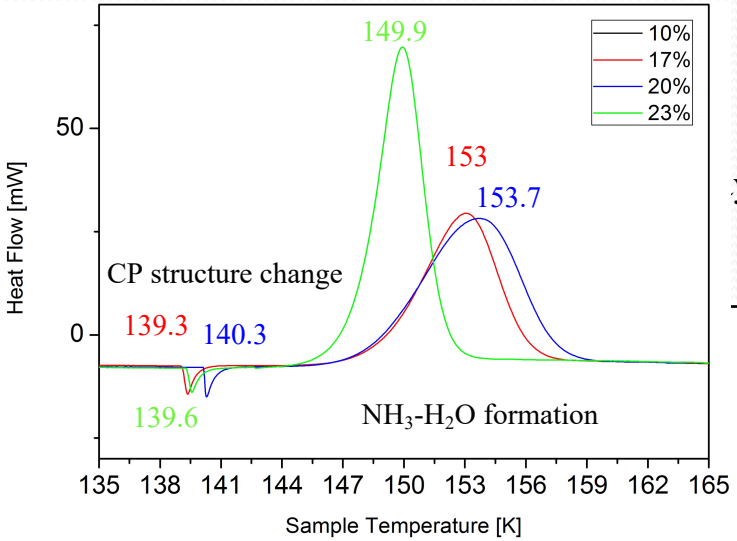
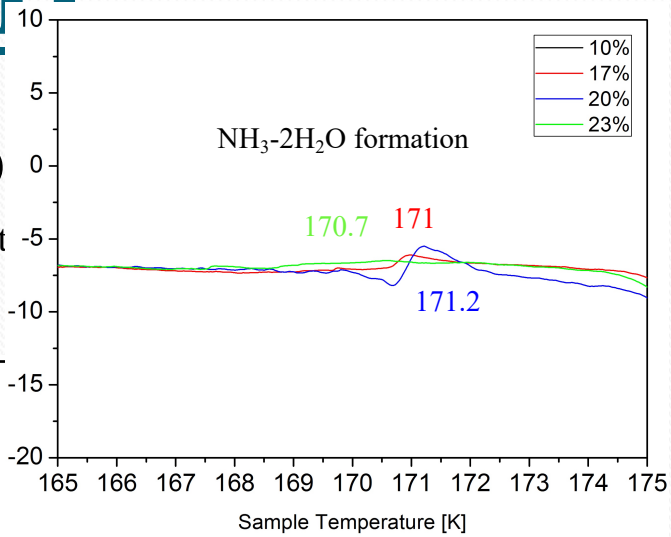


