

# ICES, CLATHRATES, AND HABITABILITY

(RETENTION, SCAPE AND CYCLING OF WATER AND ESSENTIAL ELEMENTS)

Olga Prieto-Ballesteros

Centro de Astrobiología-INTA-CSIC. Madrid. Spain

[prietobo@cab.inta-csic.es](mailto:prietobo@cab.inta-csic.es)

*Missions to Habitable Worlds. 28-29 October 2015. Budapest, Hungary*

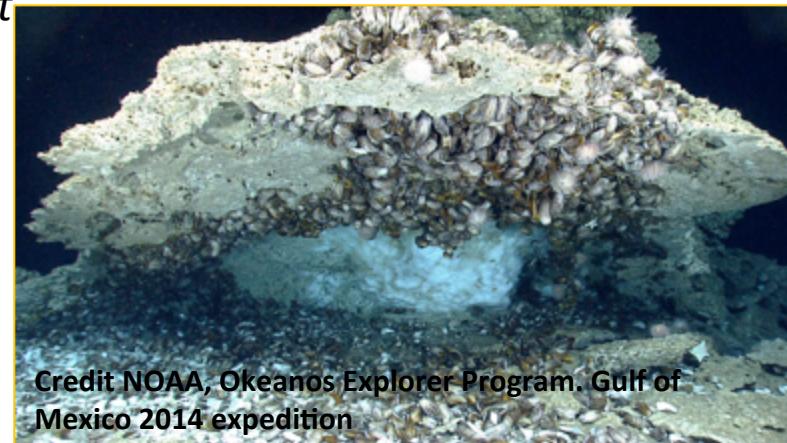
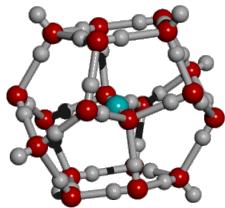
*EU COST TD 1308*

# CLATHRATE HYDRATES

*"Clathrate hydrates are ice like solids in which a host hydrogen-bonded H<sub>2</sub>O lattice entraps a nonpolar guest gas molecule such as CH<sub>4</sub> or CO<sub>2</sub>*

from *Encyclopedia of Astrobiology* (2011)

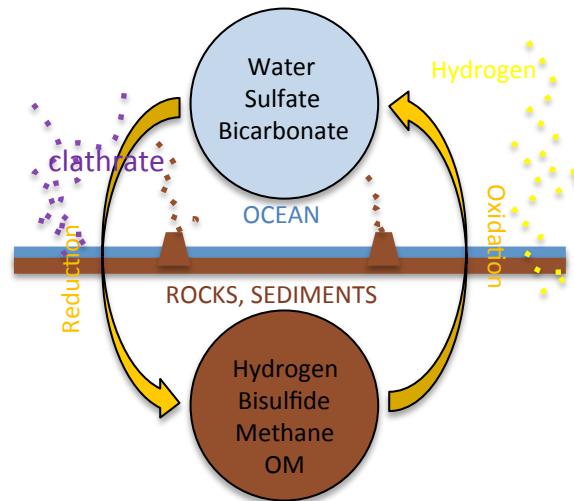
P/T stability conditions



Credit NOAA, Okeanos Explorer Program, Gulf of Mexico 2014 expedition

Relevance for habitability:

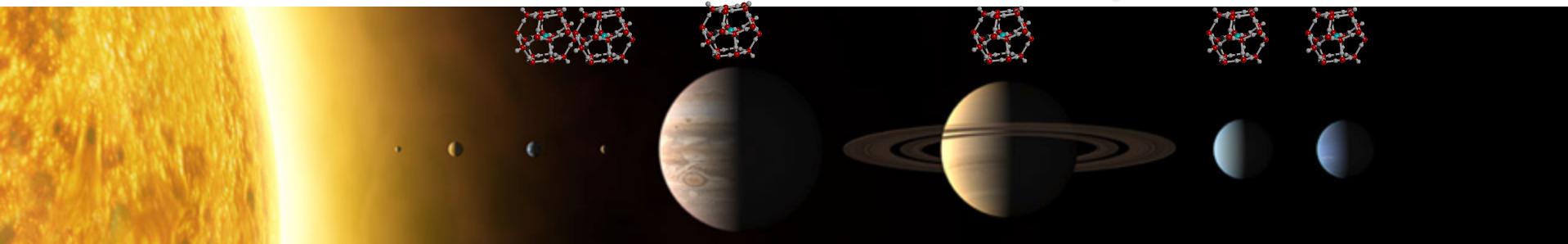
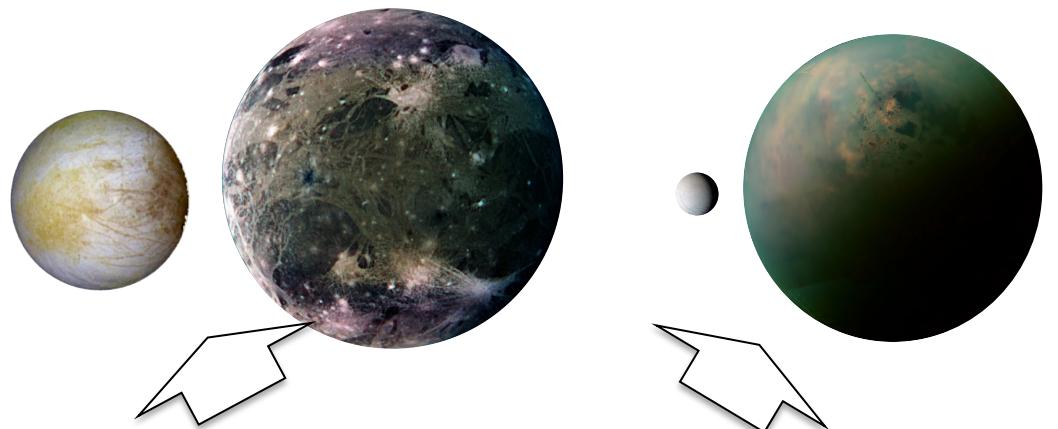
- Chemical compounds essential for life
- Properties that affect the planetary evolution
- Role in biogeochemical cycle of elements
- Extremophiles



