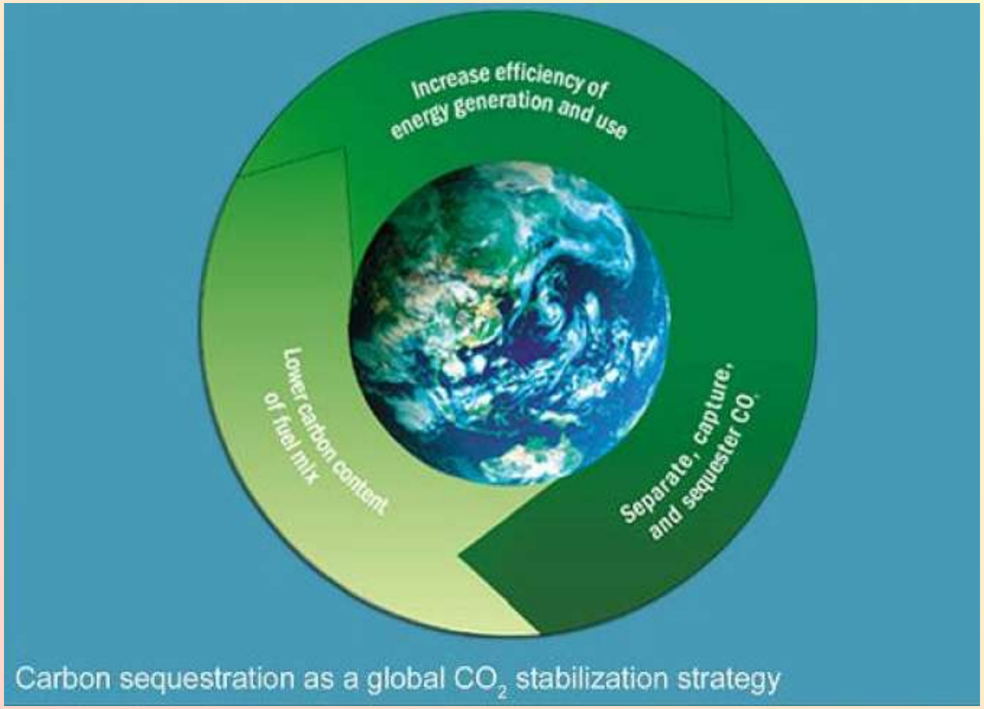
Sequestering Carbon dioxide into Clathrate Hydrates: Laboratory Studies



Carbon sequestration as a global CO_2 stabilization strategy

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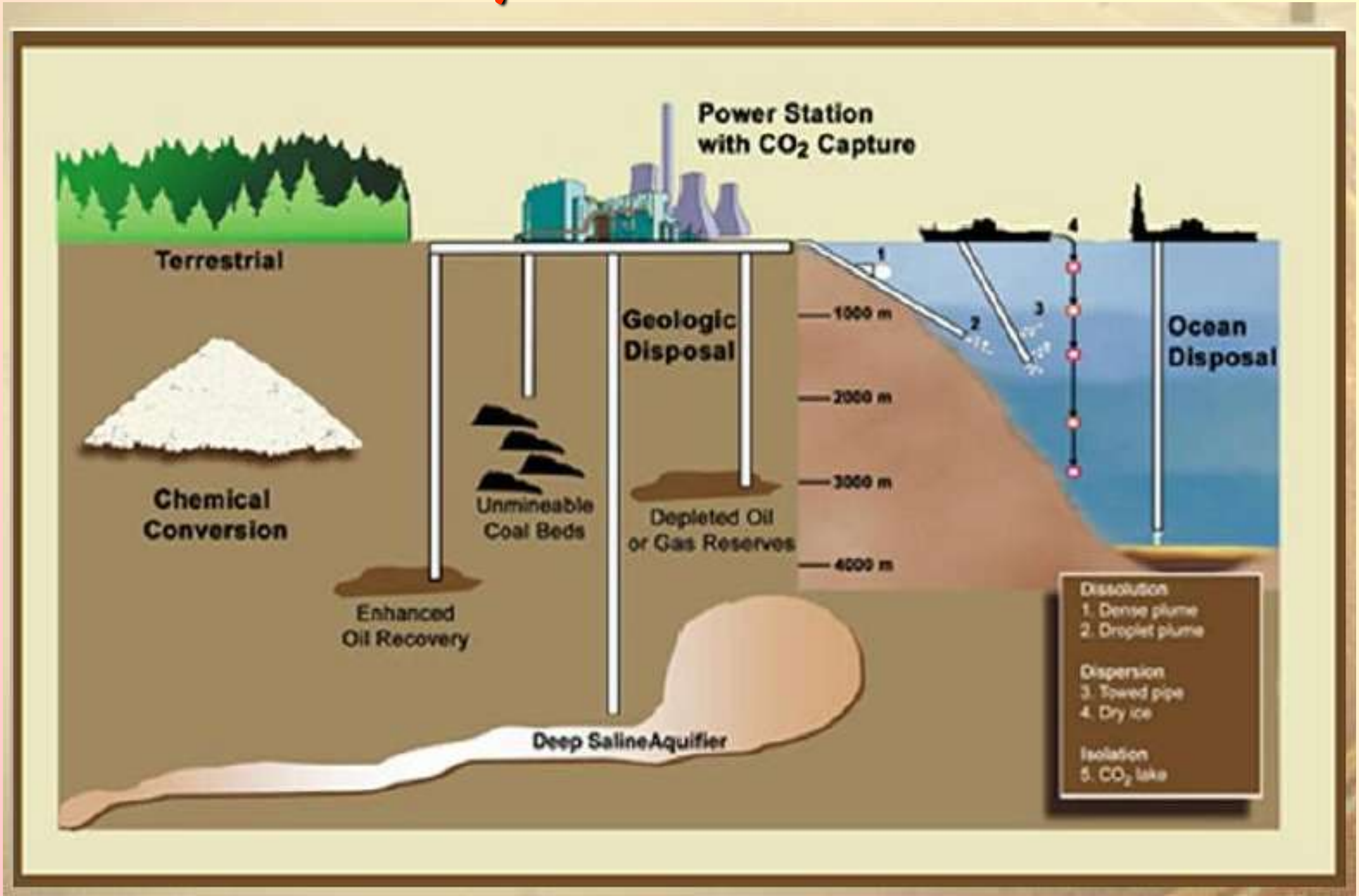
HYDERABAD – 500 007

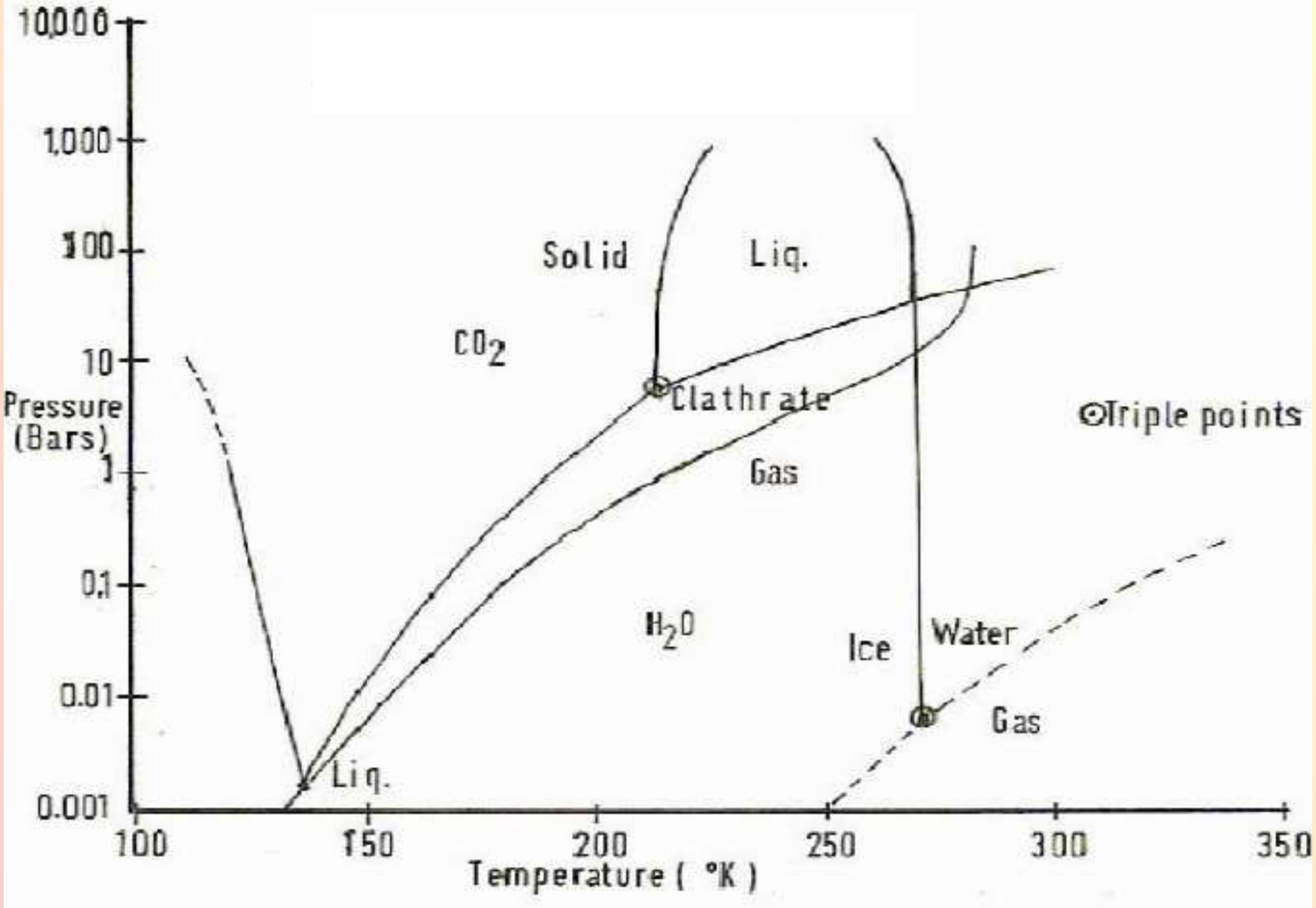
Current Sequestration Methods

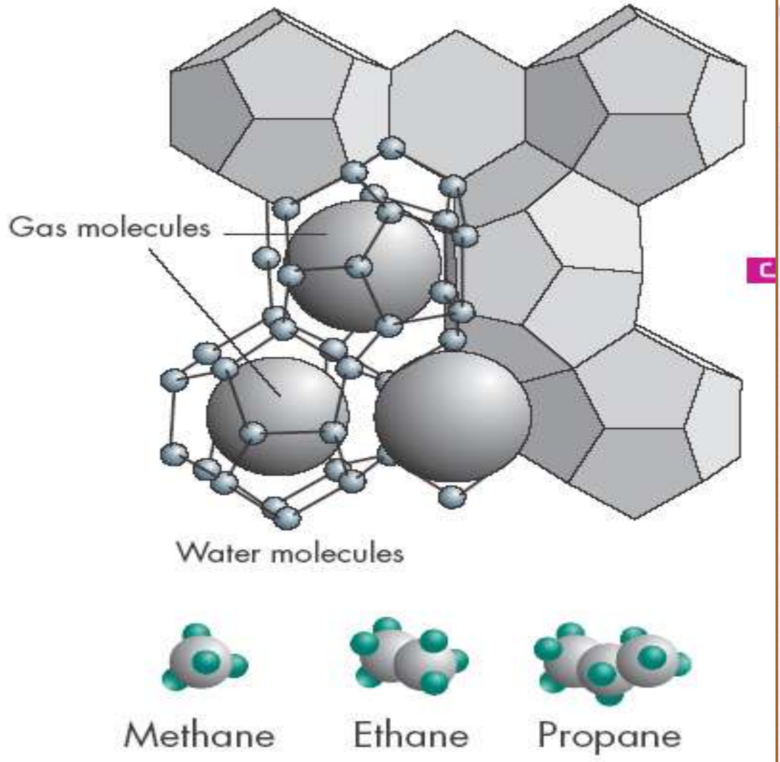


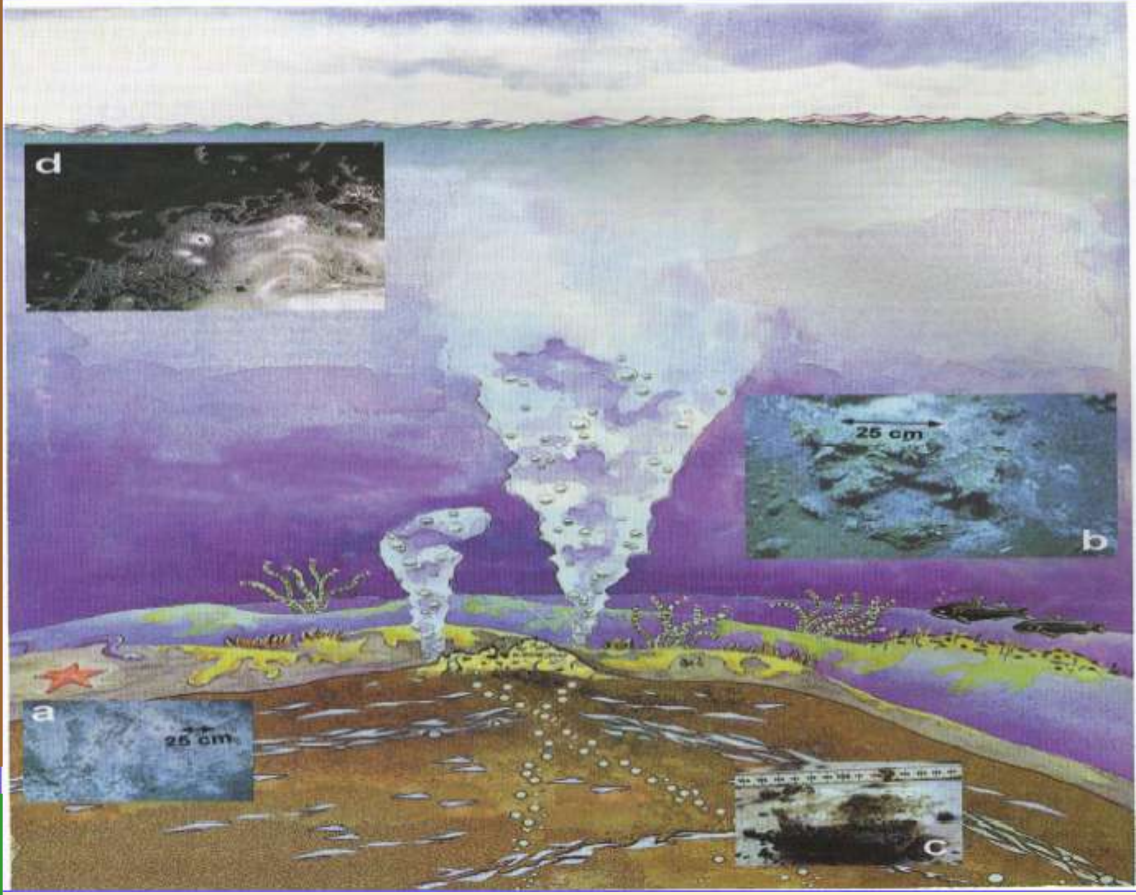
Novel Concepts:

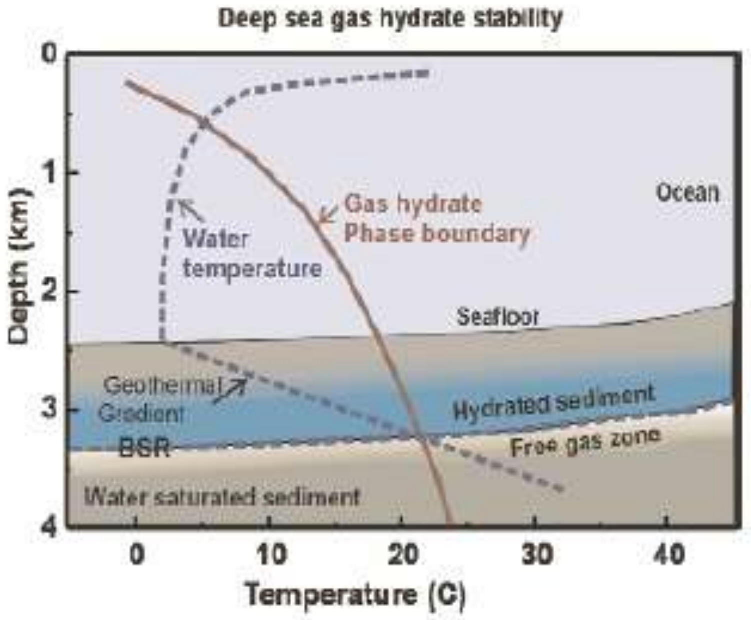
- Glacial Storage (Clathrates)
- Biogenic Methane
- Mineralization

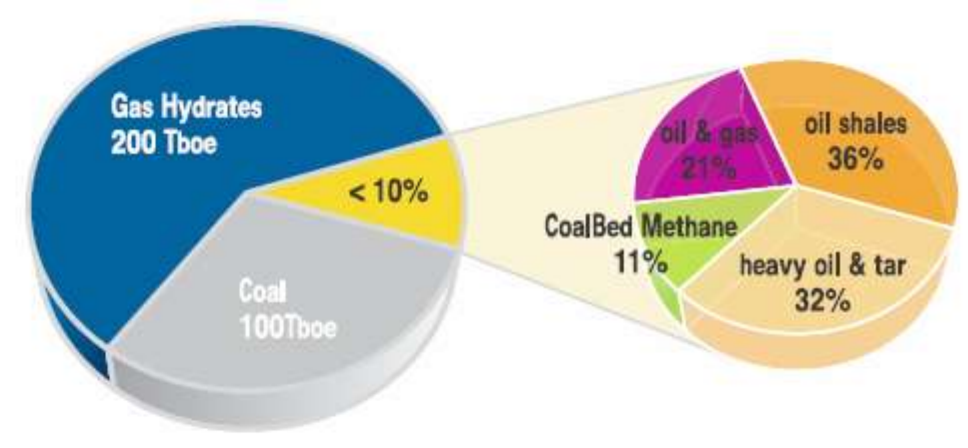
CO_2 – H_2O Phase Diagram



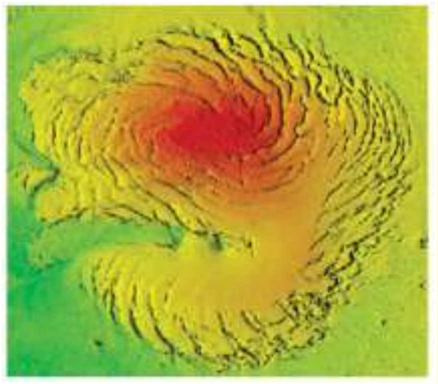

Gas molecules
Water molecules
Methane
Ethane
Propane


d
25 cm
b
a
25 cm
c

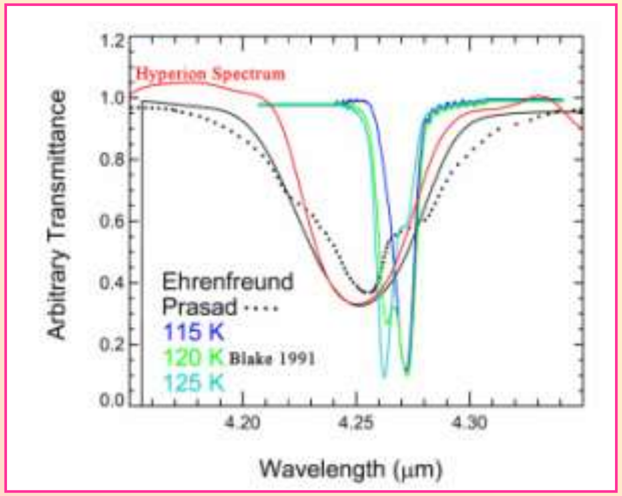

Deep sea gas hydrate stability
Depth (km)
0
1
2
3
4
Ocean
Gas hydrate Phase boundary
Water temperature
Seafloor
Geothermal Gradient
Hydrated sediment
BSR
Free gas zone
Water saturated sediment
0
10
20
30
40
Temperature (C)

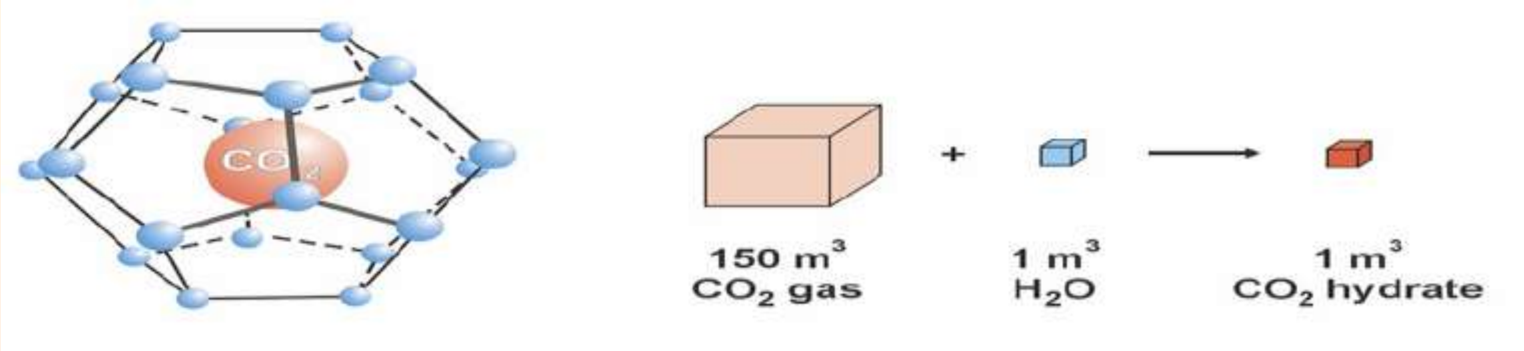

Gas Hydrates 200 Tboe
< 10%
Coal 100Tboe
oil & gas 21%
oil shales 36%
CoalBed Methane 11%
heavy oil & tar 32%

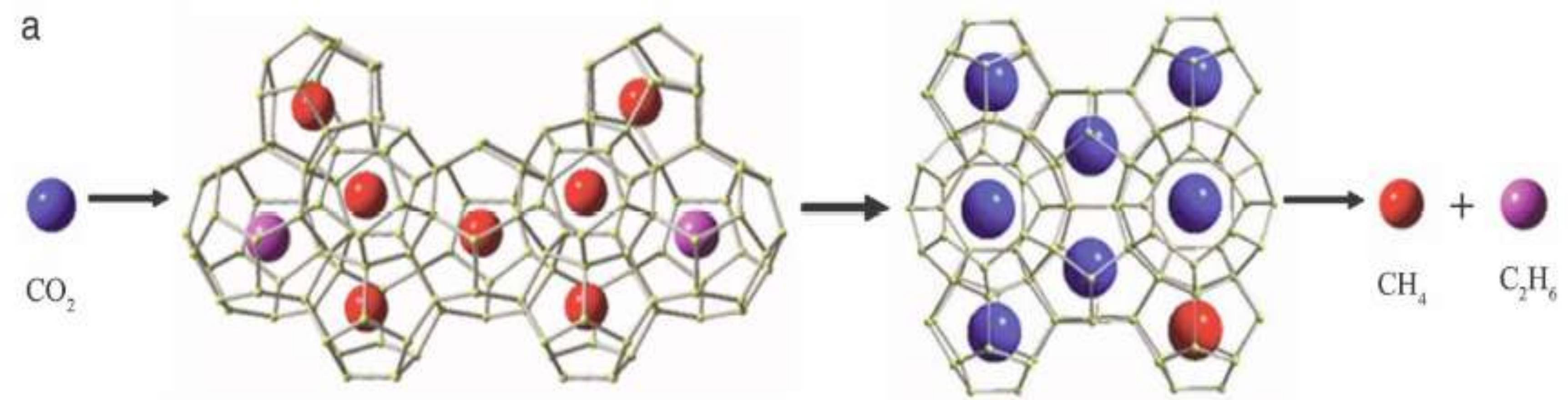
Glacial Clathrate Storage: a better carbon store

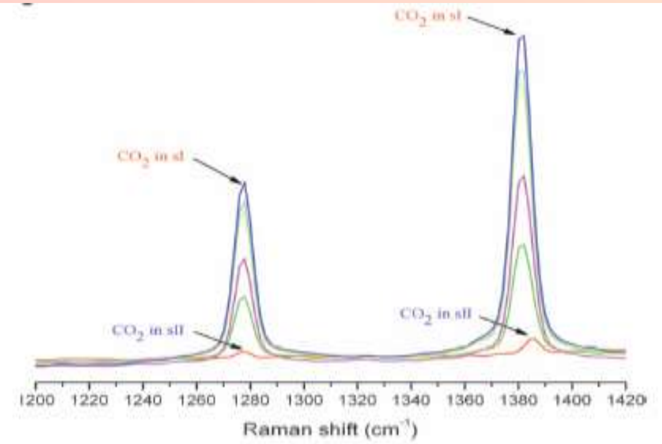


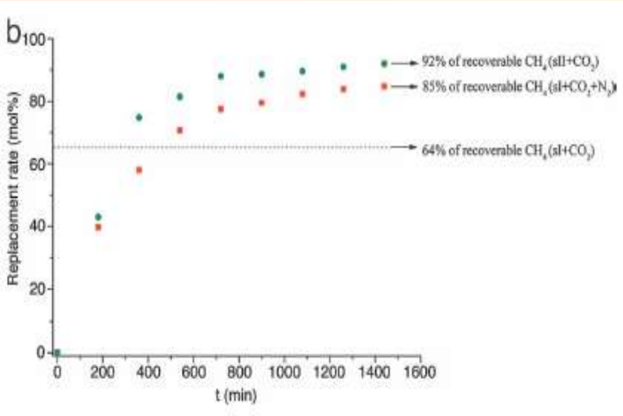
- Clathrates naturally form in Glaciers
- Storage times up to 1 million years
- Stability of Clathrates within Glaciers
- Practically unlimited storage of CO_2
- Low environmental impact
- Low energy requirement to create store
- Stored carbon is recoverable




CO_2
150 m^3 CO_2 gas
+
1 m^3 H_2O
1 m^3 CO_2 hydrate


a
CO_2
CH_4
+
C_2H_6


CO_2 in sI
CO_2 in sI
CO_2 in sII
CO_2 in sII
1200
1220
1240
1260
1280
1300
1320
1340
1360
1380
1400
1420
Raman shift (cm^{-1})


b
Replacement rate (mol%)
0
20
40
60
80
100
t (min)
0
200
400
600
800
1000
1200
1400
1600
92% of recoverable CH_4 (sII+CO_2)
85% of recoverable CH_4 (sI+CO_2+N_2)
64% of recoverable CH_4 (sI+CO_2)

What are the issues related to the presence of gas hydrates?