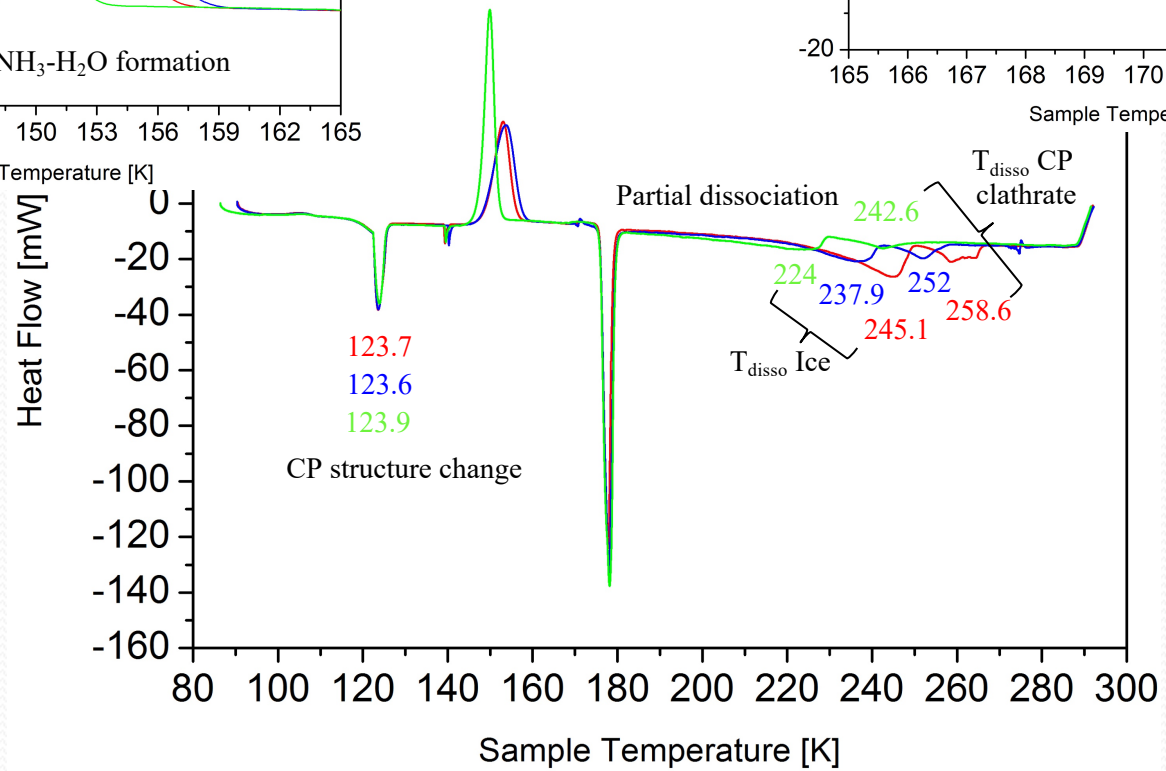
CP-H_2O-NH

Calorimetry (D

y at 223 K during 24h//cool t



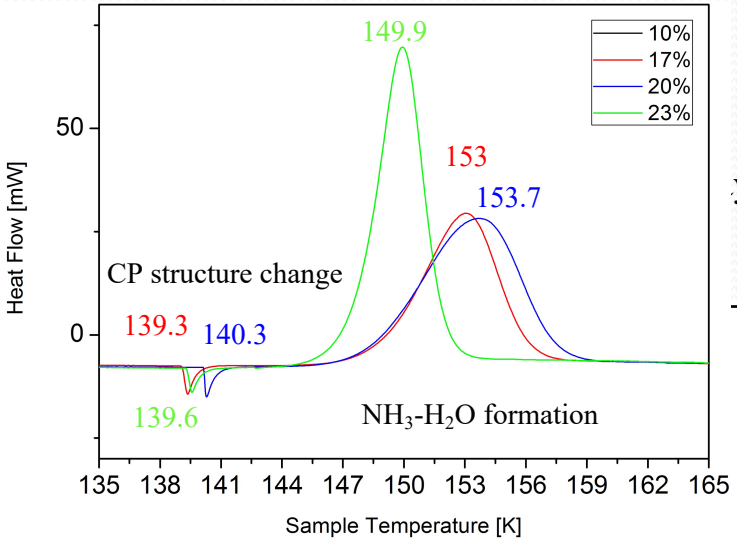


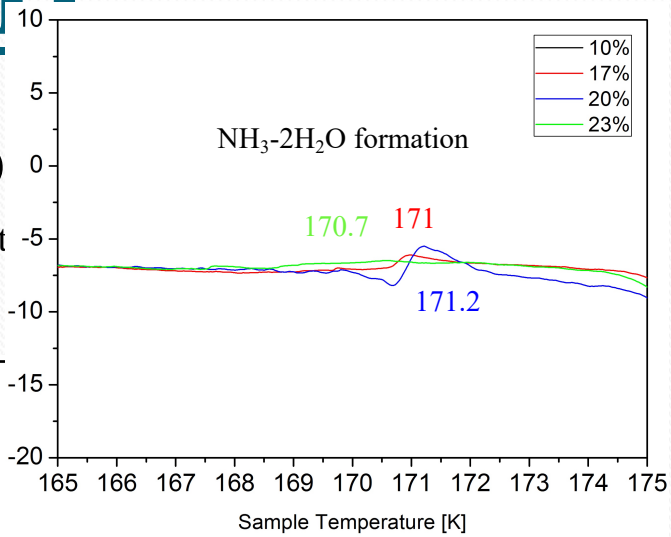


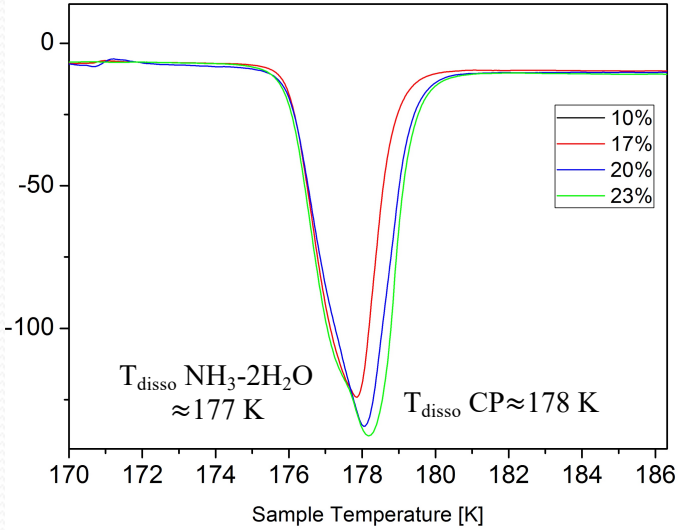
CP-H_2O-NH

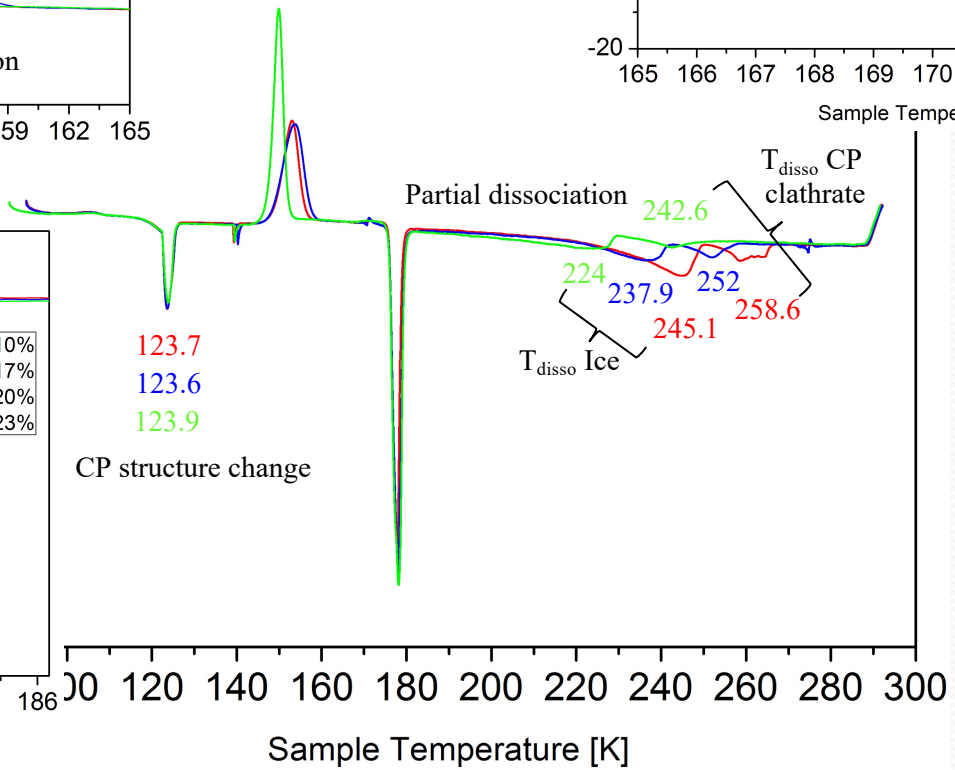
Calorimetry (D