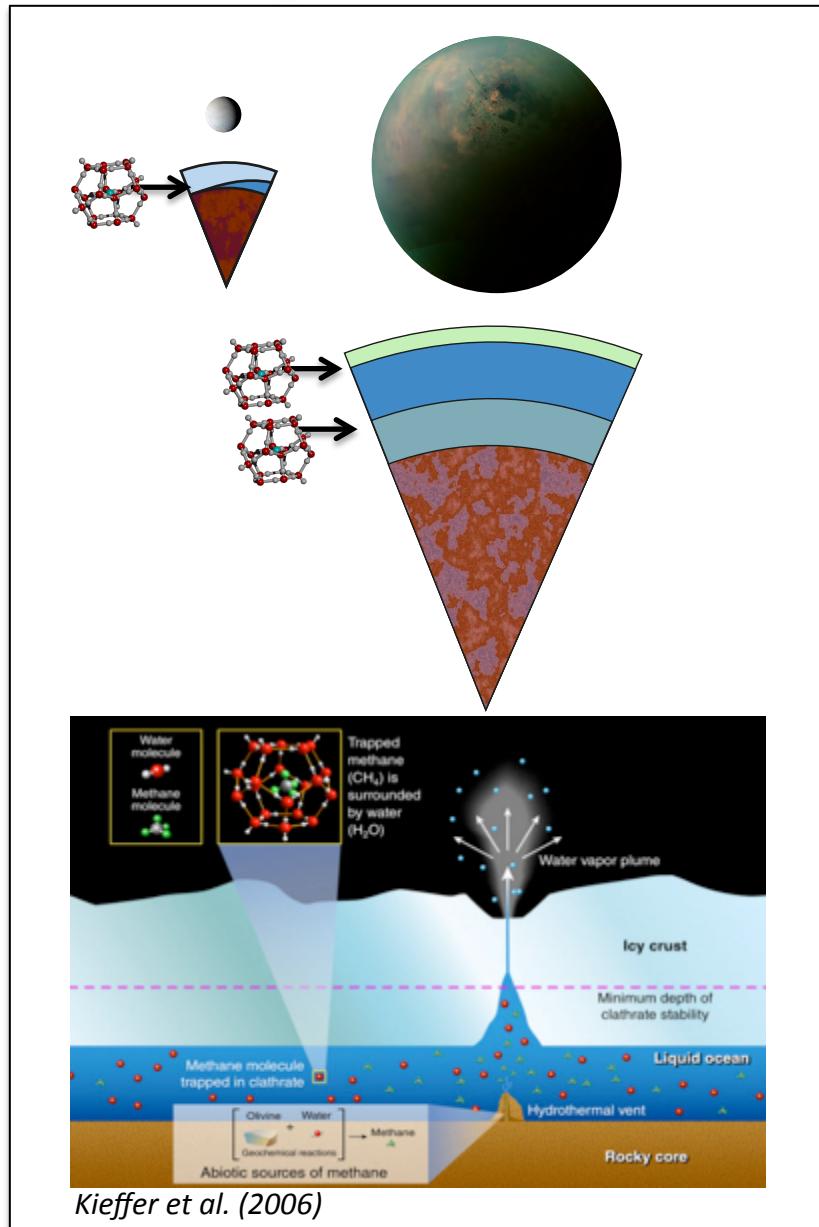
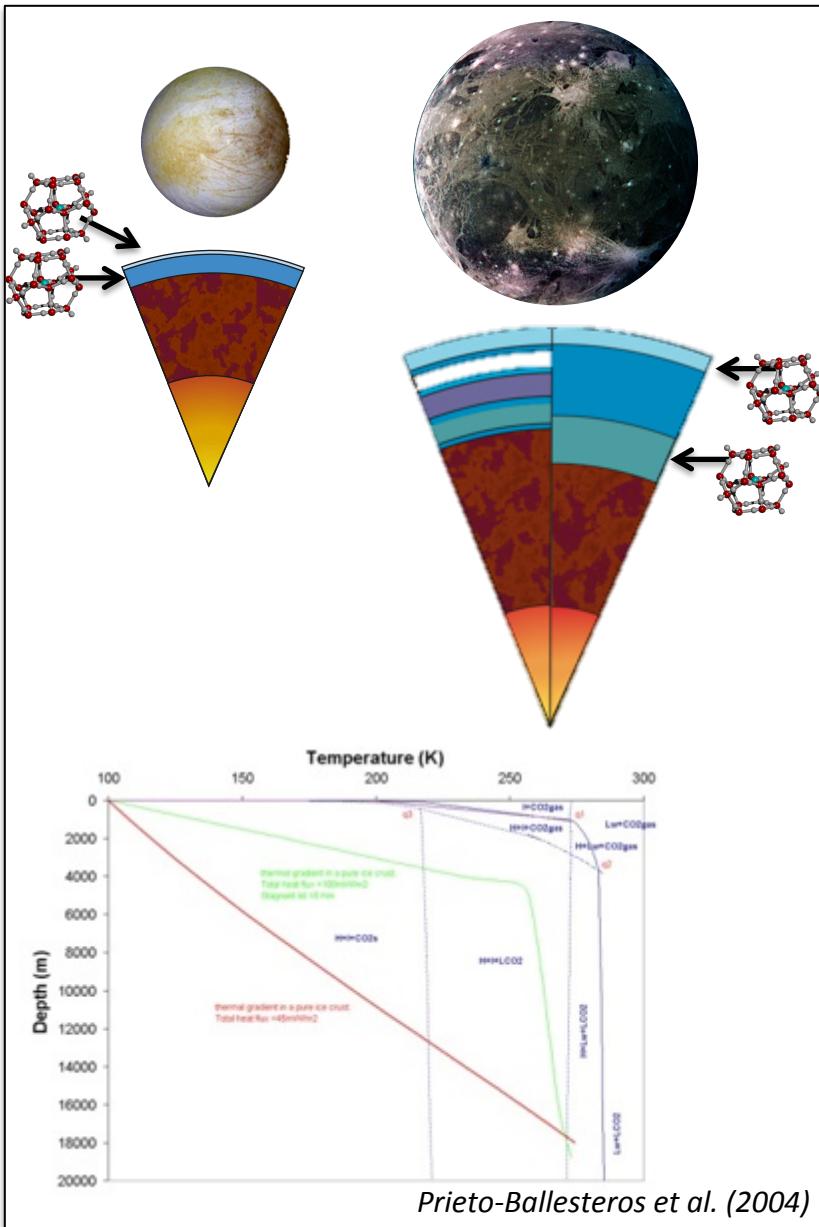
# Clathrate zone

- They can be present where stability field and compounds are present
- Ices on surfaces
- Volatiles can have different origin: endogenous, exogenous; primordial, products of material alteration

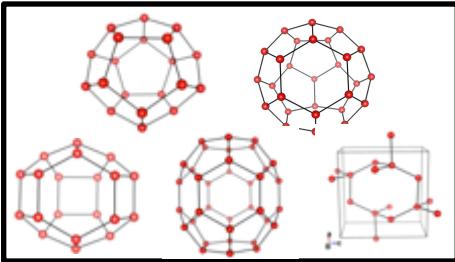
Compounds surf/exosf		H <sub>2</sub> O	CO <sub>2</sub>	SO <sub>2</sub>	NH <sub>3</sub>	CH <sub>4</sub>	O <sub>3</sub>	CO	N <sub>2</sub>	O <sub>2</sub>
Freezing Temperature (K)		273	215	200	195	91	80	68	63	55
Jupiter	Europa	Y	Y	Y			Y			Y
	Ganymede	Y	Y				Y			Y
	Callisto	Y	Y	Y						
Saturn	Small moons	Y	Y				Y			
	Enceladus	Y	p		plumes	p		p	p	
	Titan	Y				Y				
Uranus	Small moons	Y	Y							
Neptune	Triton	Y	Y			Y		Y	Y	
Pluto		Y				Y		Y	Y	
Comets		Y	Y		Y	Y		Y	Y	



# Clathrate zone / Habitability zone



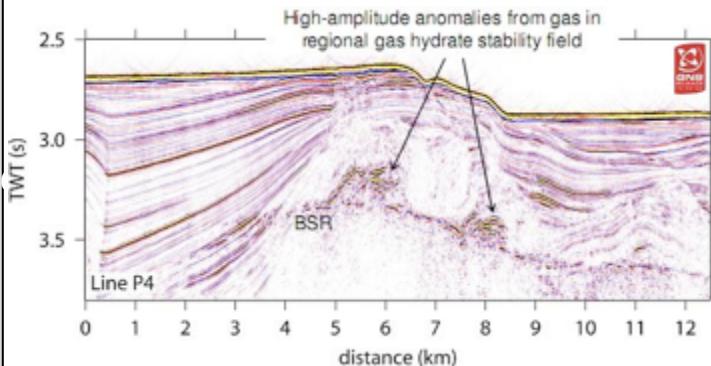
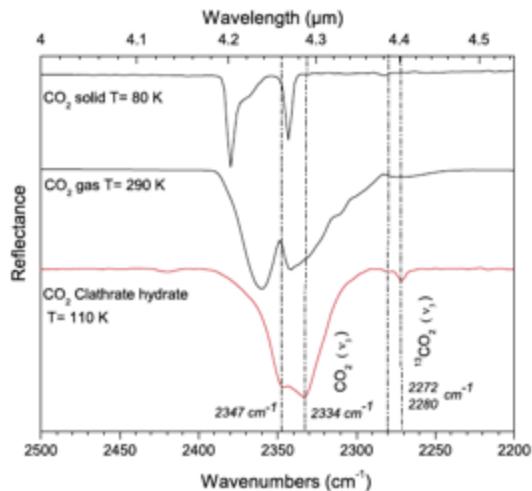
# Attributes