Deep offshore extraction

Extreme conditions encountered at these depths require an adaptation of the drilling muds. The range of temperature (down to - 1°C) and pressure (up to 400 bars) favor the formation of gas hydrates. The water contained in the drilling muds traps the gas molecules coming from the reservoirs. The plugging of the lines as well as the annular may cause interruption of the drilling operation and even destruction of the rig equipment.

Flow assurance

The production, processing and distribution of gas is a high pressure operation. Under pressure, pipelines can be plugged with gas hydrate in the form of ice. Today every oil and gas company has a flow assurance department responsible for detecting and predicting the formation of gas hydrates in the pipelines and the processing equipment.

Natural gas hydrates

More and more countries are interested in the investigation of gas hydrates trapped in marine sediments and in permafrost. Gas hydrates occur abundantly in nature, both in artic regions and in marine sediments. Methane trapped in marine sediments as a hydrate represents a huge carbon reservoir. The worldwide amounts of carbon bound in gas hydrates is conservatively estimated at twice the total amount of carbon to be found in all known fossil fuels on earth. Methane hydrate is stable in ocean floor sediments at water depths greater than 300m.

Storage and transportation of natural gas

One way of reducing the cost of natural gas transport is to carry it as natural gas hydrates (NGH). The gas hydrate process reduces the volume of natural gas by about 169 times and stores the hydrates within a range of potential temperatures and associated pressures. Such transportation and storage are easier and safer than liquefied natural gas (LNG) handling. But more has to be known about the formation of gas hydrates to optimize the industrial process, and particularly their stability and conditions of safety during transportation and storage.

Global warming

The stability of gas hydrates and their effect on global warming may become an issue and needs to be investigated. Depending on the stability of the gas hydrates, a 1 or 2°C increase in the temperature of the ocean might possibly cause the release of methane into the atmosphere with all the ensuing impacts on climate changes.

CO$_2$ ocean sequestration

CO2 ocean sequestration is one method being explored to control the build-up of CO2 in the atmosphere. The formation of a CO2 hydrate from fossil fuel CO2 disposal with a solid hydrate as the sequestered form is evaluated. The success of the option of pumping liquid CO2 into the oceans depends above all on the chemical stability of the CO2 hydrate.

Cold energy storage

As gas hydrates show high latent heat during formation and dissociation, they are considered very interesting materials for cold energy storage.

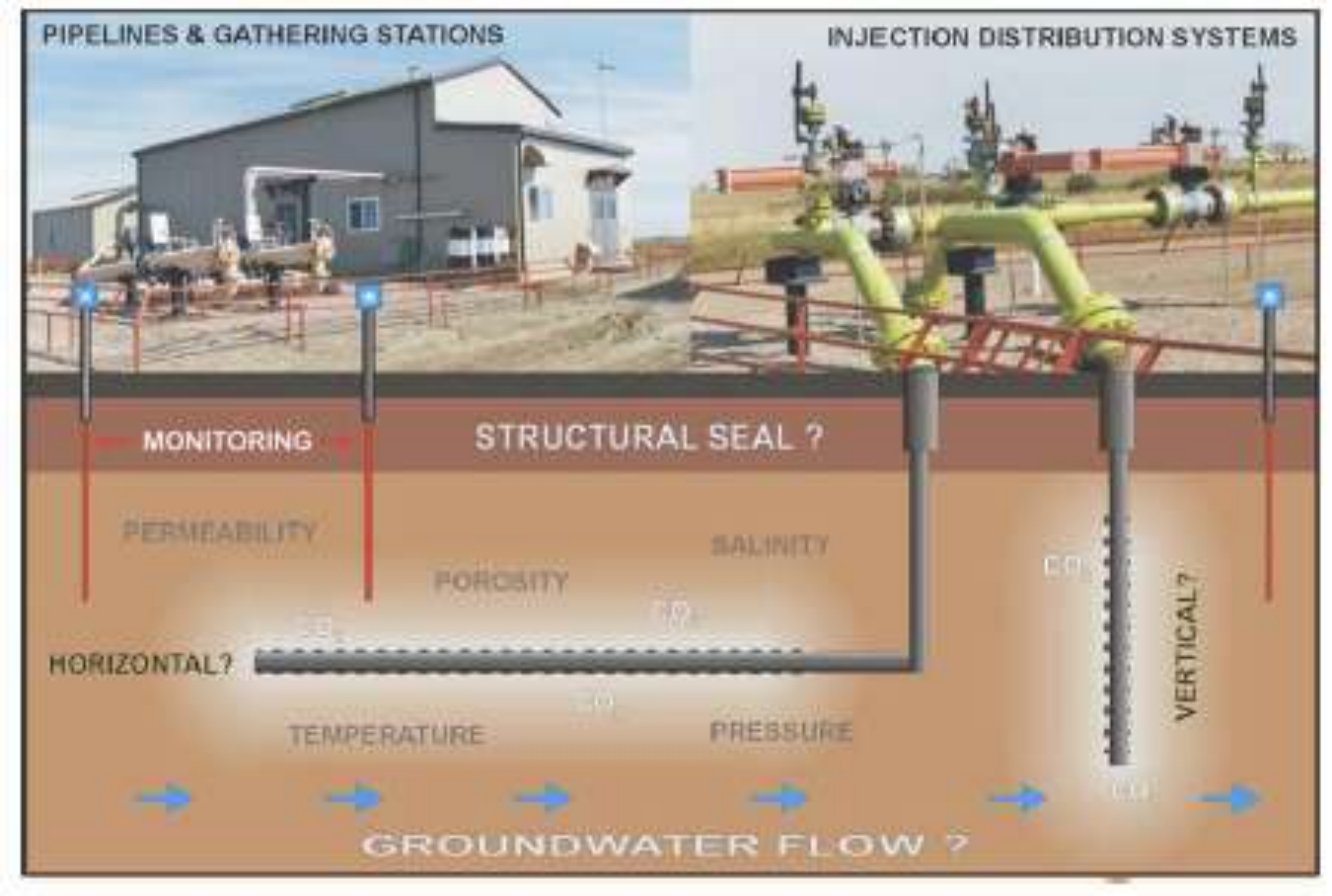
Desalination

Gas hydrate technology can be used to produce fresh water. Using an appropriate gas, water molecules go into a hydrate phase during hydrate formation from salt water, while minerals dissolve in the water concentrate.

For all the scientists working on the above mentioned topics, it is absolutely vital to have as much information as possible on gas hydrate formation / dissociation such as:

- thermodynamic properties
- kinetics data with any type of mixture (even including solid particles)

Conceptual diagram – (Geological)



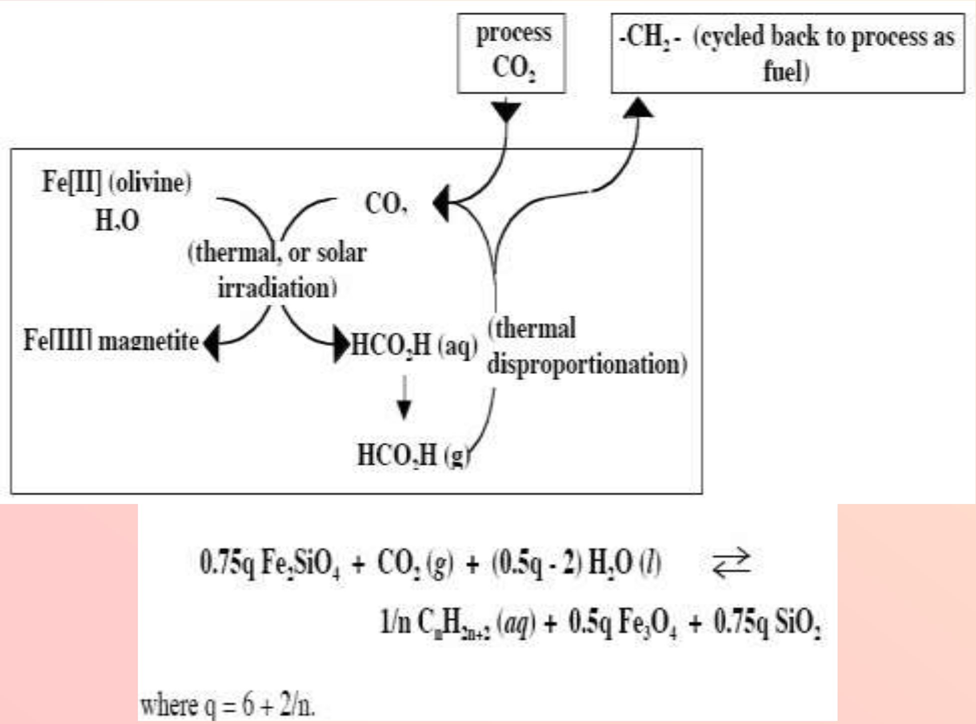
$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$$

(Olivine) (Magnesite)

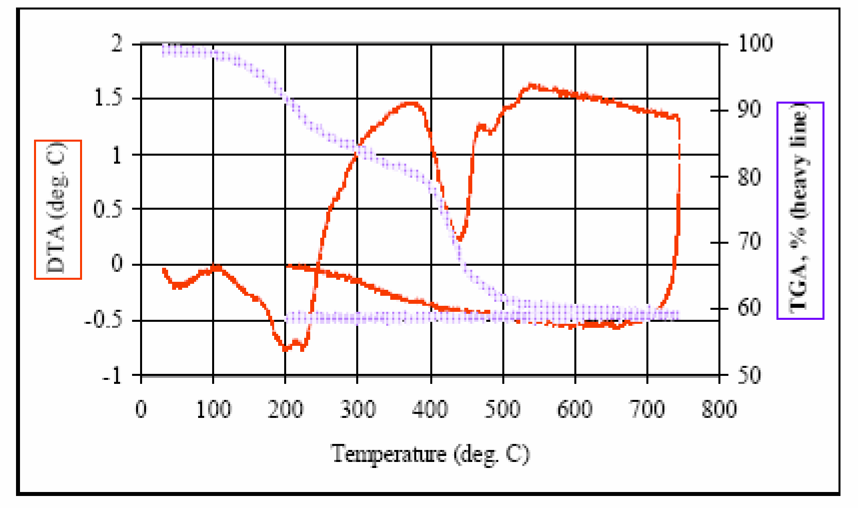
$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$$

(Serpentine) (Magnesite)



$$0.75q\ Fe_2SiO_4 + CO_2\,(g) + (0.5q - 2)\ H_2O\,(l) \rightleftarrows \frac{1}{n}\ C_nH_{2n+2}\,(aq) + 0.5q\ Fe_3O_4 + 0.75q\ SiO_2$$

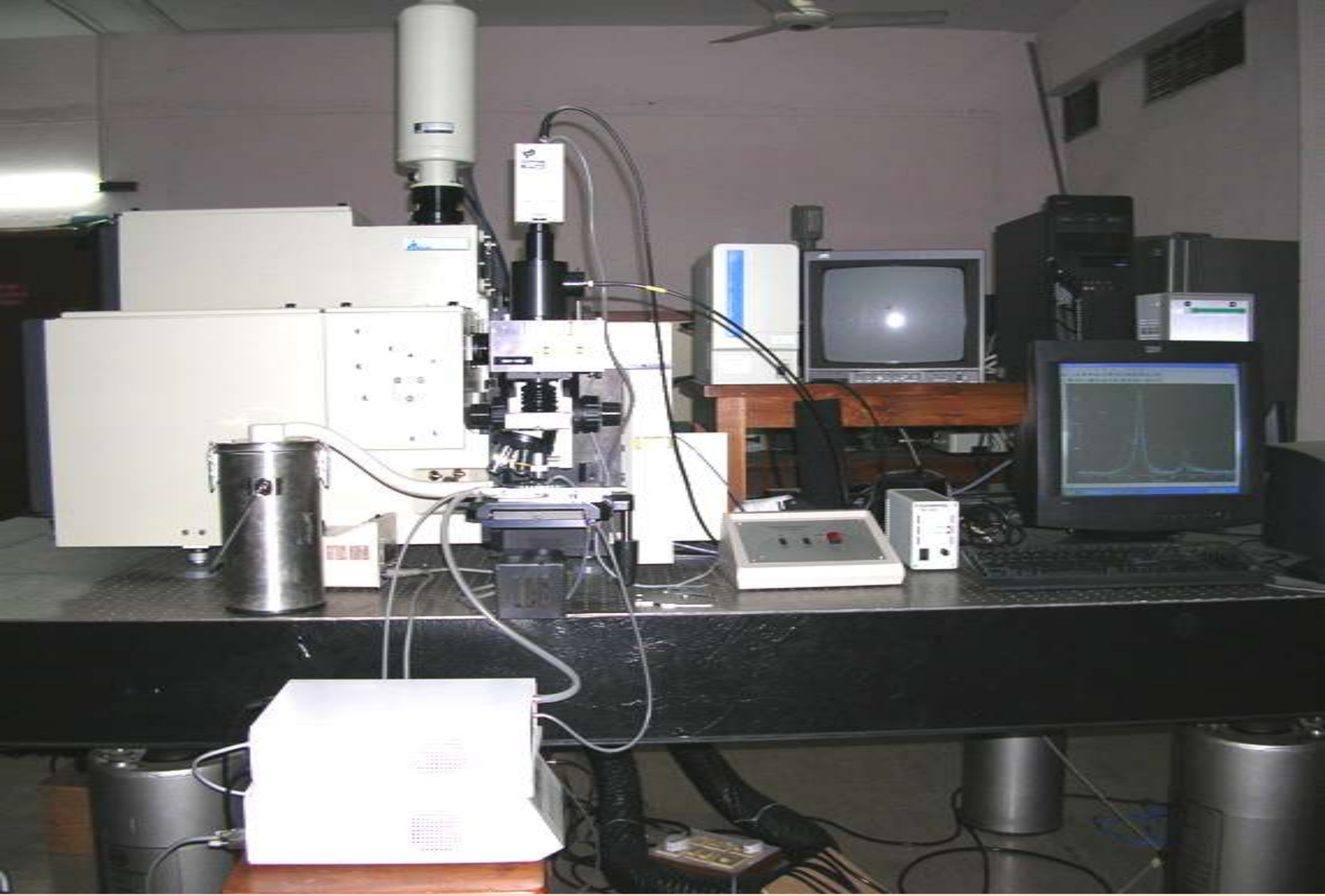
where $q = 6 + 2/n$.