y at 223 K during 24h//cool t









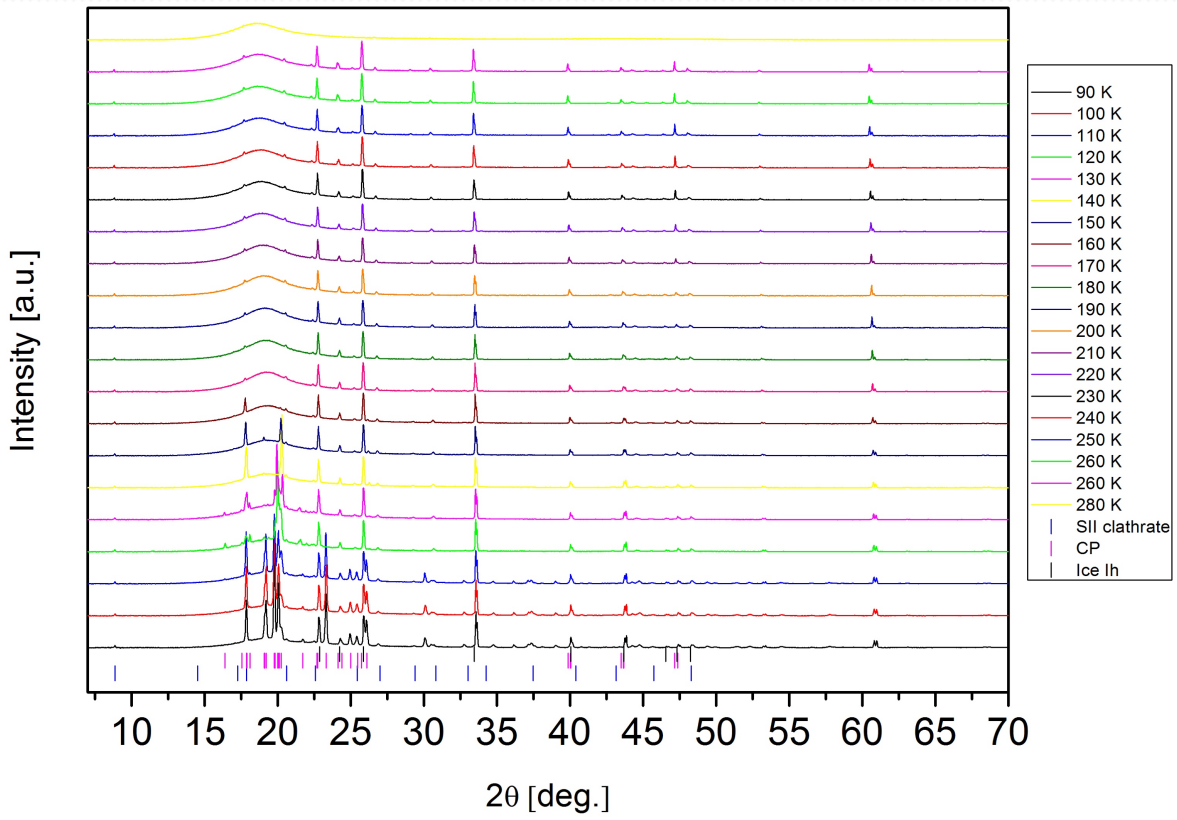
CP-H_2O

- X-rays Diffraction
  - Run: Growth at 263 K during a night and then pattern (1s/step, [7-70deg.]) every 5 K from 90 K to 280 K with 10min of temperature stabilization

- ✓ 90 K: CP solid, Ice Ih, CP clathrate

- ✓ 120 K: CP structure change
- ✓ 140 K: CP structure change
- ✓ 170 K: CP melt

- ✓ 280 K: CP clathrate melt



CP-H_2O-NH_3

- X-rays Diffraction
  - Run: Quench at 90 K and then pattern (1s/step, [7-70deg.]) every 10 K until 280 K with 10min of temperature stabilization