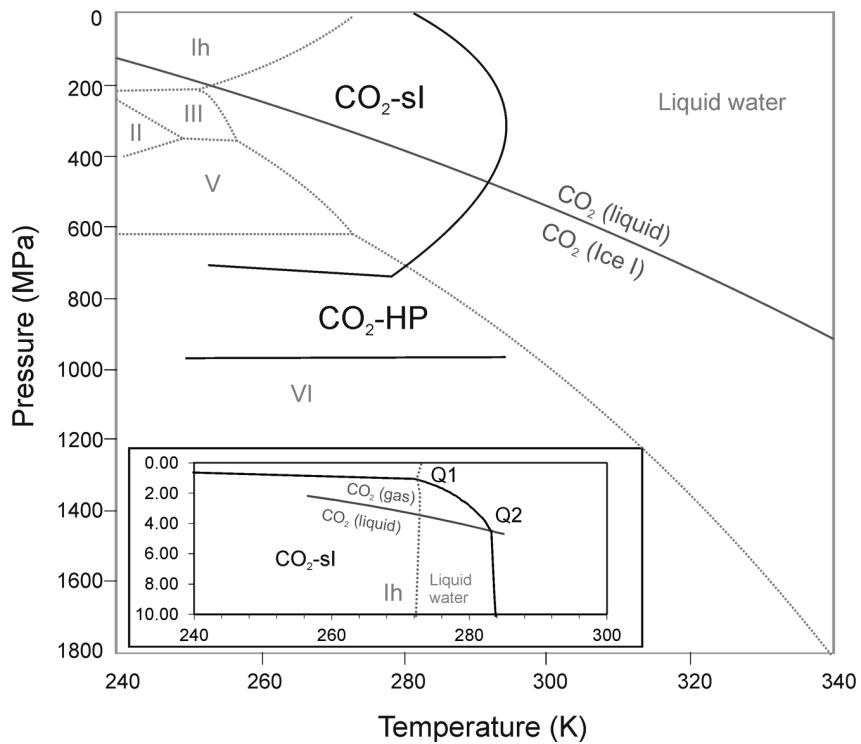
Type	Symmetry	nH2O/cell	P (GPa)
sI 5 <sup>12</sup> 6 <sup>2</sup>	Pm3m	46	0-0.9 (CH4) 0-0.7 (CO <sub>2</sub> )
sII 5 <sup>12</sup> 6 <sup>3</sup>	Fd3m	136	0-0.5 (CH4) metastable
sH 6 <sup>3</sup> 5 <sup>6</sup> 4 <sup>3</sup>	P6/mmm	34	0.9-1.6 (CH4)
FIS channel	ImcM	8	1.6-42 (CH4) 0.7-1.0 (CO <sub>2</sub> )

Guest gas	Structure	Density, kg m <sup>-3</sup> partial occupancy	Density, kg m <sup>-3</sup> full occupancy
CH <sub>4</sub>	sI	901	920
N <sub>2</sub>	sII	951	1001
CO <sub>2</sub>	sI	1084	1134
Ar	sII	1021	1093
Kr	sII	1280	1430
Xe	sI	1654	1805

Property	Clathrate	Ice Ih
Thermal conductivity W/m/K	0.5	2.2
Thermal expansion coeff. K <sup>-1</sup>	44 x 10 <sup>-6</sup>	31 x 10 <sup>-6</sup>
Young's modulus (269 K) Pa	8.4 x 10 <sup>9</sup>	9.5 10 <sup>9</sup>
Bulk modulus (272 K)	5.6	8.8
Shear modulus (272 K)	2.4	3.9
Poisson's ratio	0.33	0.33
Dielectric constant (272 K)	58	94



# High pressure environments



Modified from Bollengier et al. (2013)

Giant icy moons contain HP ices phases

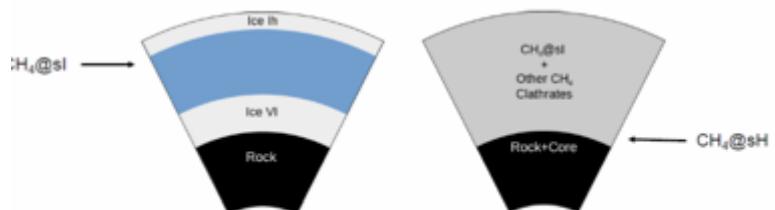
Crystal structure and properties are different than LP clathrates

Guest	Phase	P (GPa)	T (K)	d (g/mL)
CH4	sH	0.86-2.26	Room	1.018-1.083
	FIS	2.17-42	Room	1.117-1.962
CO2	sl	-	77-240	1.119-1.54
	FIS	-	173	1.825

Ice	Density (g/cm <sup>3</sup> )
V	1.24 at 0.35 GPa (where Lw = 1.13)
VI	1.31 at 0.6 GPa (wher Lw= 1.18)
VII	1.65 at 2.5 GPa



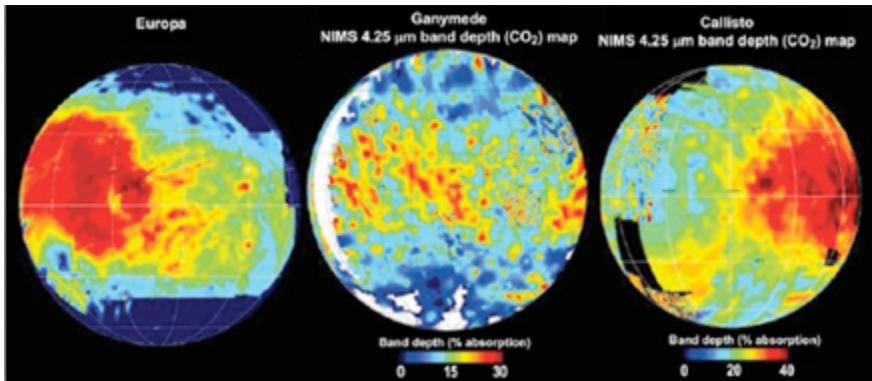
Ganymede models (after Sohl et al. 2002, Vance & Brown 2013, Vance et al. 2014)  
Arrows show the clathrate gravitational stable position



Titan geophysical models (after Fortes 2012)  
Arrows indicate gravitational stable position of clathrates

Izquierdo et al. (2015)

