How marine gas hydrates form in Nature

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Rice U. Hydrate Workshop Nov. 12, 2003

HYDRATE FORMATION CONDITIONS

- gas hydrate forms in methane-saturated formation waters under conditions of high P and low T
- stability conditions widespread (>70% of earth's surface), but methane content limits occurrence
- methane present in marine sediments only where accumulate rates > 40-50 m ma^{-1} (otherwise sulfate not depleted and methane not generated or oxidized)

Outline: Main points

1. Modes of marine gas hydrate occurrence

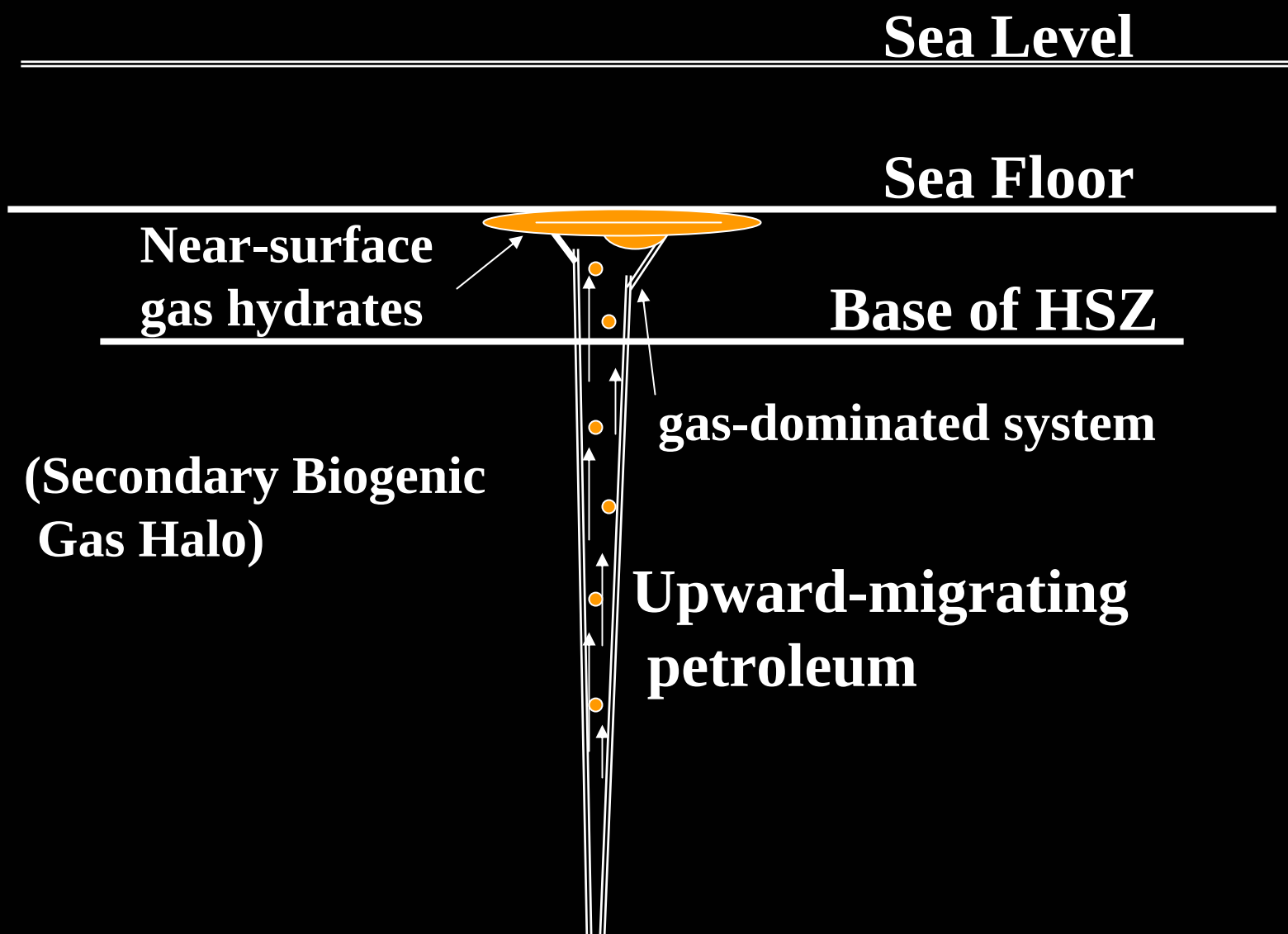
2. Hydrates as a safety factor preventing overpressure