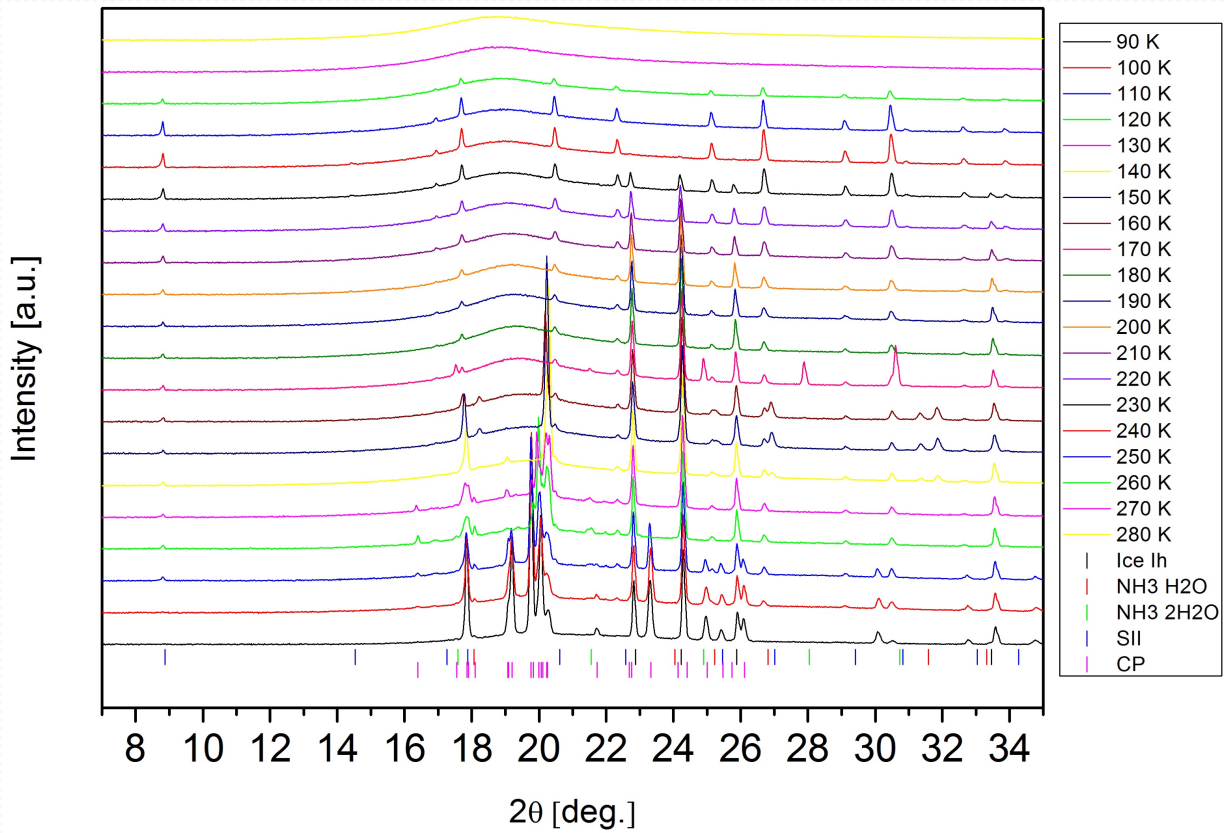
Example: 17wt% NH_3

- ✓ 90 K: CP solid, Ice Ih
- ✓ 110 K: CP clathrate formation

- ✓ 120 K: CP structure change
- ✓ 140 K: CP structure change
- ✓ 170 K: CP melt

- ✓ 270 K: CP clathrate melt

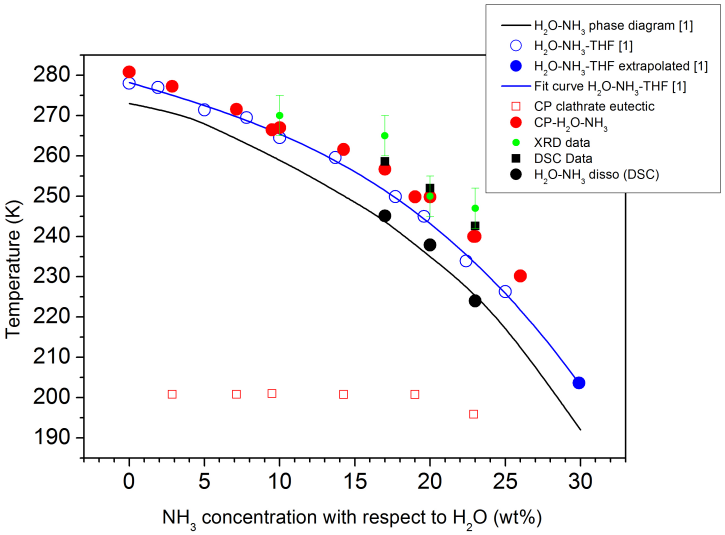
- ✓ [140 K-160 K]: NH_3-H_2O
- ✓ [160 K-170 K]: NH_3-$2H_2O$



Concluding remarks

- Partial dissociation of CP clathrate with ammonia
  - Ammonia have the same effect as on water ice and on THF clathrate lowering the dissociation temperature of CP clathrates and promoting a partial dissociation
  - Ammonia does not have any interaction with CP (hydrophobic)
  - Ammonia seems not to interact neither with the skeleton of the clathrate cage (at these concentrations)

- Perspectives:
  - DSC: some experiments to do to have a whole data set
  - Verifying the temperatures of partial dissociation (eutectic point) and complete dissociation making a sample with more CP clathrate and with a slower increase of the temperature during the XRD run.
  - Start the study of the effect of ammonia on methane clathrate hydrates
  - Geophysical modeling