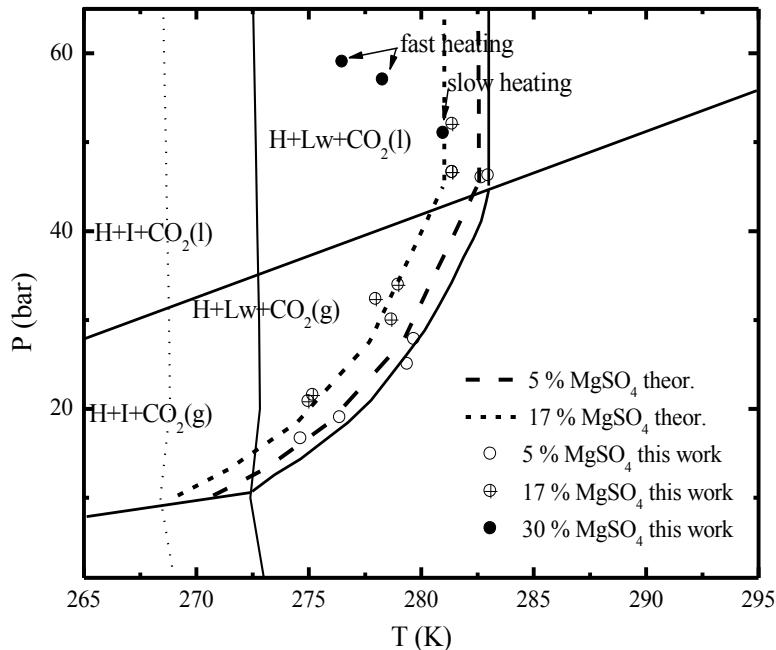
# Salty environments



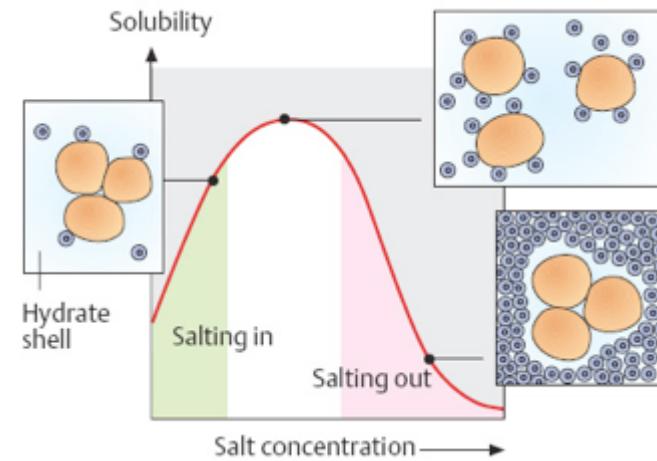
Aqueous solutions are not pure: volatiles, gasses

Salts affect the stability of clathrates

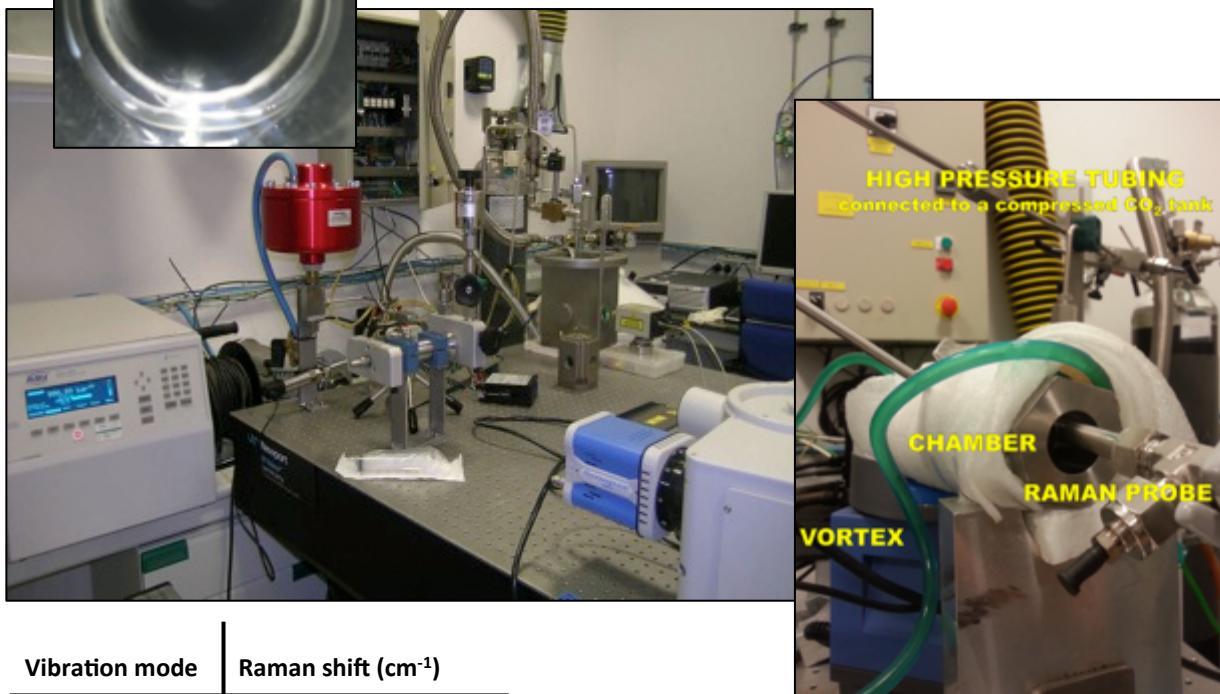
Salting out effect on the icy moons



Muñoz-Iglesias et al. (2014)



# Salting-out



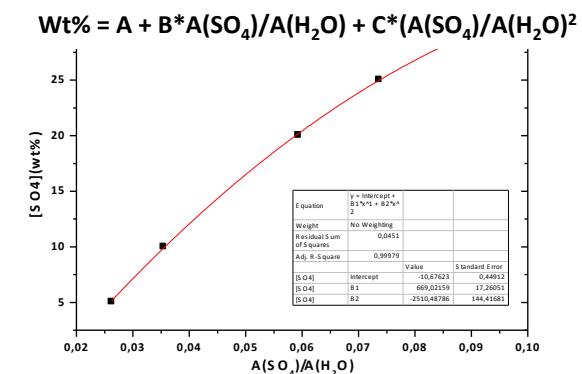
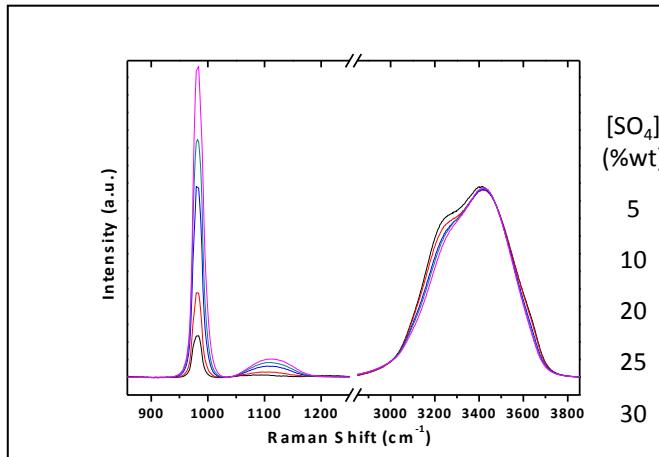
HP simulation chambers