3. Evidence for and importance of shallow microbial processes for marine gas hydrate occurrence

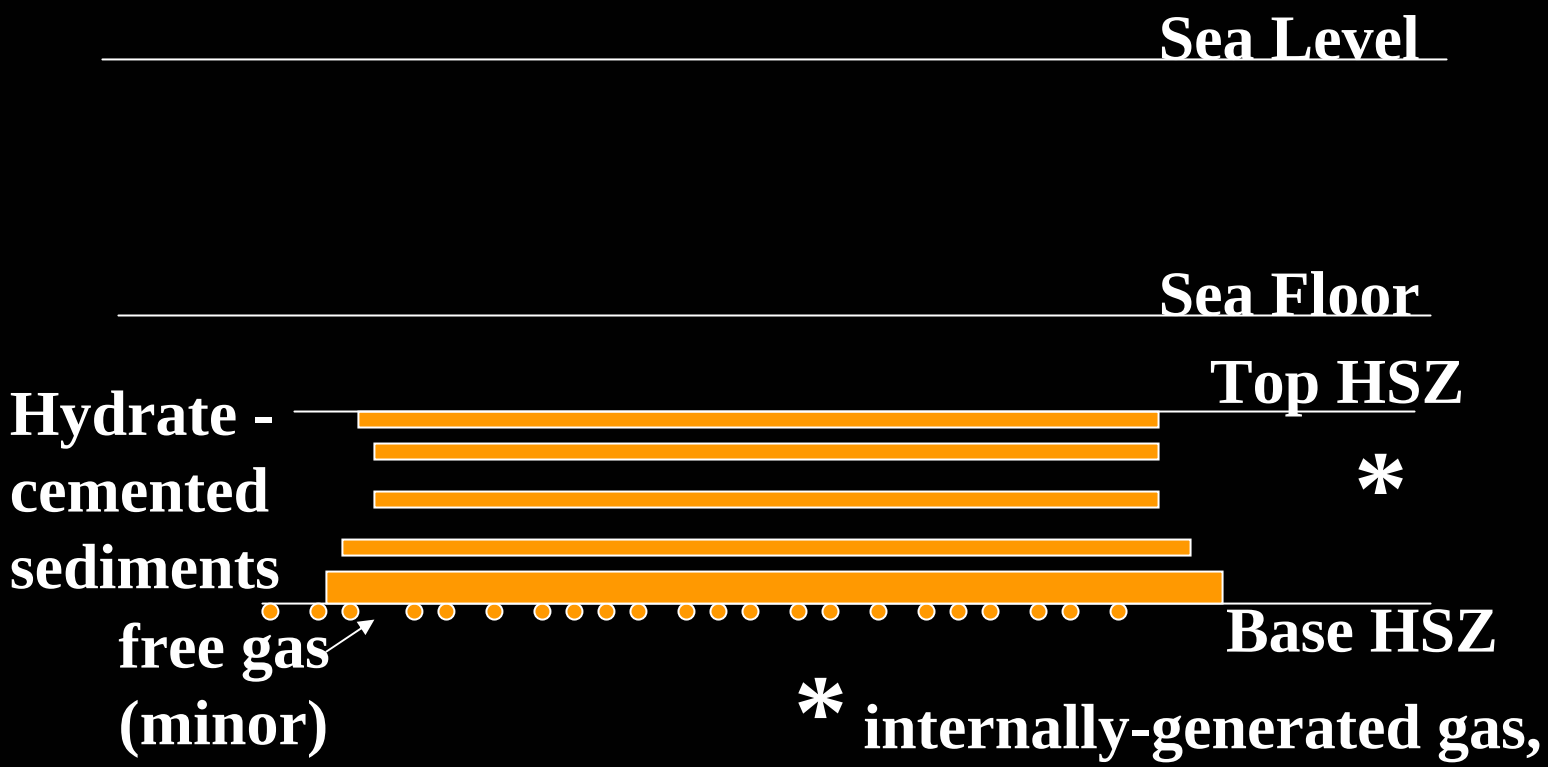
MARINE GAS HYDRATE OCCURRENCE--2 MODES

- **Near-surface, thermogenic gas hydrates, gas-dominated system;**
- **BSR-related, biogenic gas hydrates, water-dominated system.**