Hydromagnesite [3MgCO3.Mg(OH)2.3H2O]

Objectives:

- Firstly, to study the kinetics of carbonation reactions in laboratory test vessels by varying the parameters like temperature and pressures. The reactants & products will be analyzed in detail to estimate the over-all retention time of captured carbon dioxide.
- The second objective is to develop an understanding into guest - host interactions in gas hydrate system. Recovery of hydrocarbons from '*Gas hydrates*' is a technological problem as the volume of gas released on dissociation of hydrates is exceedingly large.



Raman spectrometer

FTIR spectrometer

De-(Re) hydration induced structural modifications in Natural Zeolites from Deccan Traps

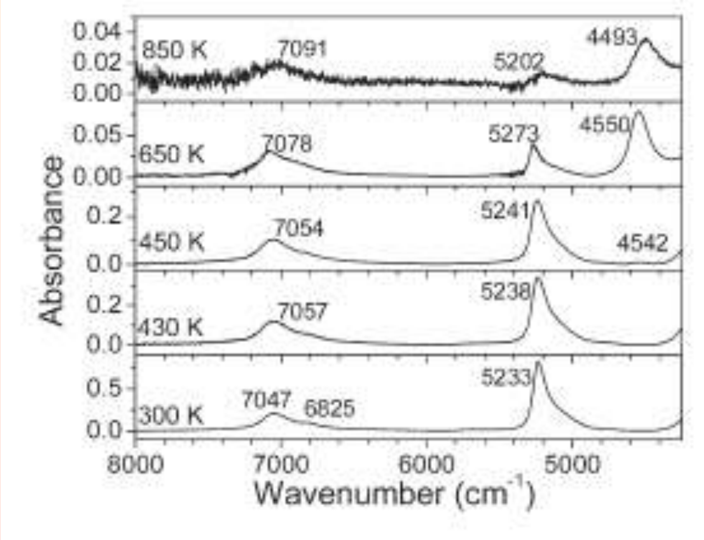
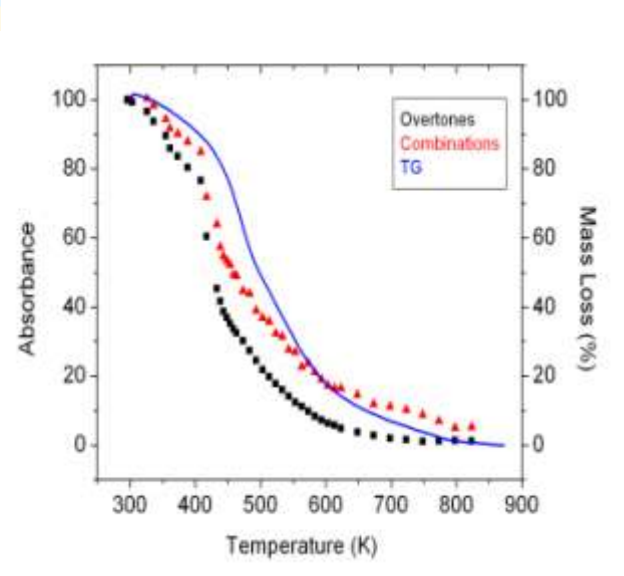
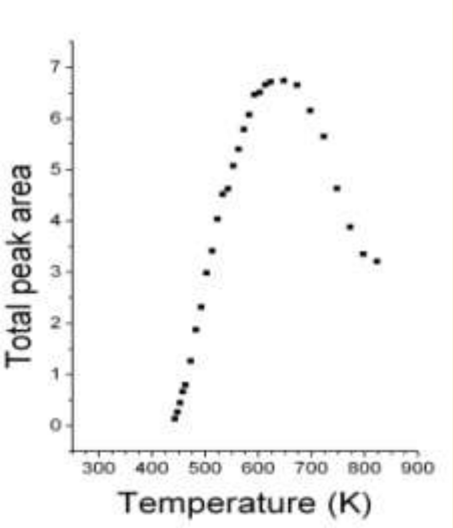


FIGURE 4. Background corrected spectra of stilbite collected at different temperatures of dehydration (300, 430, 450, 650, and 850 K) in the wavenumber region 4000–8000 cm^{-1}.





Stilbite (STI): $Na_2Ca_8(Al_8Si_{54}O_{144})60H_2O$

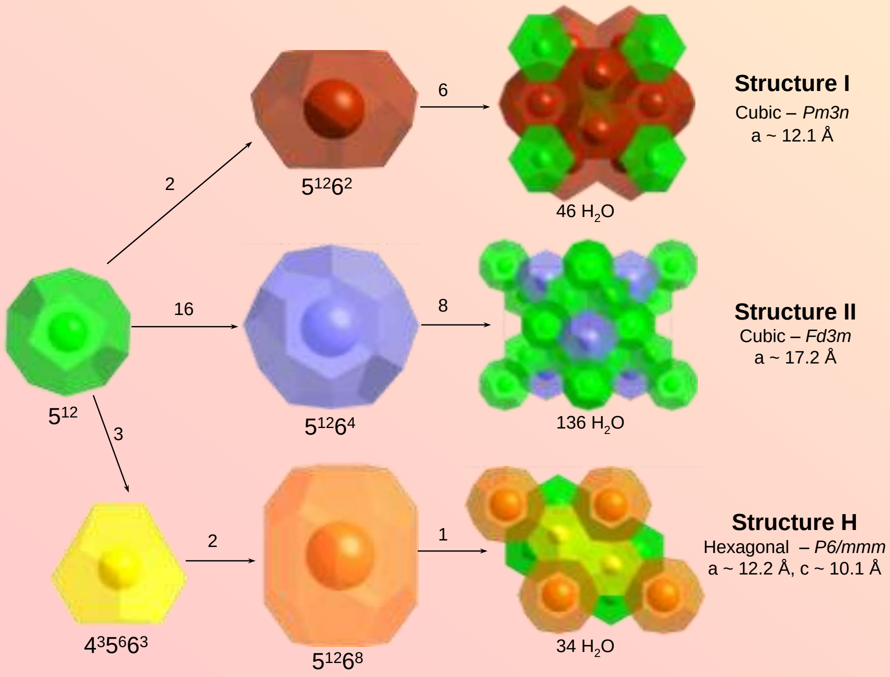
Conclusions:

- **Structural Modifications in natural zeolites are at second (high) stage dehydration**
- **Si is more prone for protonation than Al**

Prasad et al., Am Mineral, 90, 1636-1640 (2005); Eur J Mineral, 18, 265 - 272 (2006); Micropor Mesopor Mater (2006)

Clathrate Hydrate Structures:

Hydrate Type	Structure I		Structure II		Structure H		
Cavity	S	L	S	L	S	M	L
	5^{12}	$5^{12}6^{2}$	5^{12}	$5^{12}6^{4}$	5^{12}	$4^{3}5^{6}6^{3}$	$5^{12}6^{8}$
# Cavities / Unit Cell	2	6	16	8	3	2	1
Average Radius (A)	3.95	4.33	3.91	4.73	3.91	4.06	5.71