Raman spectroscopy analysis

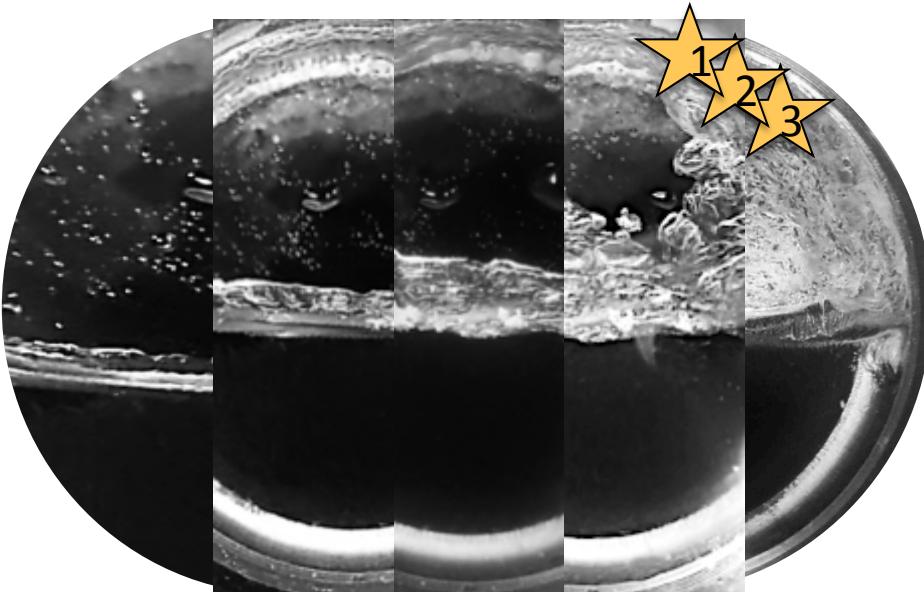
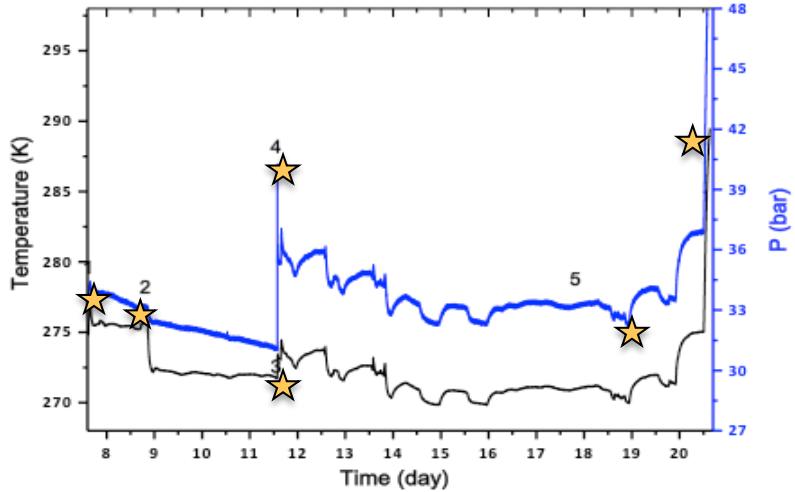
Calibration

Salting out experiments:  
H<sub>2</sub>O-CO<sub>2</sub>-MgSO<sub>4</sub> (Europa)

Vibration mode	Raman shift (cm <sup>-1</sup> )
$\nu_1\text{-SO}_4^{2-}$	981.9 (aqueous)
	983 ( $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$ )
	986 ( $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ )
	990 ( $\text{MgSO}_4\cdot 11\text{H}_2\text{O}$ )
Fermi doublet-	1285/1388 (gas)
	1280/1386(liquid)
CO <sub>2</sub>	1275/1383(aqueous)
	1276/1381(clathrate)
O-H stretch	2900-3900



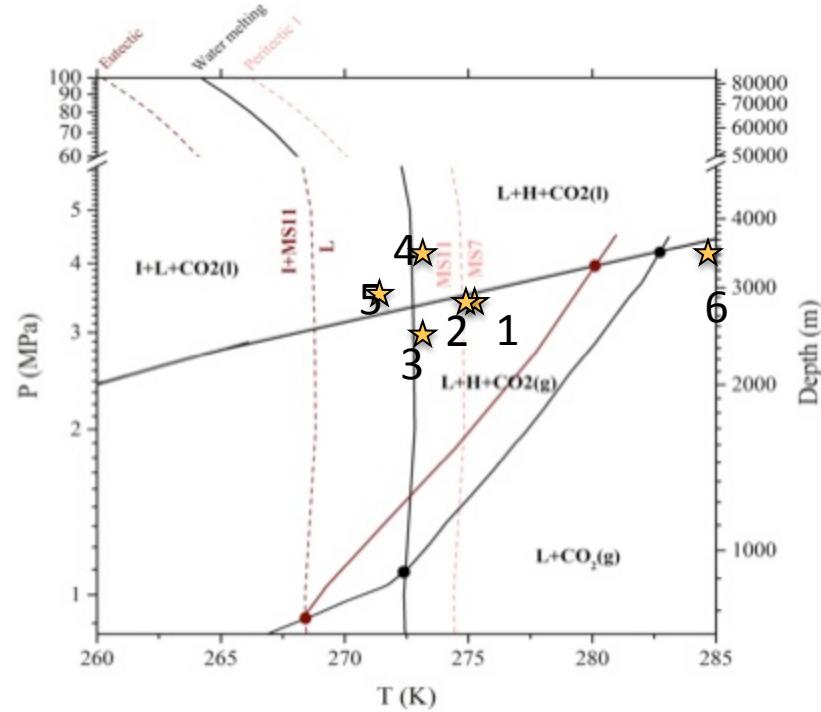
# Salting out



Several runs of CH formation/dissociation

P and T is recorded every second

Spectra and pictures are taken during the runs



# Related geological activity

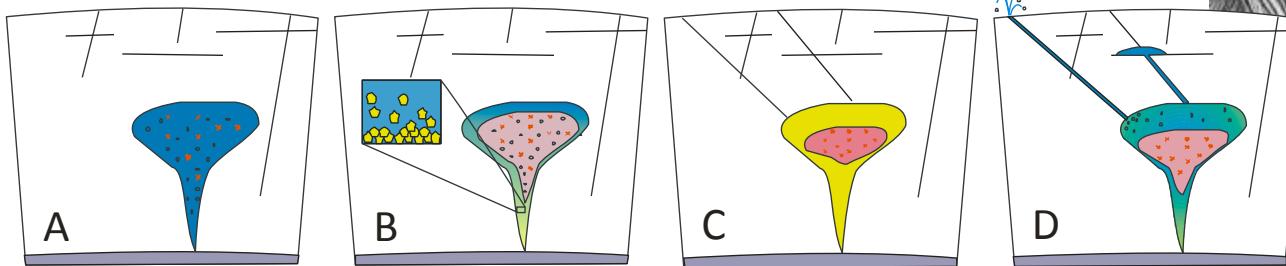
Molar volumes (cm<sup>3</sup>/mol) of the mineral assemblages which were formed during the evolution of the aqueous solutions at 5, 17 and 30 wt% of MgSO<sub>4</sub>, in the absence and presence of CO<sub>2</sub>-clathrate.

5 wt% MgSO <sub>4</sub>	V (solid mixture) 86 wt% ice/clat + 14 wt% MS11	V (ice/clat + L <sup>b</sup> ) 71 wt% ice/clat + 29 wt% L	V (L <sup>b</sup> /clat) 100 wt% L/clat
Ice	102.9	121.5	96
CO <sub>2</sub> -clathrate	23	38.3	38.3
17 wt% MgSO <sub>4</sub>	V (solid mixture) 53 wt% ice/clat + 47 wt% MS11	V (L <sup>b</sup> /clat) 100 wt% L/clat	
Ice	89.9	83.7	
CO <sub>2</sub> -clathrate	40.8	47.6	
30 wt% MgSO <sub>4</sub>	V (solid mixture) 17 wt% ice/clat + 83 wt% MS11	V (MS11 + L <sup>c</sup> /clat.) 32 wt% L/clat + 68 wt% MS11	V (MS7 + L <sup>c</sup> /clat.) 32 wt% L/clat + 68 wt% MS7
Ice	75.7	69.6	66.9
CO <sub>2</sub> -clathrate	60.2	52	29.5

Geological features formed because of volume changes occurring when a salty cryomagma at several concentrations of MgSO<sub>4</sub> freezes in the absence or presence of CO<sub>2</sub>-clathrate hydrates.