Sea floor, thermogenic gas hydrates



Biogenic (BSR-related) gas hydrates



MARINE GAS HYDRATE OCCURRENCE--2 MODES

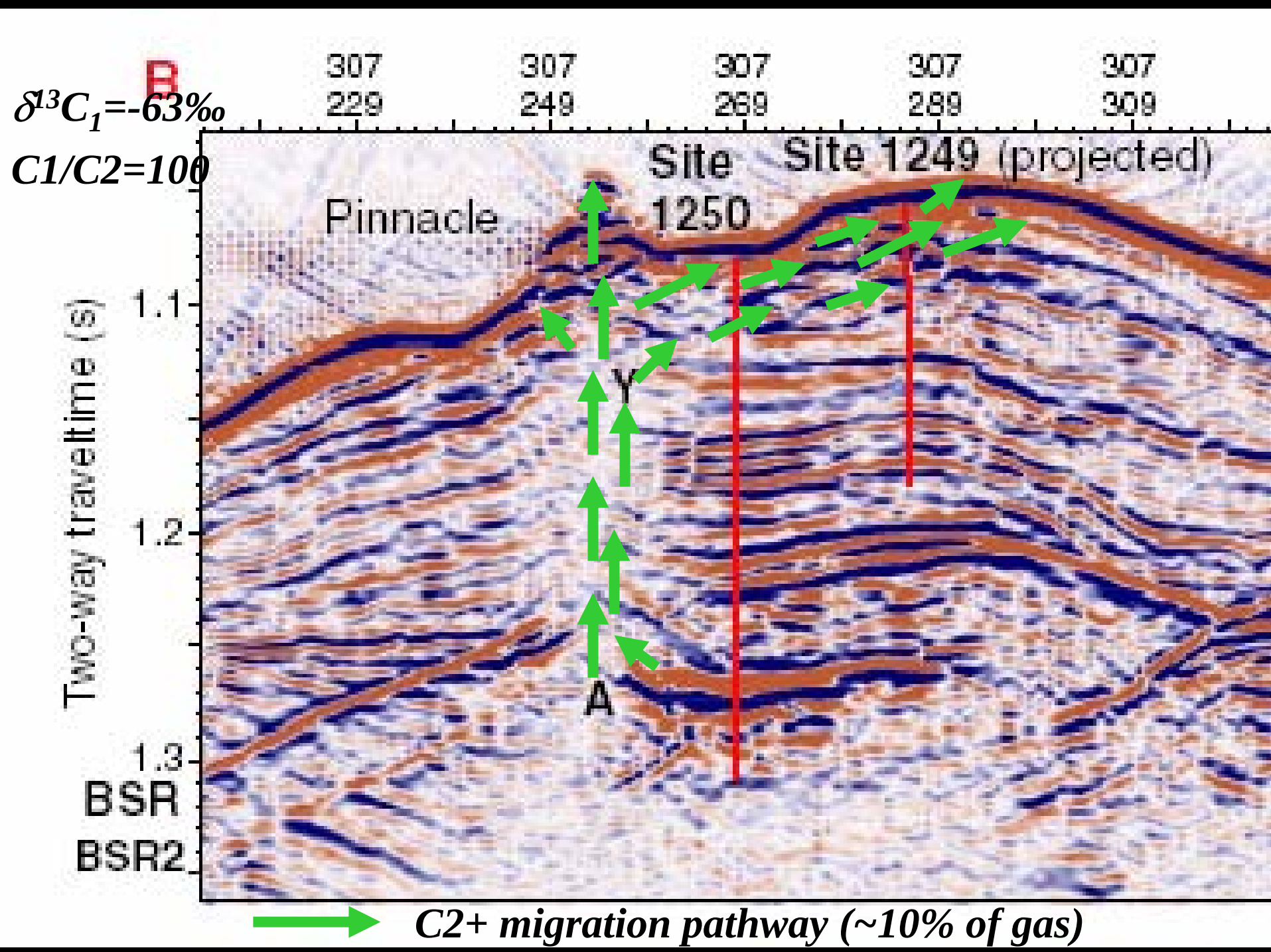
- ***transport dominated*** hydrates, usually near-surface with thermogenic gas