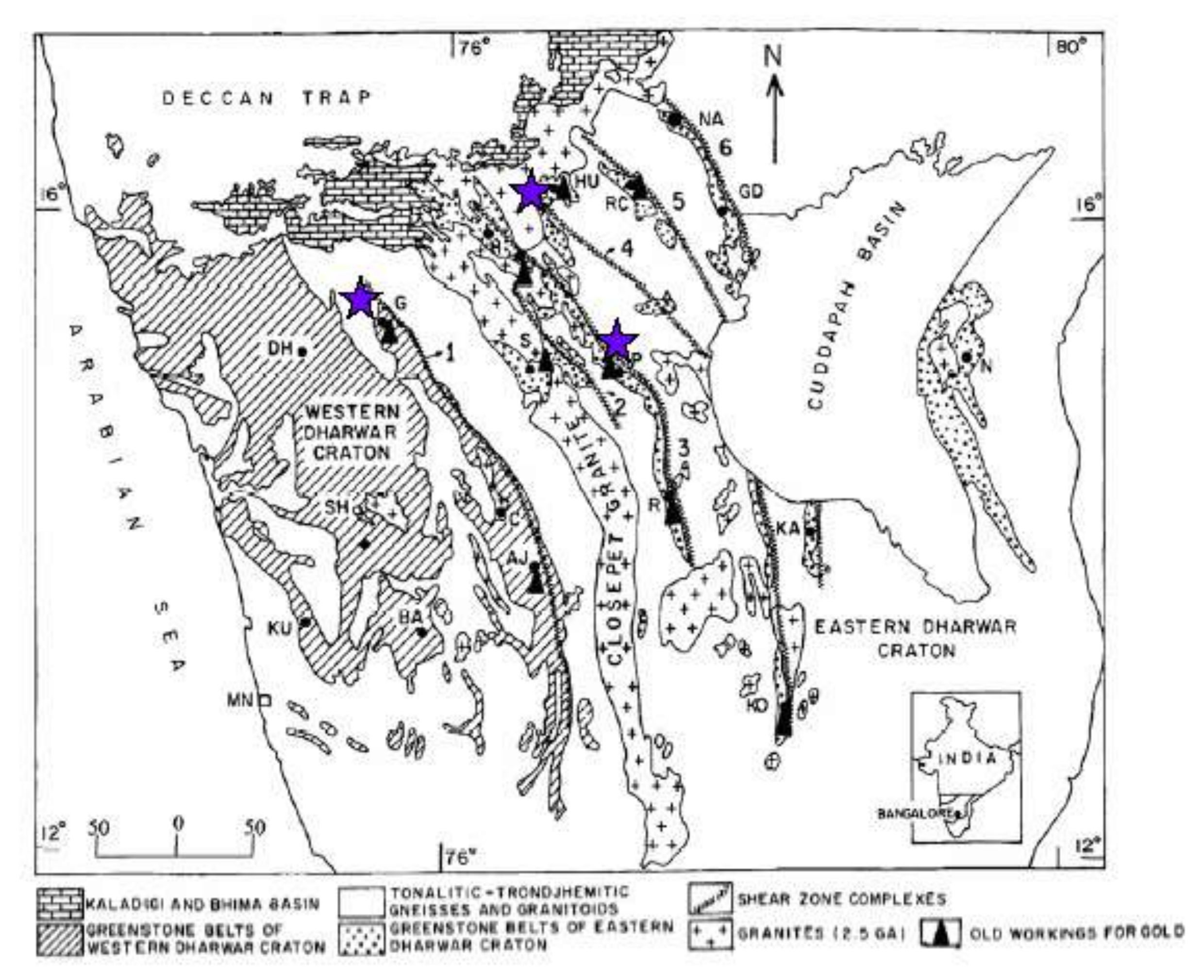
Optimum ratio – 0.76 to 1.00

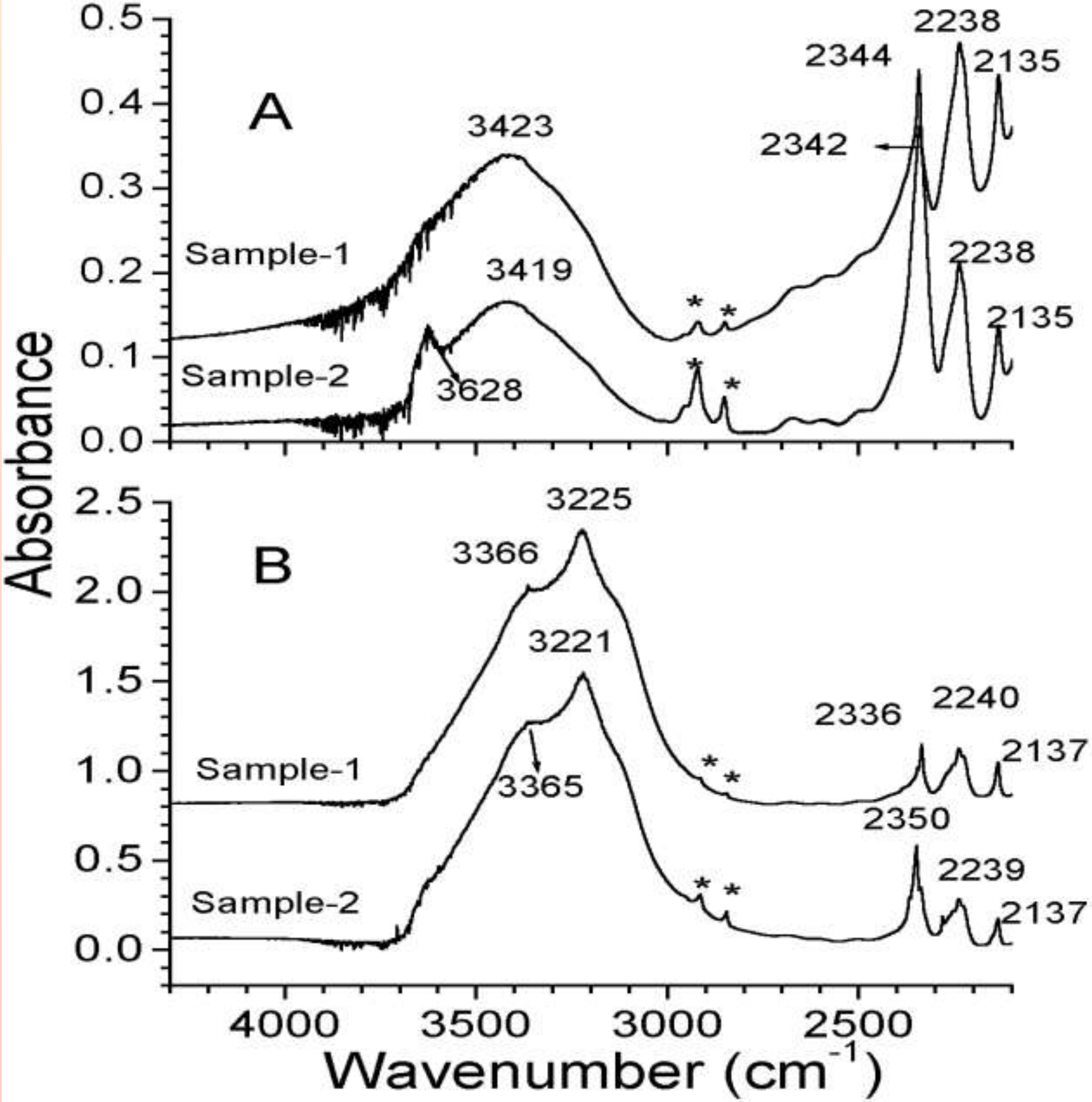
Molecule	Dia (A)
CO_2	5.12
CH_4	4.36
C_2H_6	5.5
C_3H_8	6.28
N_2	4.10
Kr	4.0
Ar	3.8

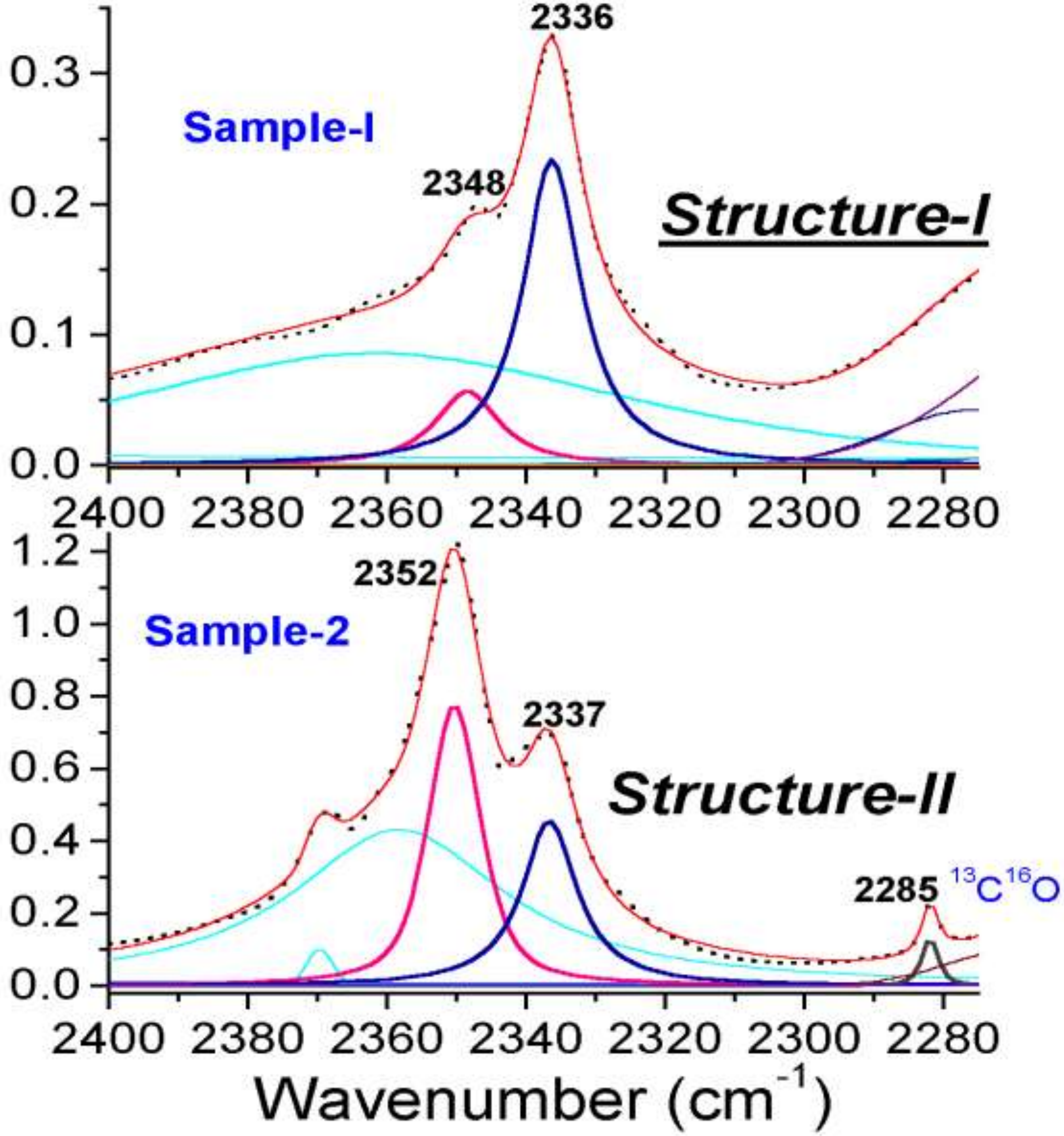
Structure I	
S	**1.004**
L	0.874
Structure II	
S	**1.02**
L	**0.76**

CO_2

FTIR Studies on CO_2 – H_2O in Quartz veins



A
B
Absorbance
Wavenumber (cm^{-1})
Sample-1
Sample-2
3423
3419
3628
2344
2342
2238
2135
*
3225
3366
3221
3365
2336
2240
2137
2350
2239
0.0
0.1
0.2
0.3
0.4
0.5
0.0
0.5
1.0
1.5
2.0
2.5
4000
3500
3000
2500

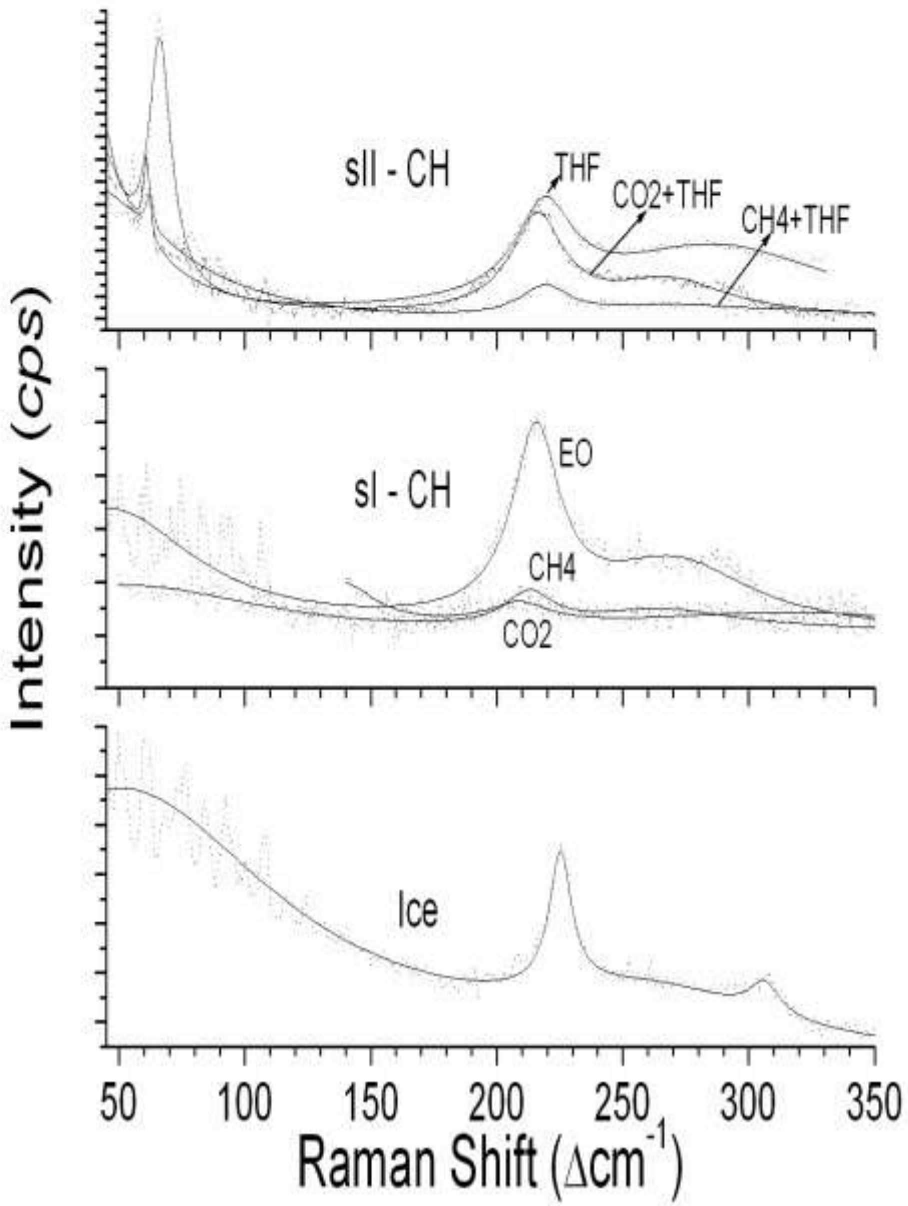

2336
Sample-I
2348
Structure-I
0.3
0.2
0.1
0.0
2400 2380 2360 2340 2320 2300 2280
1.2
1.0
0.8
0.6
0.4
0.2
0.0
2352
Sample-2
2337
Structure-II
2285 $^{13}C^{16}O$
2400 2380 2360 2340 2320 2300 2280
Wavenumber (cm^{-1})

Acrylic Cell @ 1 MPa

Propane Hydrate


VIA MADRAS
O/N. 57.55
001
Draw No. 7A
Draw No. 7B
17.11.2006
Companion

Can one distinguish sI & sII from RS ?



Guest Molecule	Observed Raman Peak (cm^{-1})		CH Struct
	Position (width)	Position (width)	
THF	219 (27)	66 (10)	sII
Propane	209 (29)	60 (6)	sII
CH_4 + THF	219 (20)	62 (4)	sII
CO_2 + THF	216 (27)	61 (3)	sII
EO	214 (28)	--	sI
CH_4	213 (24)	--	sI
CO_2	208 (28)	--	sI
Ice	225 (10)	--	--

YES - Raman mode around ~ 60 cm^{-1} is the unique feature for sII hydrates

Prasad et al., Current Science, 94 (2008) 1495

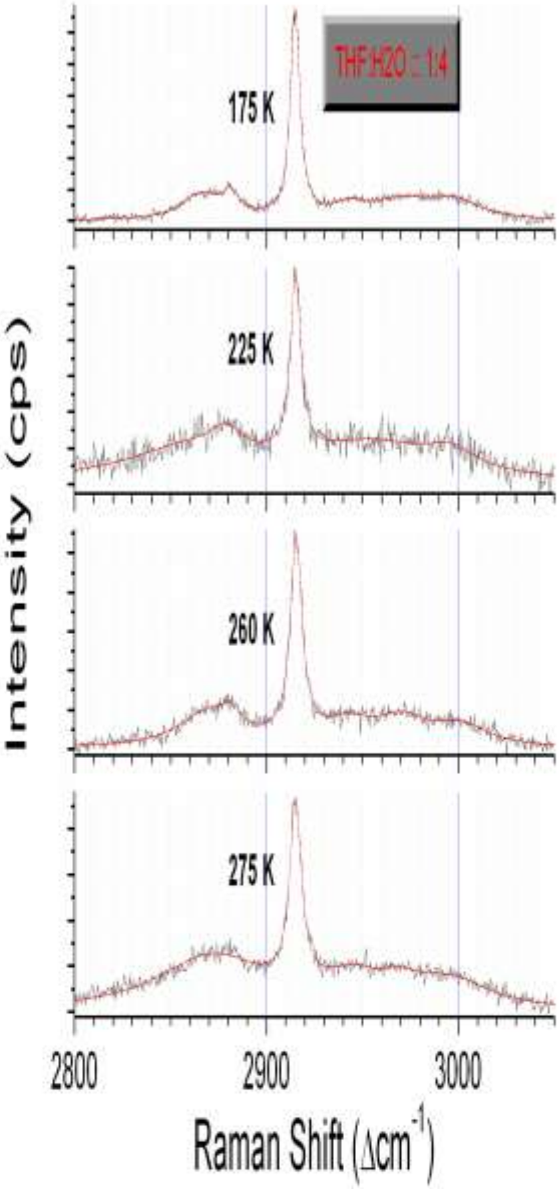
Can methane occupy vacant cages in mixed hydrates ??