		Volume liquid solution	Volume solid assemblage	Volume change	Geological feature formed
5 wt% MgSO <sub>4</sub>	Ice	96	103	(+)	Fracture
	CO <sub>2</sub> -clathrate	38	23	(-)	Collapse
17 wt% MgSO <sub>4</sub>	ICE	84	90	(+)	Fracture
	CO <sub>2</sub> -clathrate	48	41	(-)	Collapse
30 wt% MgSO <sub>4</sub>	ICE	67	76	(+)	Fracture
	CO <sub>2</sub> -clathrate	29	60	(+)	Fracture

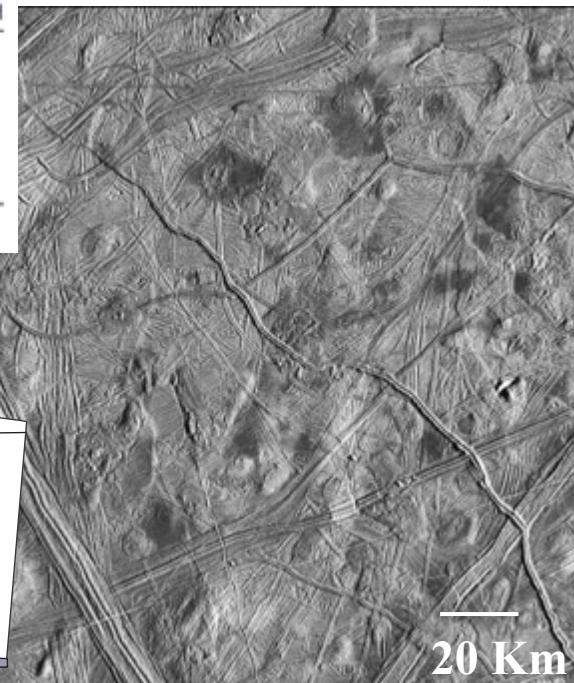
Symbols: (+) positive volume change, (-) negative volume change.



Molar volume changes when minerals form  
Features related: collapses, fractures

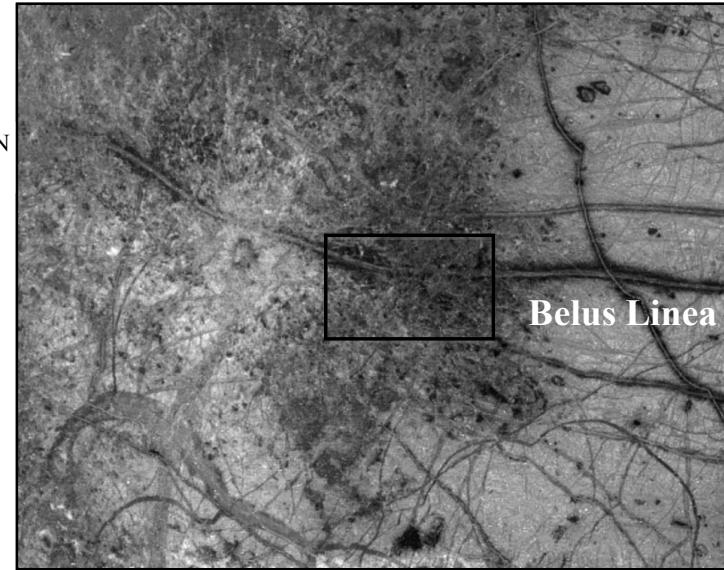
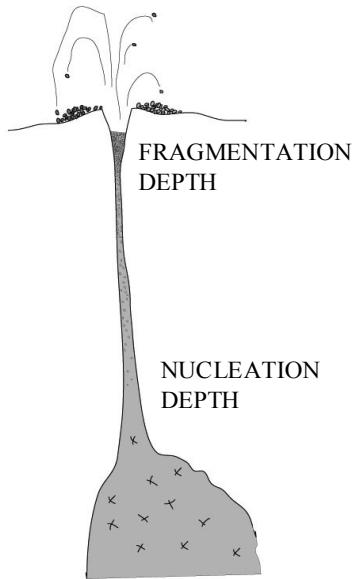
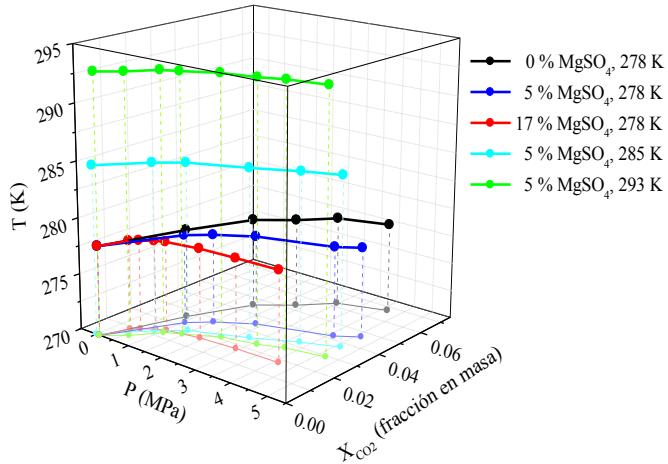
Differentiation of cryomagmas

Buoyancy of clean gassy water



20 Km

# Related geological activity



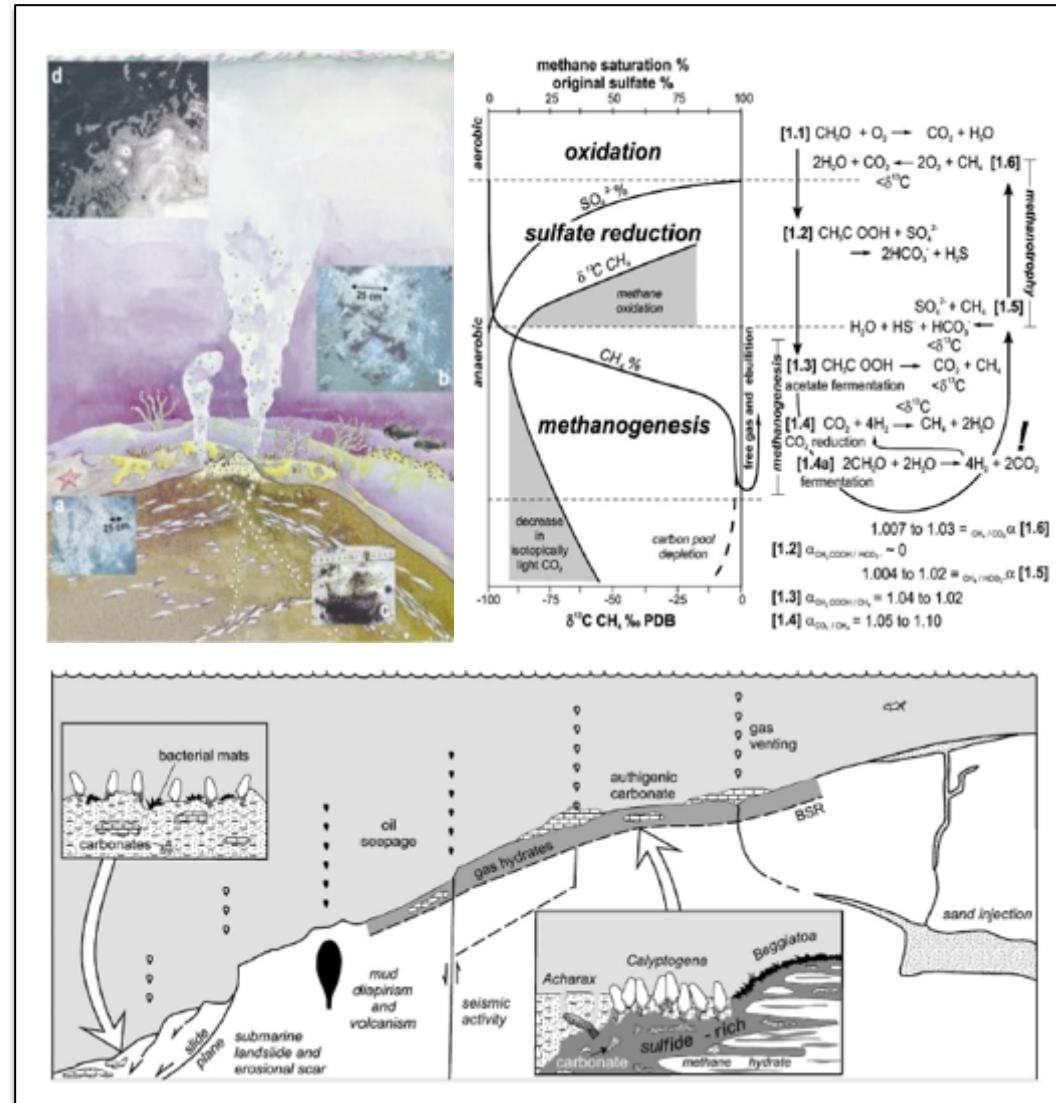
$$1/\beta = [(R T / P) \times x_{CO_2(g)} / m_{W(CO_2)}] + [(1 - x_{CO_2}) / \rho \quad (\text{Head and Wilson , 2003})]$$