- ***reaction dominated*** hydrates, microbial methane, usually with BSR

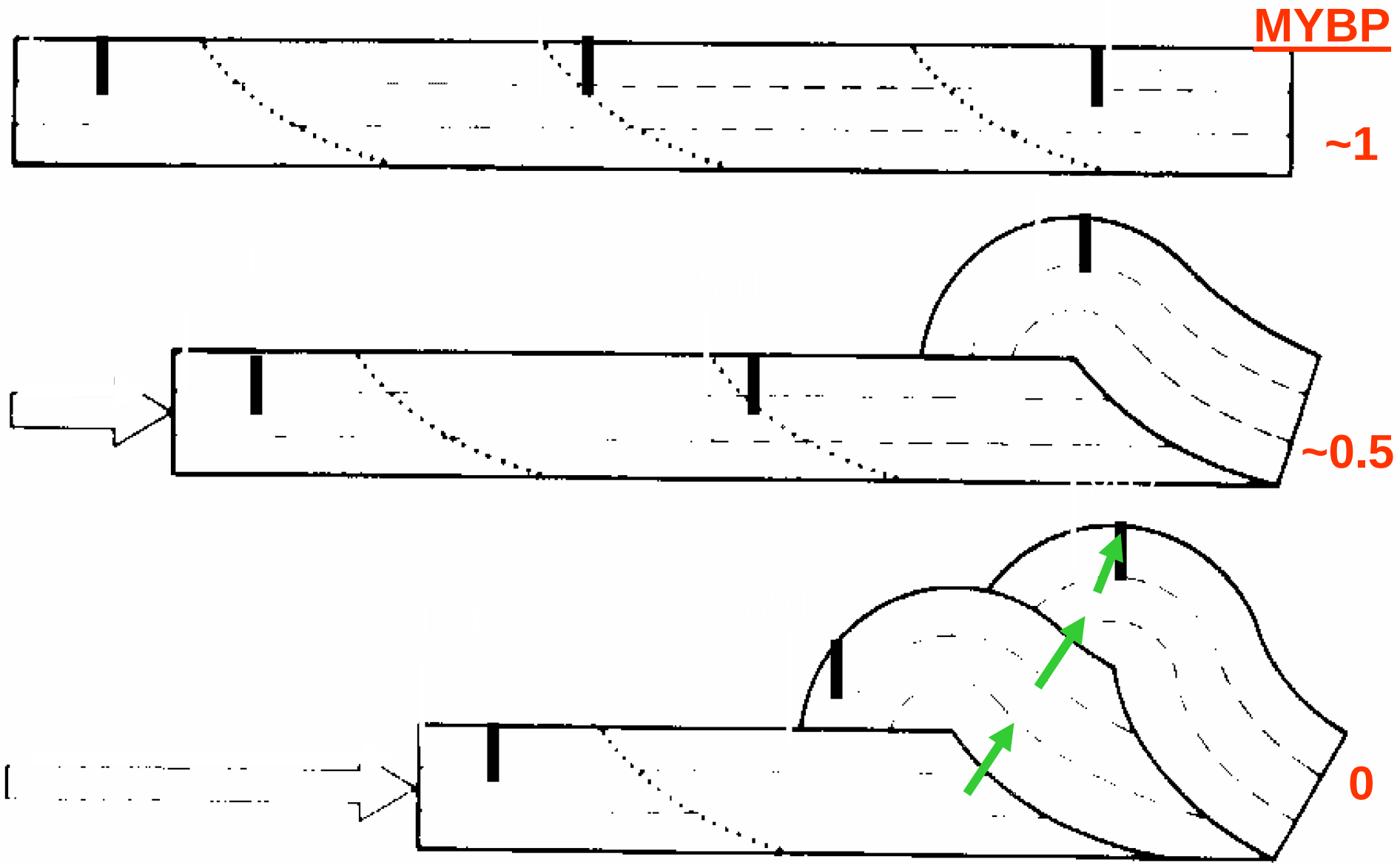
ODP Leg 204 Results

- Gas hydrates abundant (>20%) in shallow zones (0-40 mbsf) only at/near summit—***transport dominated***

- Away from summit, gas hydrates present at lower concentration (0-3%) in deeper zones (45-195 mbsf)—***reaction dominated***