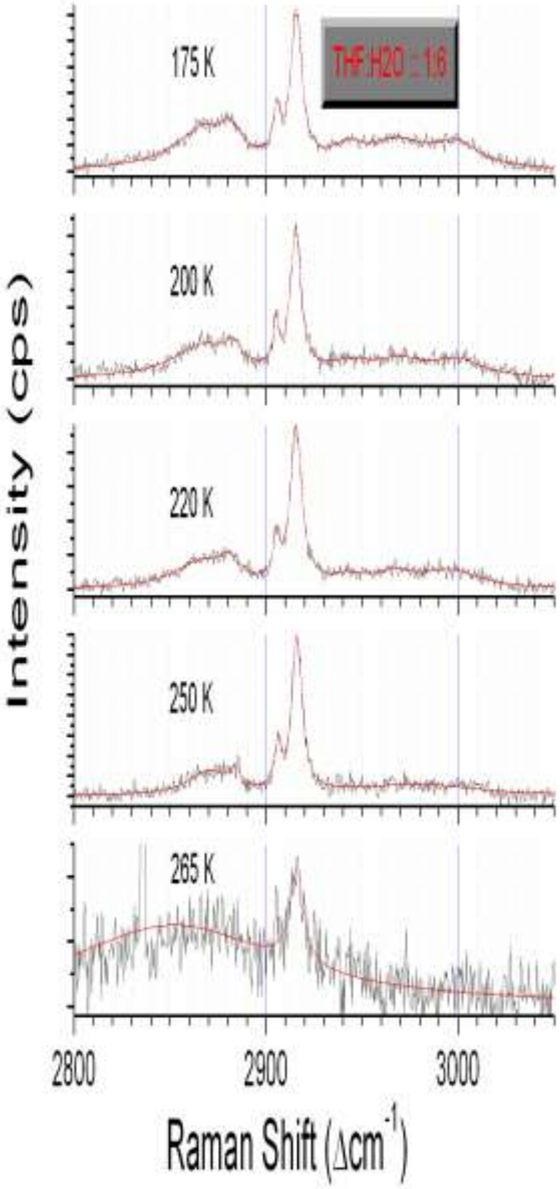
- Conflicting opinion –
mixed (sI + sII) phases
- Two hydrocarbons (THF & t-BuNH$_2$)

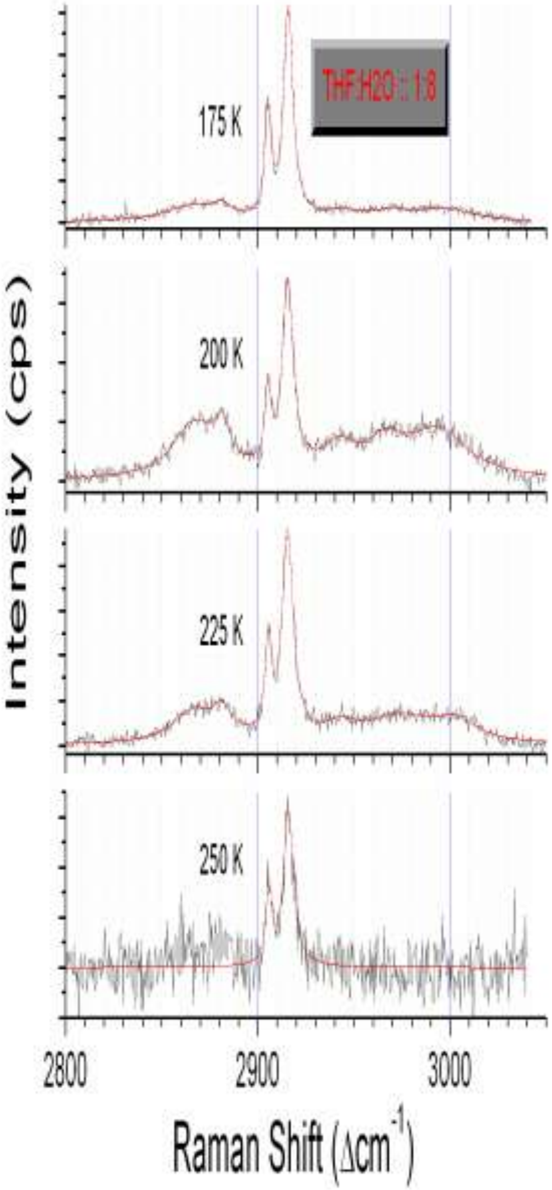
Prasad et al, Vibrational Spectroscopy 50 (2009) 319 -323

Prasad et al, J Phys Chem A 113 (2009) 11311 - 11315

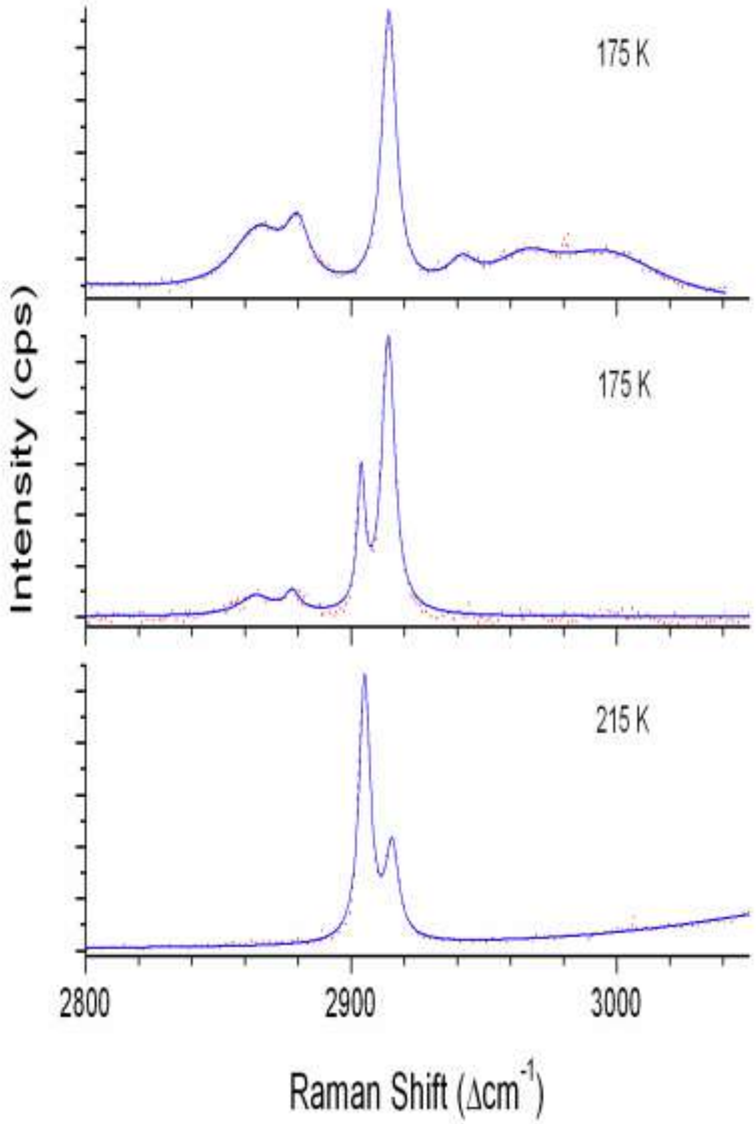
Mixed Hydrates with THF (sII)







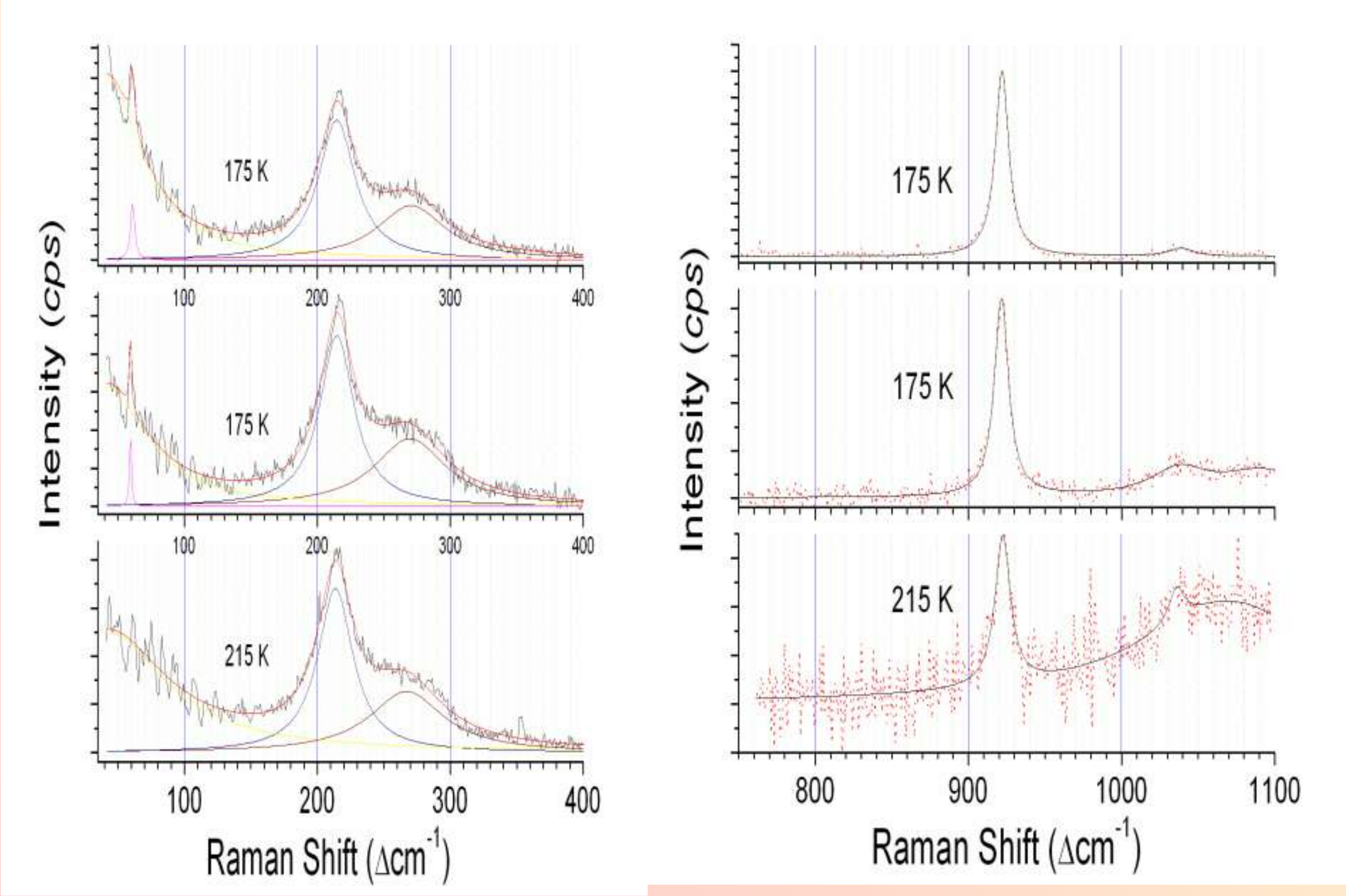
Mixed Hydrates with THF (sII)



- THF + CH_4 hydrate (sII) & methane occupies vacant 5^{12} cages. Hydrates are stable ~290 K, 0.1 MPa
- Vacant $5^{12}6^4$ cages are also occupied by methane
- A unique structural transformation sII to sI has been observed THF (1.0 mol%) + CH_4

Prasad et al., Vib Spectrosc, 50 (2009) 319

Mixed Hydrates with THF (sII)



Mixed hydrates with t-BuNH$_2$ + CH$_4$

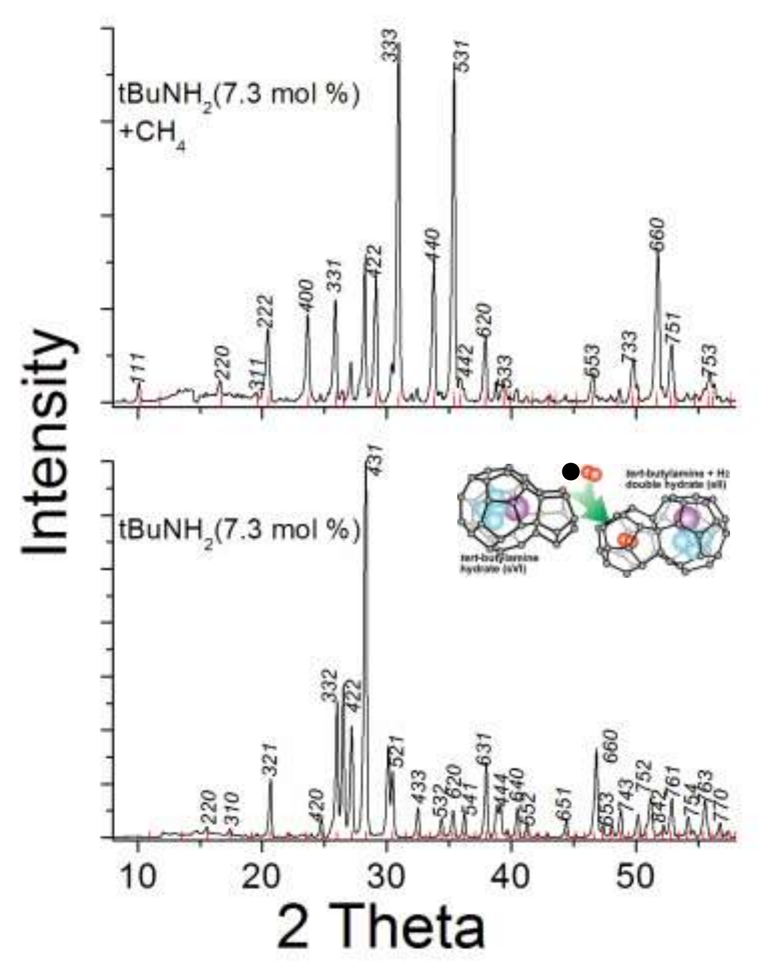
- Upon pressurizing with CH$_4$ (□ → $4^4 5^4$)