M	$MgSO_4$ (wt % )	T (°C)	$P_B$ (MPa)	Bubble depth (m)	Explosive eruption depth (m)
1	0	5	$1.0 \pm 0.1$	$817 \pm 113$	$218 \pm 28$
2	5	5	$1.52 \pm 0.08$	$1268 \pm 70$	$260 \pm 18$
3	17	5	$> 4.2$	$> 3500$	$312 \pm 28$
4	5	12	$2.9 \pm 0.1$	$2455 \pm 100$	$347 \pm 18$
5	5	20	$4.8 \pm 0.4$	$4030 \pm 320$	$378 \pm 113$

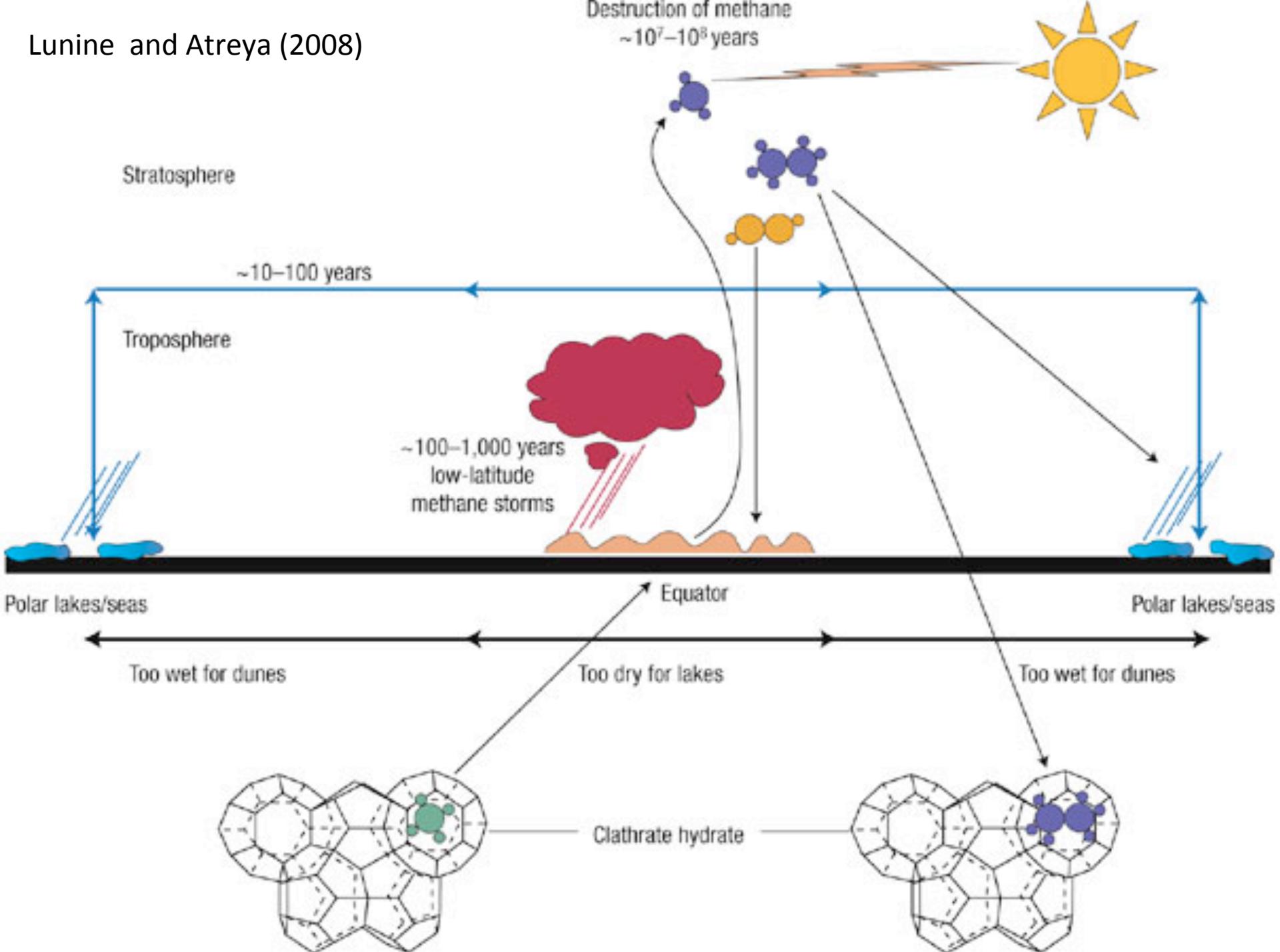


# Role in (bio)geochemical cycles

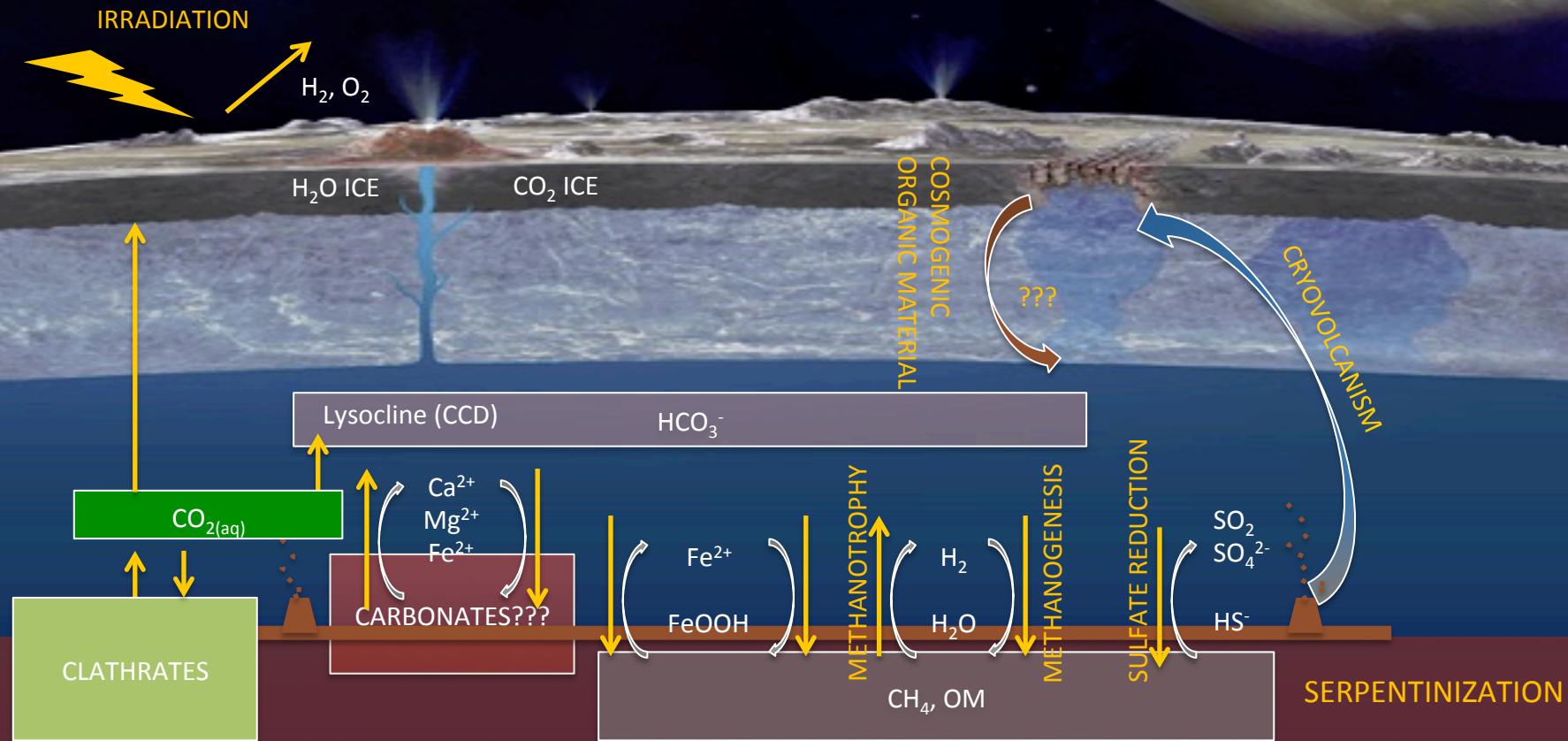
- Retain carbon molecules, e.g. hydrocarbons, and is the source of some cold seeps
- Associate to extremophiles, e.g. deep ocean today and in the past (Campbell 2005)
- Deposits are present at high latitudes and along the continental margins in the oceans (e.g., Kvenvolden, 1998)
- Environmental effects: Dissociation of clathrates may cause global warming and oceanic anoxia (Matsumoto 1995: Permian oxidation of the oceans that cause mass extinctions; oxygen was removed)