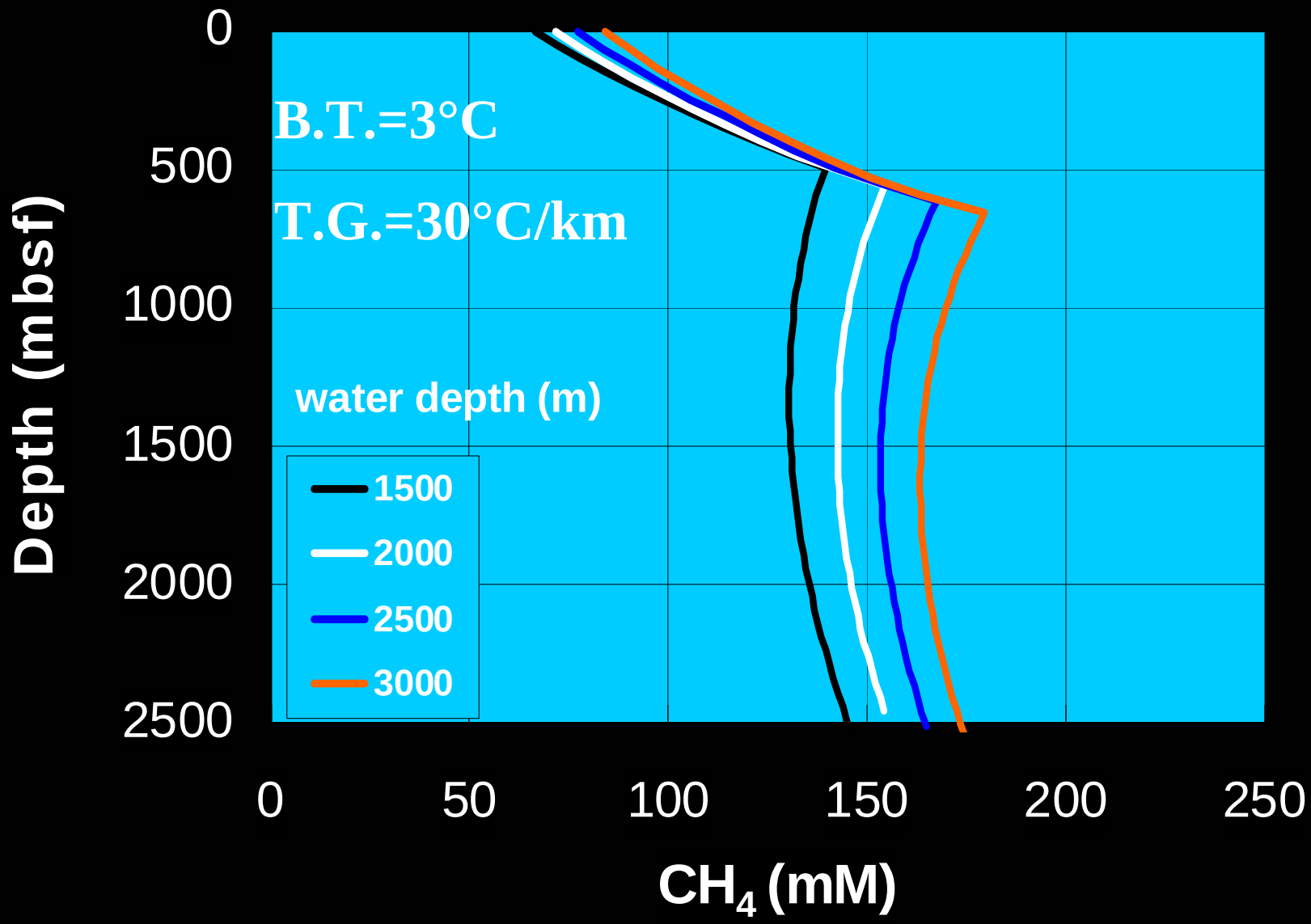

B
307
229
307
249
307
269
307
289
307
309
$\delta^{13}C_1$=-63‰
C1/C2=100
Site 1249 (projected)
Site 1250
Pinnacle
Y
A
Two-way traveltime (s)
1.1
1.2
1.3
BSR
BSR2
C2+ migration pathway (~10% of gas)

174 891 892



Imbricate Thrust Trench-Slope Model (Seely et al., 1974)