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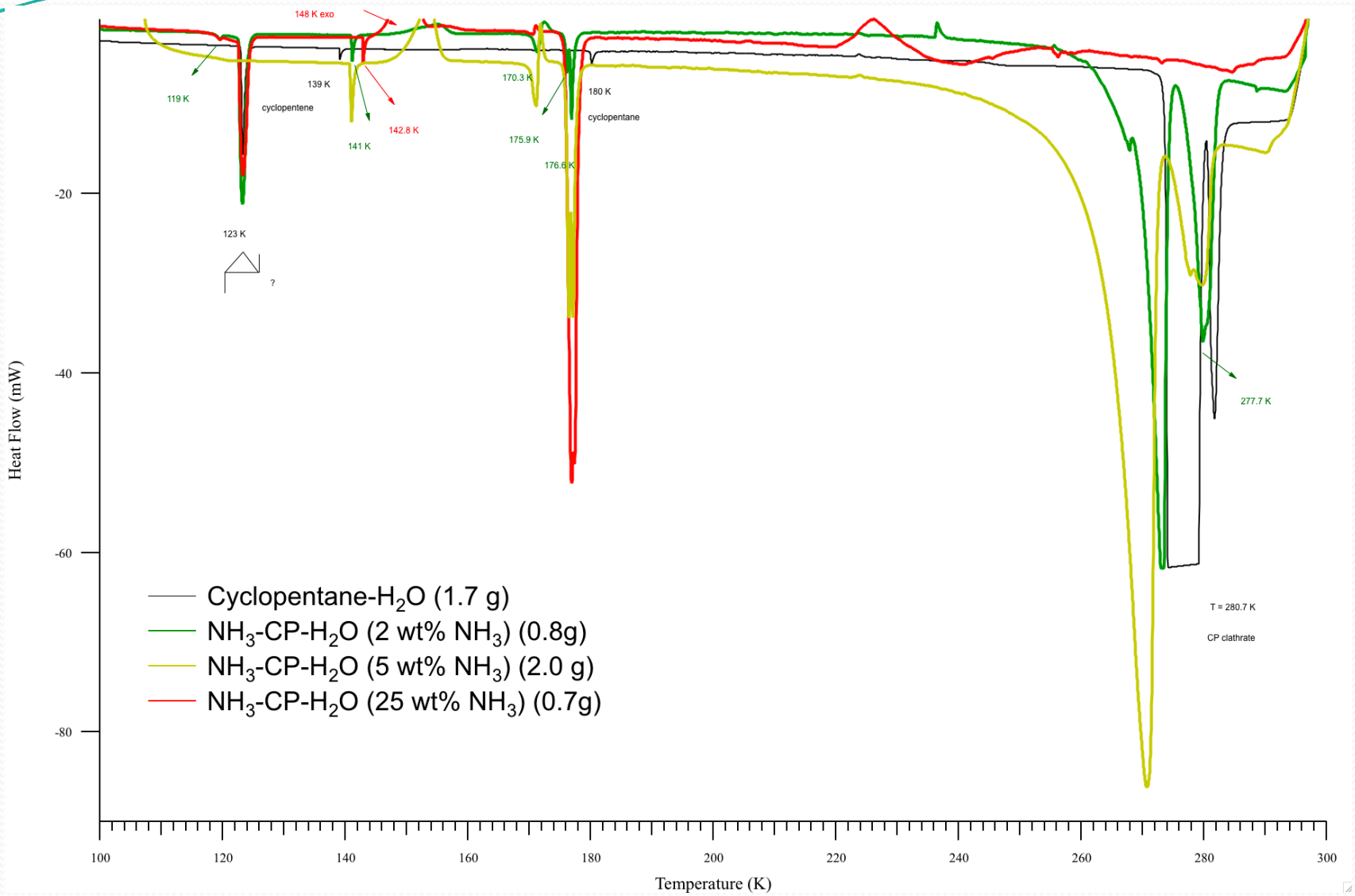
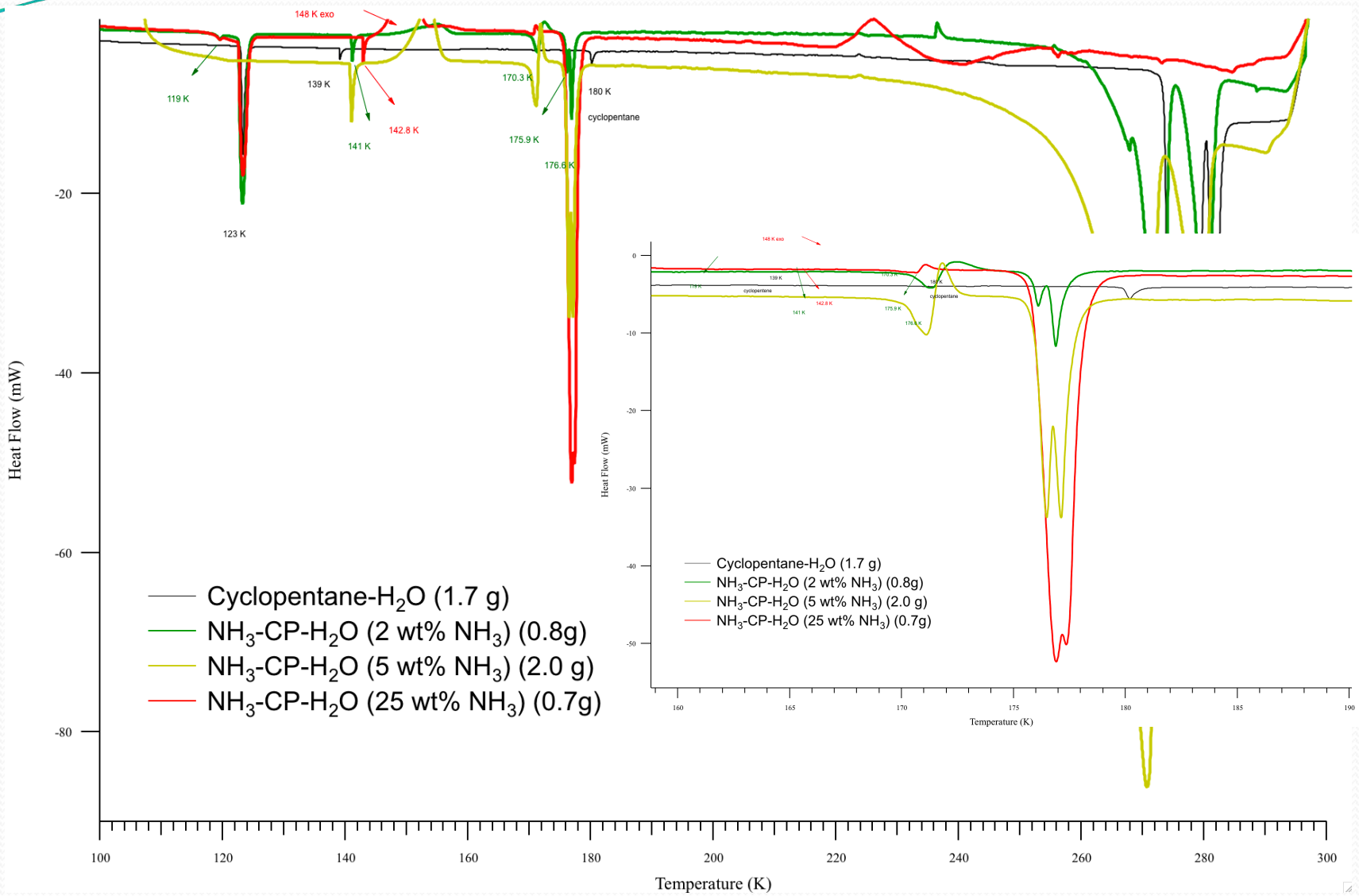
Thank you for your attention

Any questions ?