- sII – (*Fd3m*) a = 17.3984 ± 0.0177 Å

- Clathrate Hydrates with 12□ 16tBuNH$_2$.156.H$_2$O

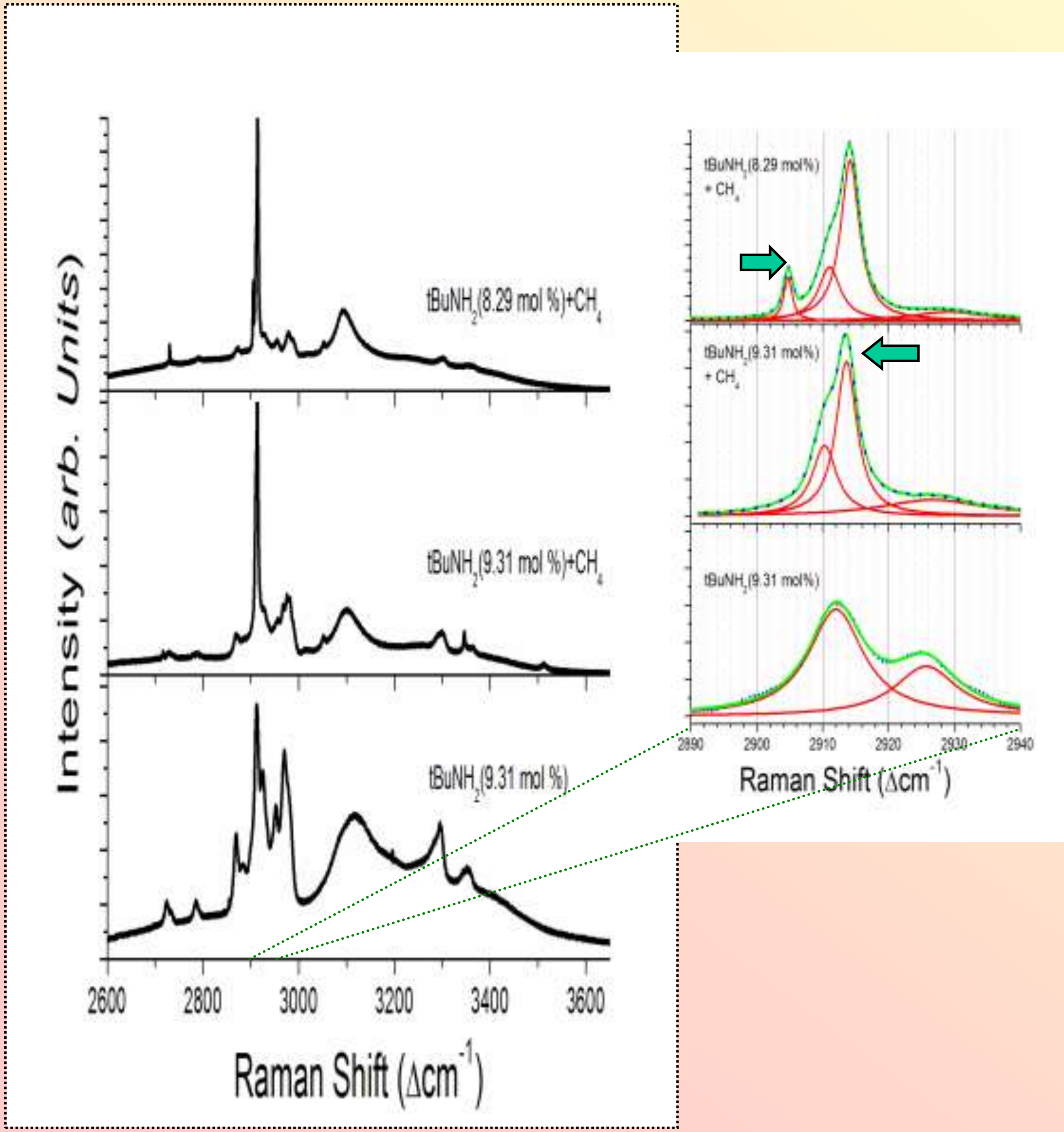
✓ sVI – (*I-43d*) a = 18.6341 ± 0.0046 Å

XRD measurements – 0.1 MPa & 120 K



Prasad et al., J Phys Chem A, in press (2009)

Raman results on (t-$BuNH_2$ + CH_4)

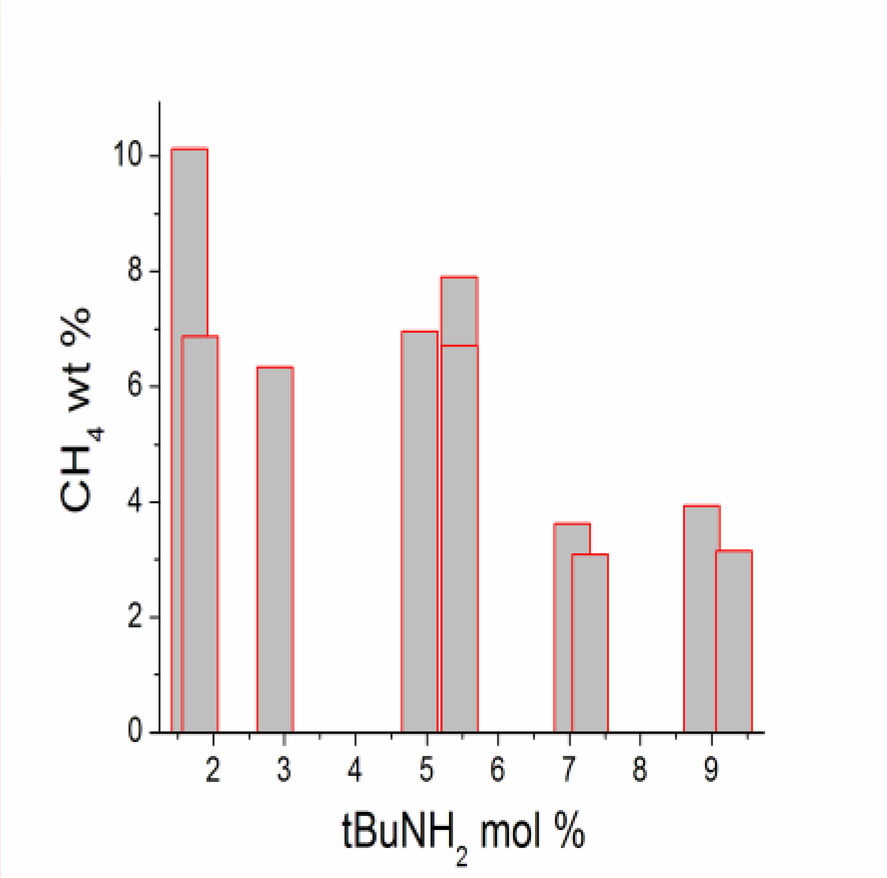


Conclusions

- t-$BuNH_2$ + CH_4 system always stabilize in sII structure. CH_4 is too large for $4^4 5^4$ cage of sVI
- CH_4 can occupy all the vacant cages of sII

Prasad et al., J Phys Chem A, 113 (2009) 11311

Gas Storage in Double Hydrates



- The storage capacity (~ 8.0 wt%) is consistent with reported cage occupancy
- Useful for shifting (P,T) conditions
- Could be useful in NGH storage and transportation

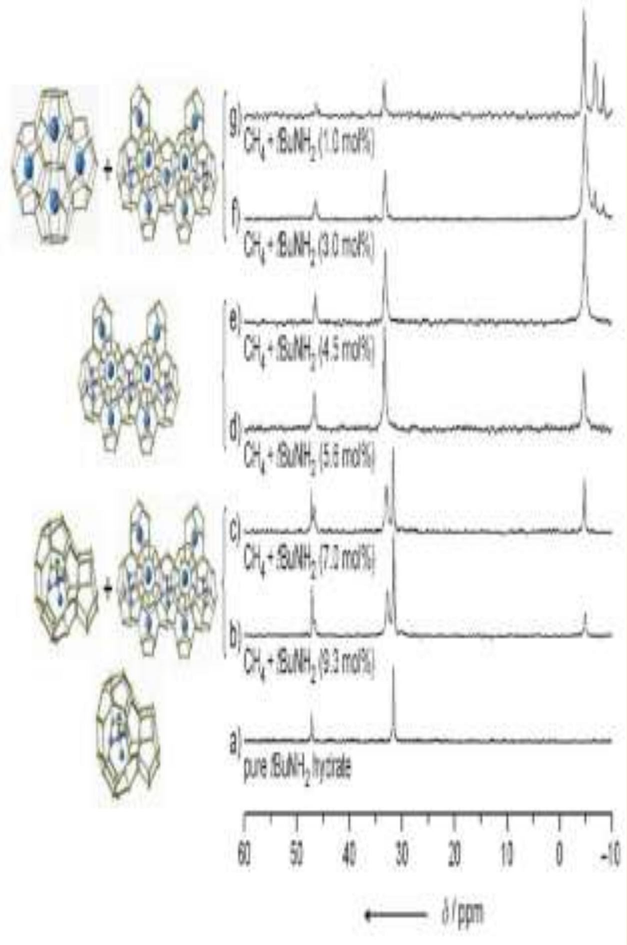
Thank You

?? !!

What is known

Tert-Butylamine + H_2O + CH_4

- Tert-butylamine – forms type VI clathrates $16(CH_3)_3CNH_2.156(H_2O)$
  - cubic (*I -4 3d*) a = 18.81 Å
  - # cages – 16 ($4^3 5^9 6^2 7^3$) & 12 ($4^4 5^4$)
- Tert-butylamine + CH_4 – forms type II clathrates $16S.8L.136H_2O$
  - cubic (*F d 3m*) a = 17.306 Å
  - tBuNH2 in 5.6 - 4.5 mol %



The storage capacity of CH_4 gas in the hydrate phase increases drastically as the initial concentration of tBuNH$_2$ decreases

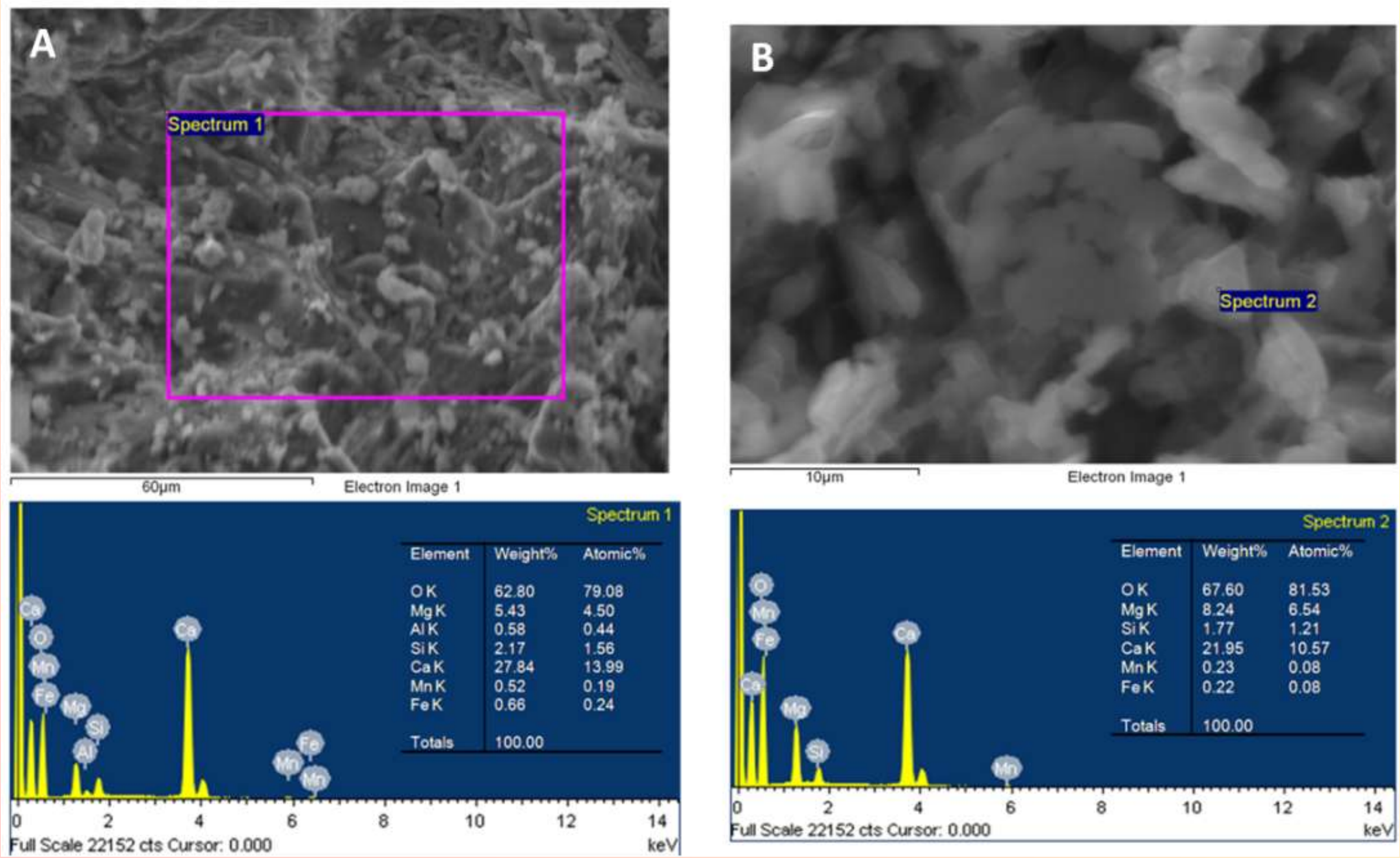
$[n(CH_4)/n(tBuNH_2)]$ ↑ upon $n(tBuNH_2)$ ~5.6 ↓ 1.0 mol%

cf. Lee et al. Angew. Chem. Int. Ed. 2005, 44, 7749 –7752

Dia molecular / (Dia of the cage – 2.8)