CH_4 solubility in porewater

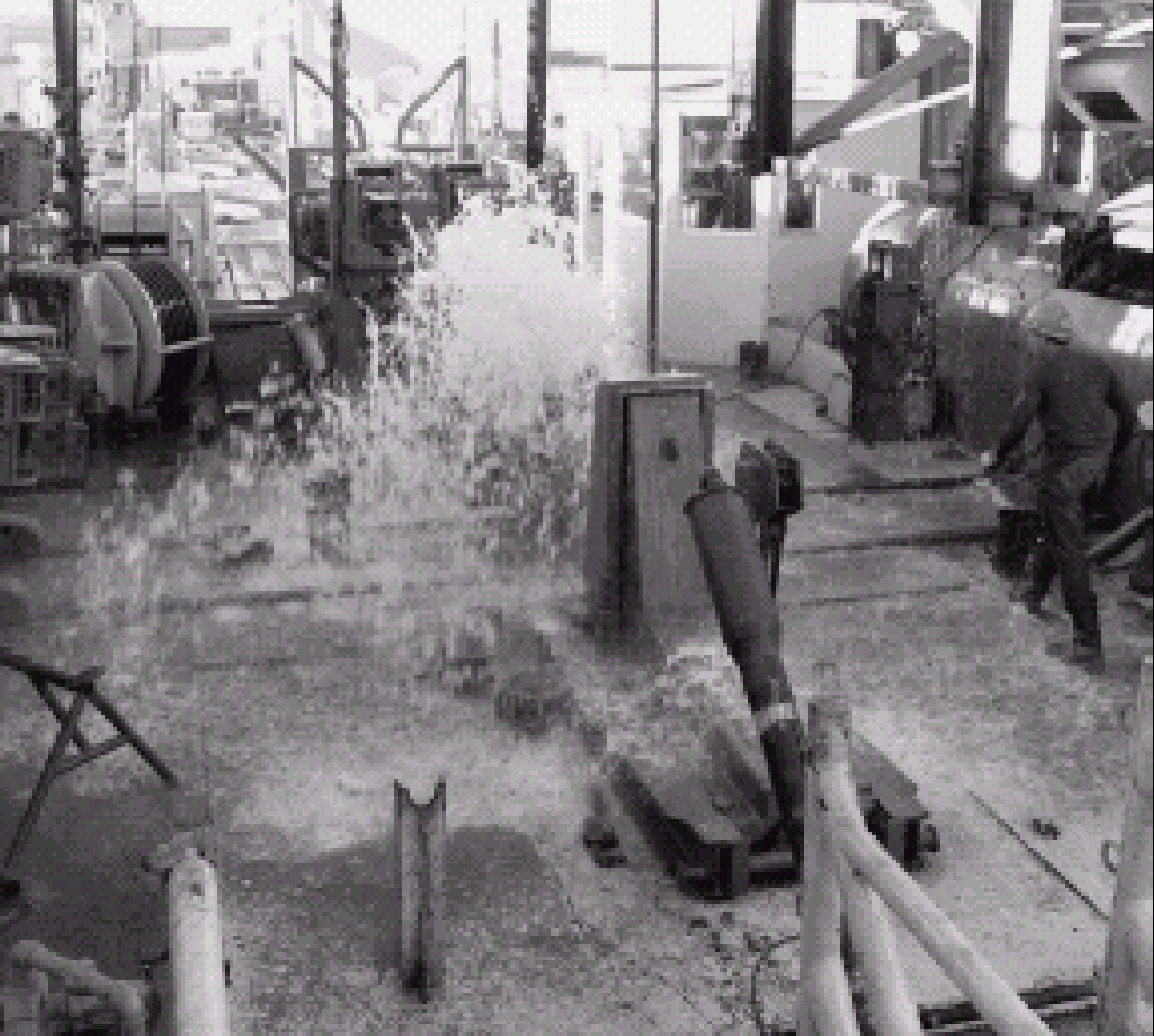


Accretionary prisms

- Combine elements of both modes of hydrate occurrence
- Enhanced CH_4 transport due to more intense dewatering of sediments and fault/fracture conduits
- More CH_4 available for hydrate by pressure reduction associated with tectonic uplift

DSDP/ODP EXPERIENCE

- Prior to Nov. 1991 no intended DSDP/ODP drilling beneath BSR due to presumed gas hazard
- Policy revised by expectation that hydrate equilibrium fixes gas pressure at hydrostatic
- No drilling/safety problems on ODP Legs where BSR/BHSZ penetration permitted (141, 146, 164, 170, 190, 196, 202, 204)