Geophysical Modeling


148 K exo
119 K
139 K
cyclopentene
142.8 K
141 K
170.3 K
175.9 K
176.6 K
180 K
cyclopentane
123 K
?
277.7 K
T = 280.7 K
CP clathrate
Cyclopentane-H2O (1.7 g)
NH3-CP-H2O (2 wt% NH3) (0.8g)
NH3-CP-H2O (5 wt% NH3) (2.0 g)
NH3-CP-H2O (25 wt% NH3) (0.7g)
Heat Flow (mW)
-20
-40
-60
-80
100
120
140
160
180
200
220
240
260
280
300
Temperature (K)


148 K exo
119 K
139 K
170.3 K
180 K
cyclopentane
142.8 K
141 K
175.9 K
176.6 K
123 K
Heat Flow (mW)
Temperature (K)
Cyclopentane-H2O (1.7 g)
NH3-CP-H2O (2 wt% NH3) (0.8g)
NH3-CP-H2O (5 wt% NH3) (2.0 g)
NH3-CP-H2O (25 wt% NH3) (0.7g)

Descent Image/Spectral Radiometer

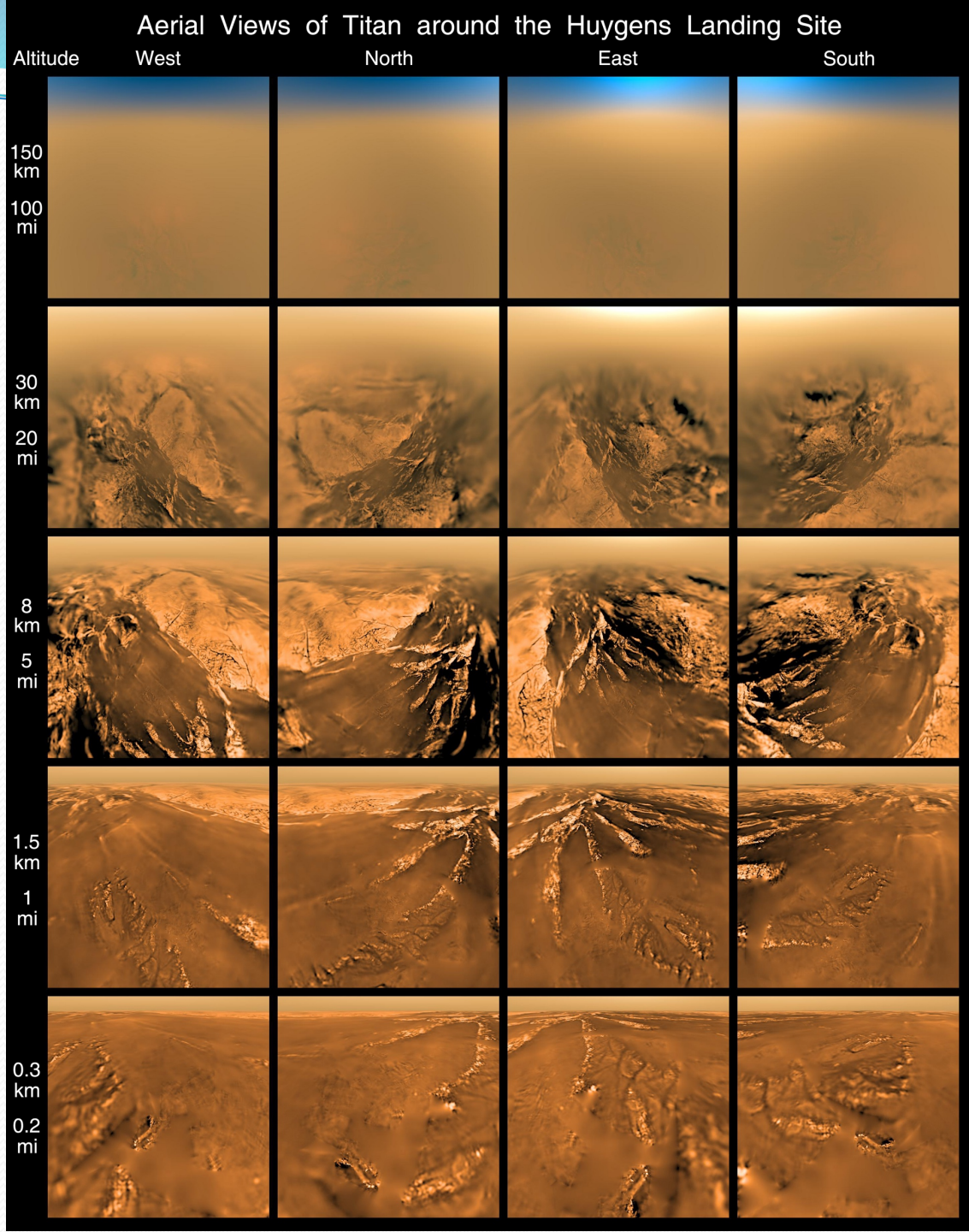


Image Credit: ESA/NASA/JPL/University of Arizona

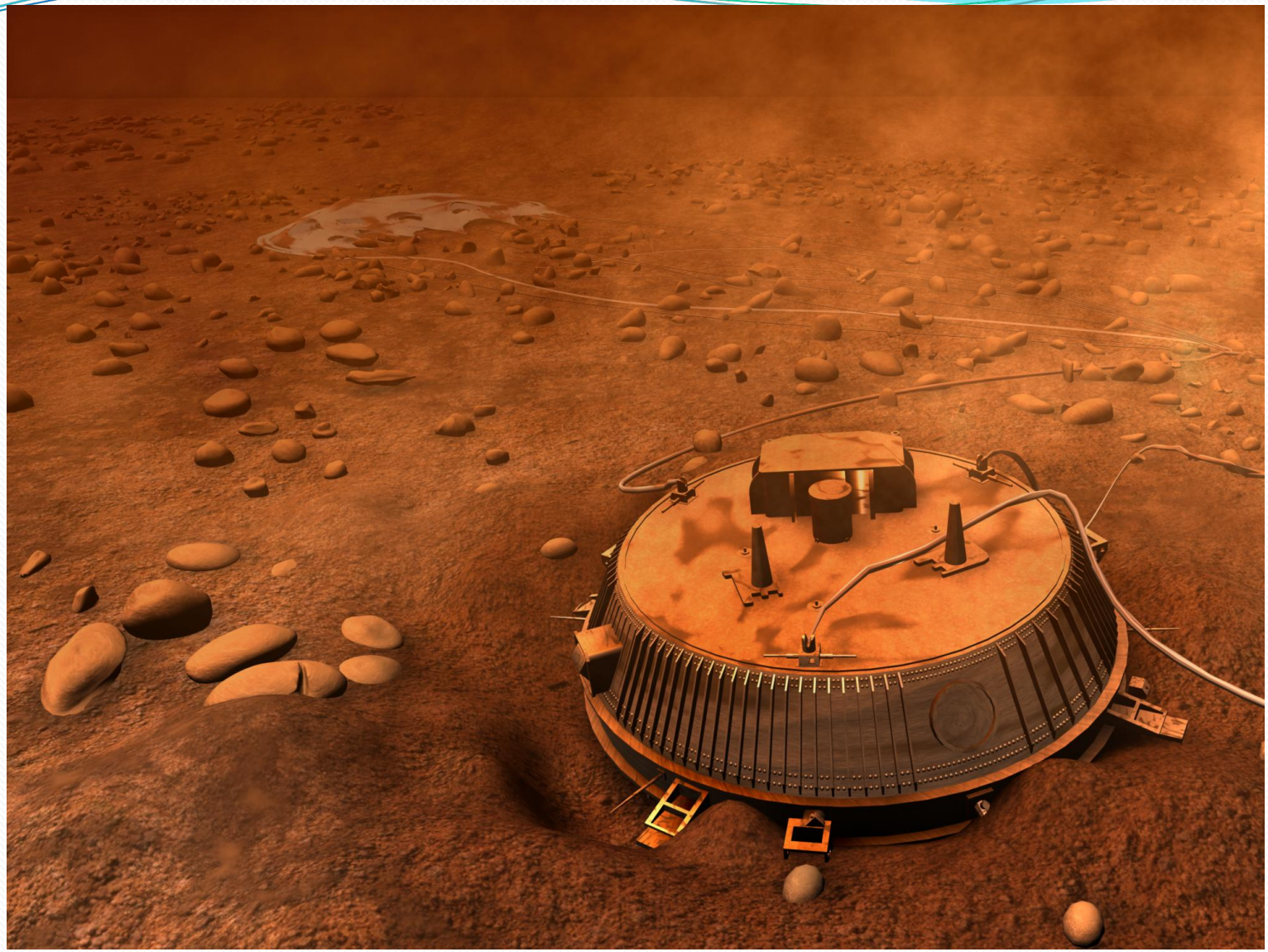


Image Credit: ESA/Artist's Concept