	Structure - II		Structure - VI	
	5^{12} (7.82 Å)	$5^{12}\ 6^{4}$ (9.46 Å)	$4^{4}5^{4}$ (5.80 Å)	$4^{3}5^{9}6^{2}7^{3}$ (10.2 Å)
Hydrogen (2.72 Å)	0.542	0.408	**0.907**	0.368
Methane (4.36 Å)	0.868	0.655	**1.453**	0.589
$tBuNH_2$ (6.72 Å)	**1.339**	1.009	**2.24**	**0.908**

Optimum ratio – 0.76 to 1.00



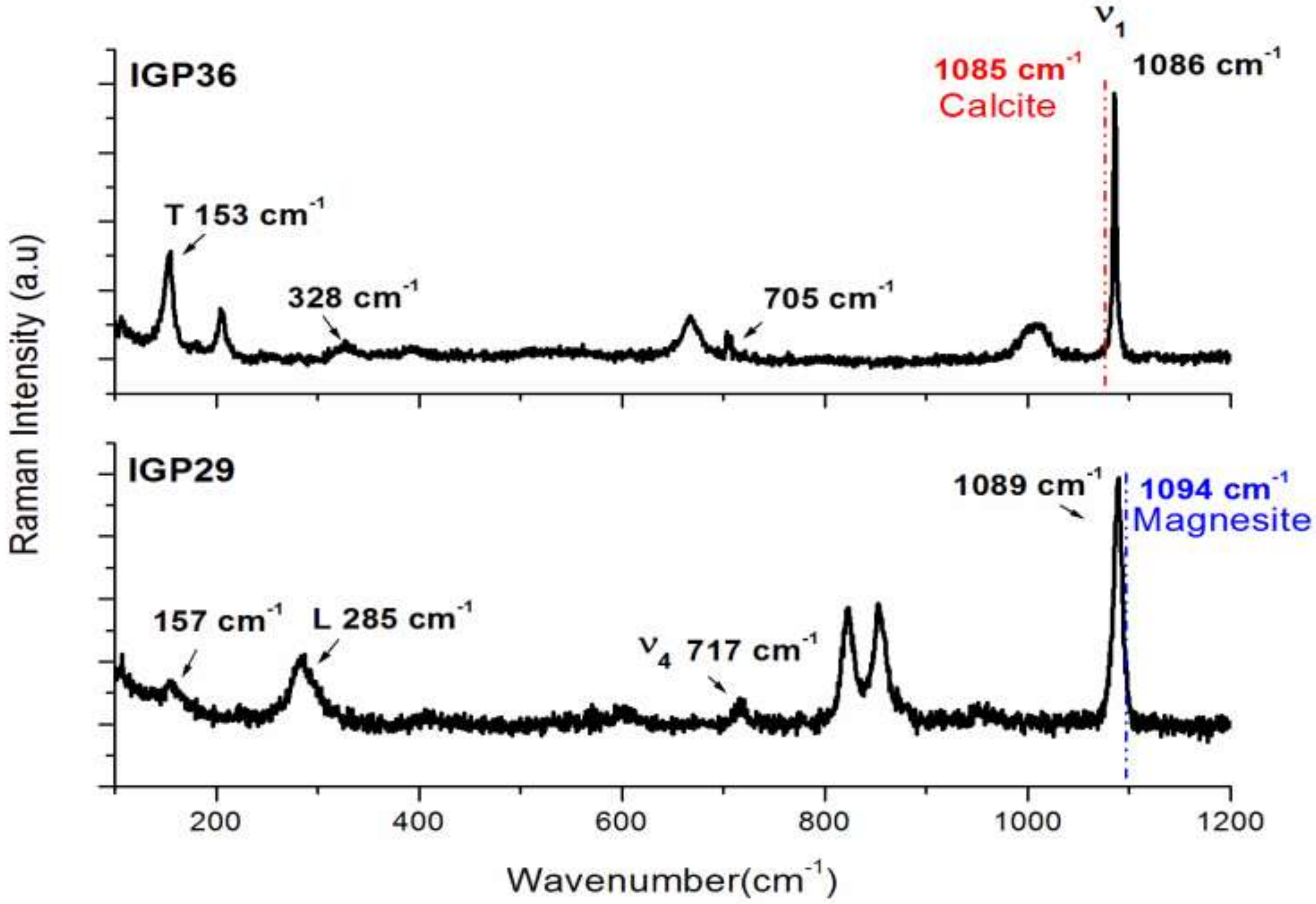
Spectrum 1

Element	Weight%	Atomic%
O K	62.80	79.08
Mg K	5.43	4.50
Al K	0.58	0.44
Si K	2.17	1.56
Ca K	27.84	13.99
Mn K	0.52	0.19
Fe K	0.66	0.24
Totals	100.00	

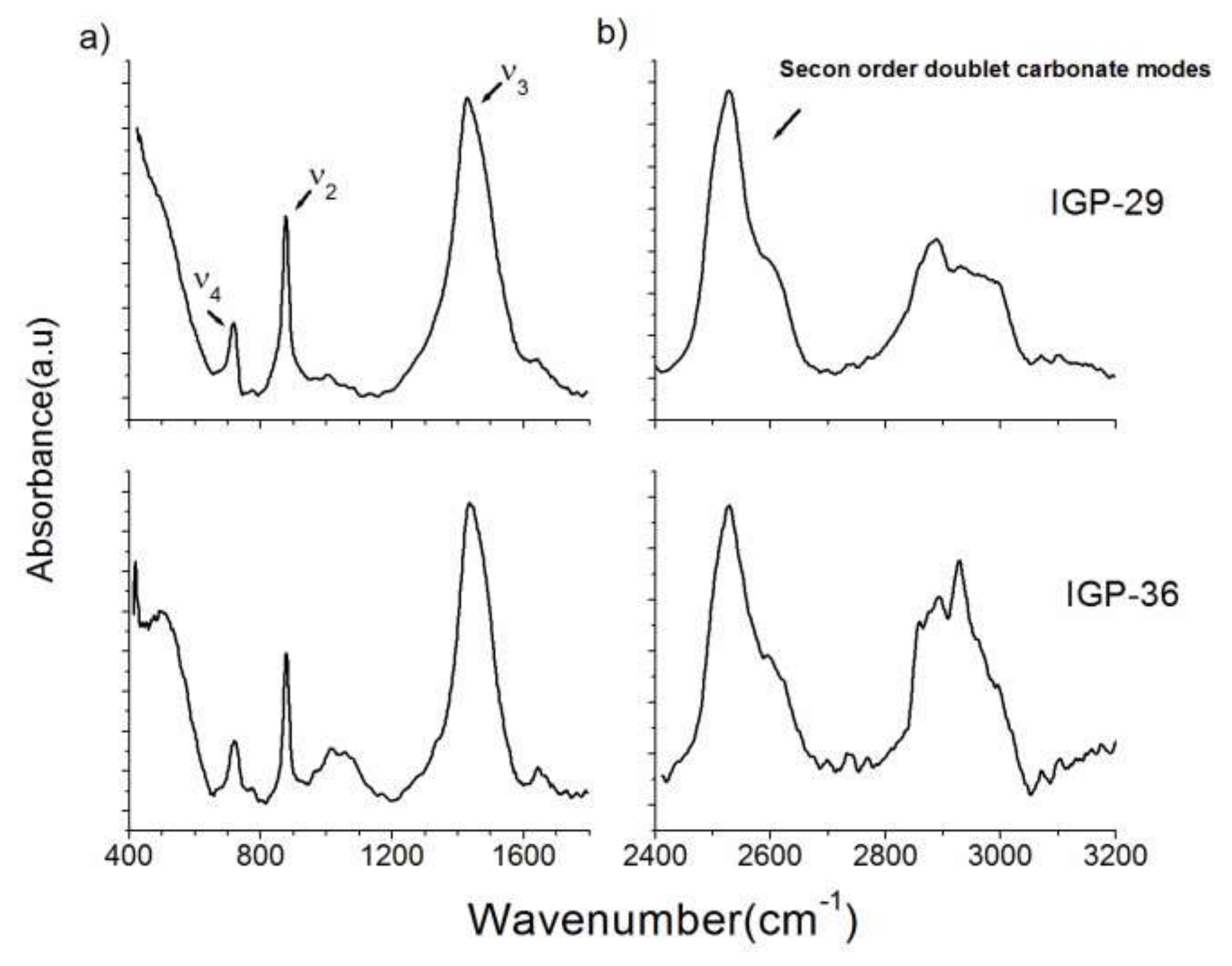
Spectrum 2

Element	Weight%	Atomic%
O K	67.60	81.53
Mg K	8.24	6.54
Si K	1.77	1.21
Ca K	21.95	10.57
Mn K	0.23	0.08
Fe K	0.22	0.08
Totals	100.00	

Micro-Raman Characterization



FTIR Characterization



Pressurizing with CH_4

Experimental Conditions

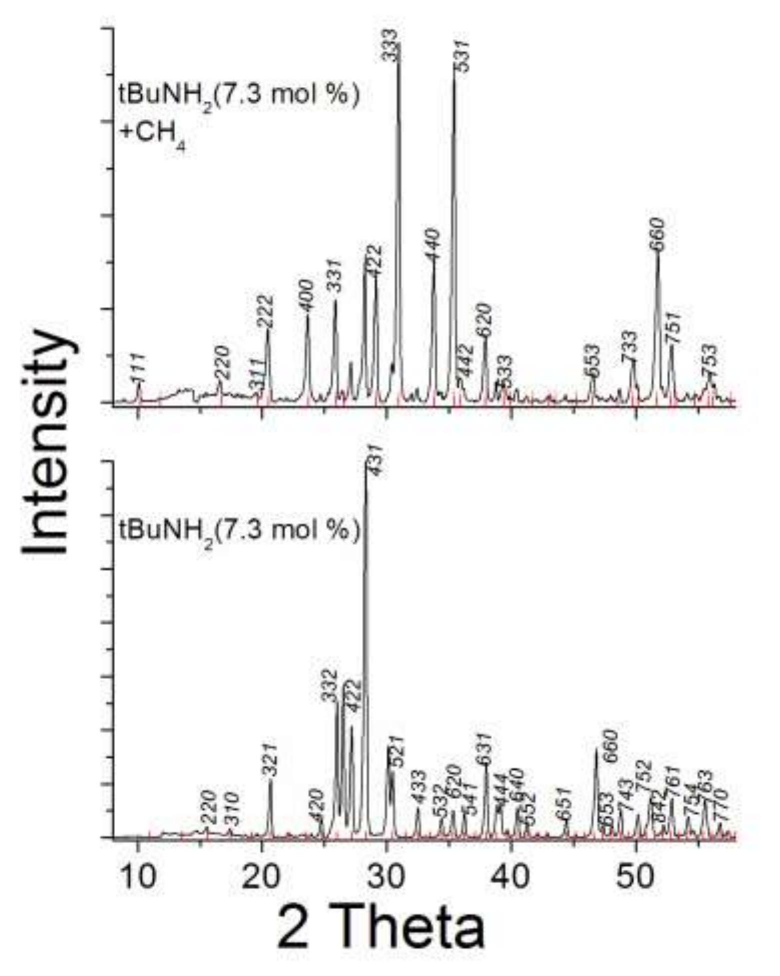
Pressure: 7.0 MPa
Temperature: 250 K

PXRD results (CH_4)

- Upon pressurizing with CH_4 (□ → $4^4 5^4$)

- sII – (*Fd3m*) a = 17.3984 ± 0.0177 Å

- Clathrate Hydrates with 12□ $16tBuNH_2.156.H_2O$
- ✓ sVI – (*I-43d*) a = 18.6341 ± 0.0046 Å



XRD measurements – 0.1 MPa & 120 K

Secondary Carbonate Formation in Picritic Basalt from DVP