Leg 174A Fountain

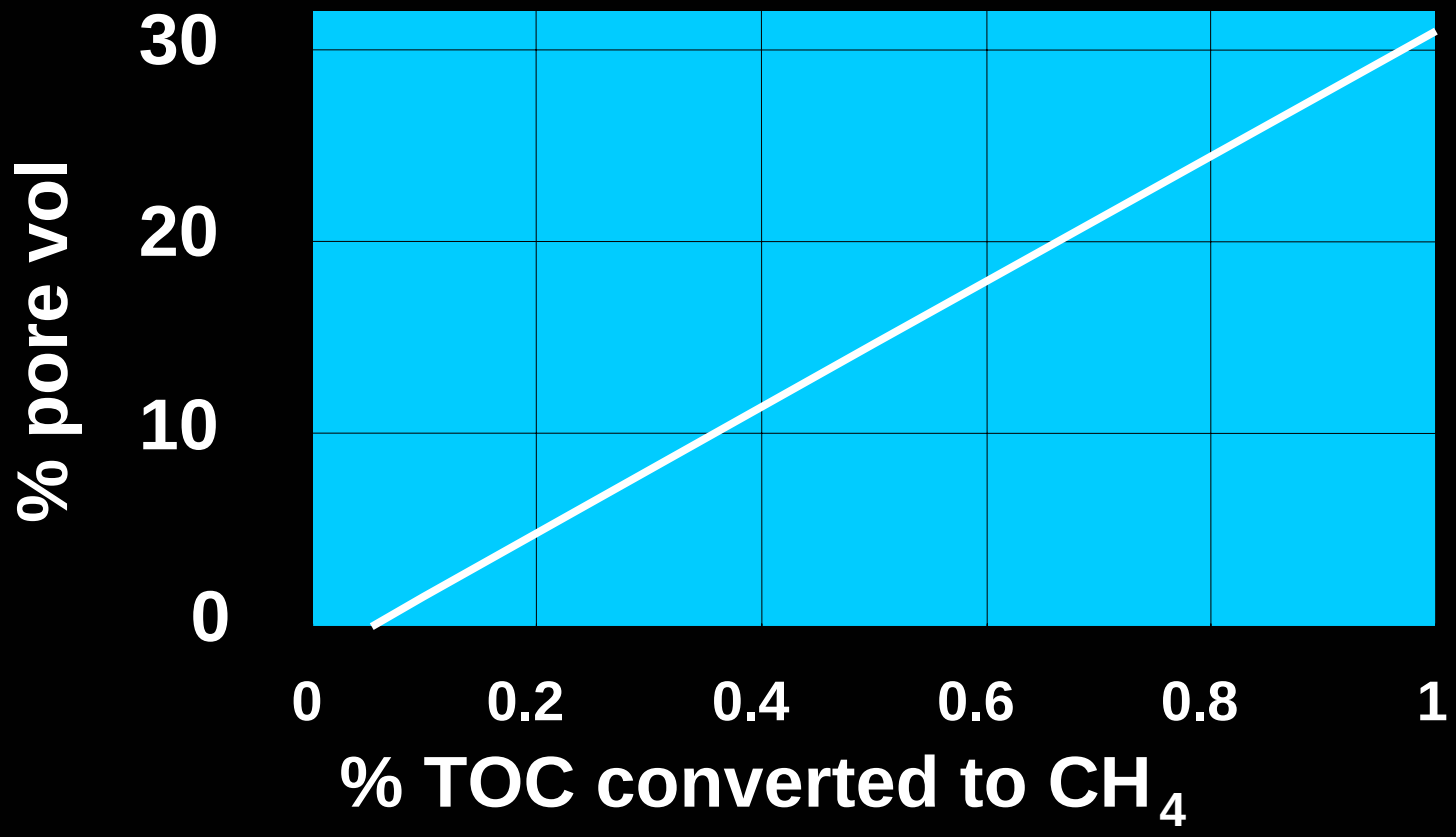
Initially 30m high gusher of water-sand

Equilibrium control on gas pressure and saturation

- 3-phases (gas-liquid-solid) required if hydrates present at base HSZ.
- Pressure fixed (hydrostatic) at base HSZ.
- Thick gas column unstable beneath gas hydrate--buoyancy causes reaction and removal of gas to form more hydrate.
- Gas beneath HSZ at residual saturation levels