clathrate hydrates be major sinks of chemical building blocks



- Most of the C come from the accretion time
- Chemical models propose that hydrothermal fluids altered the silicate mantle and OM
- Oxidation is promoted by the escape of H<sub>2</sub> to space
- CO<sub>2</sub> transforms to HCO<sub>3</sub><sup>-</sup> because the equilibration of pH from acidic to 8 (Zolotov and Shock 2004)

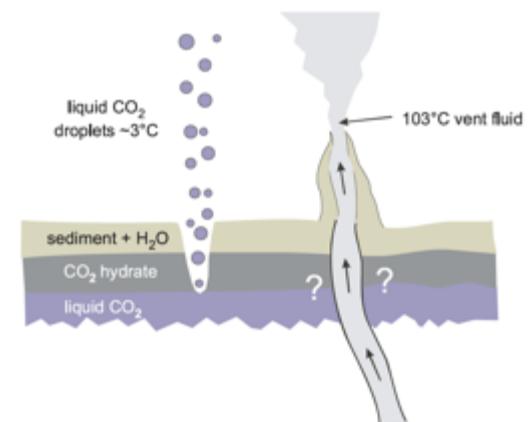
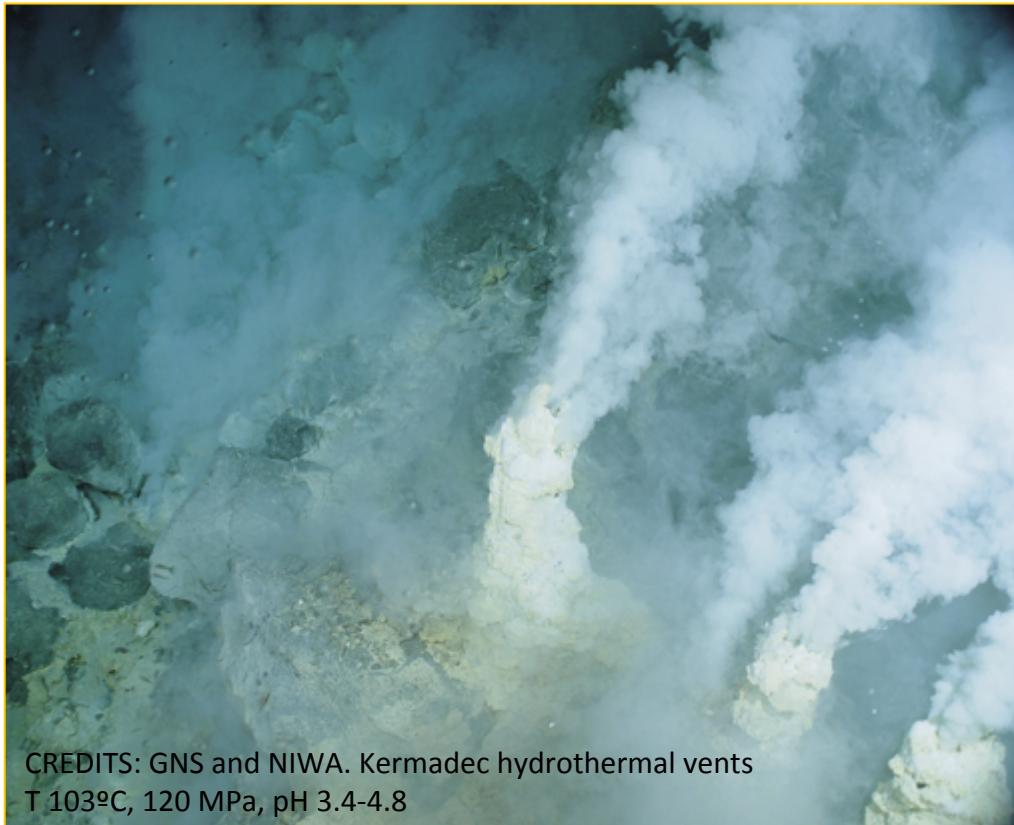


Modified from Zolotov and Shock (2004), Hand et al. (2009)

ROCKS

# Role in (bio)geochemical cycles

- Retain/release essential elements
- Fractionate volatile molecules (e.g. Ikeda et al 1999, in Vostok ice)
- Modify acidity of aqueous solutions (e.g. Lupton et al. 2008, in Kermadec hydrothermal vents)
- Concentrate nutrients in the remaining solution (if salts, activity of water is reduced)



CREDITS: GNS and NIWA. Kermadec hydrothermal vents  
T 103°C, 120 MPa, pH 3.4-4.8