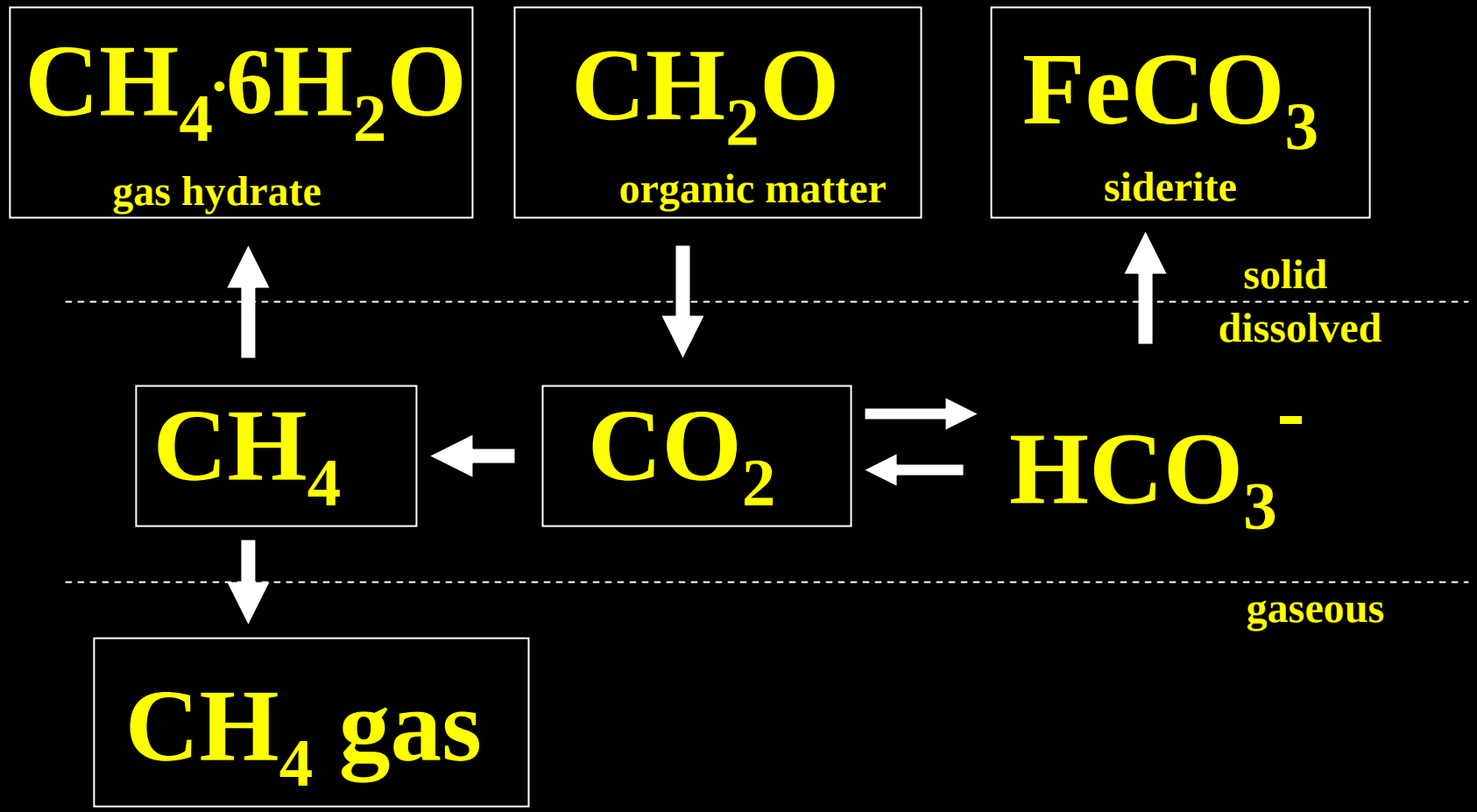
microbial CH_4 generation

- **Remineralization of 0.1 wt% TOC gives 217 mM CH_4**



*assuming 50% porosity, 2.6 g/cc grain density

Carbon flow during Methanogenesis



Sediment phase partitioning

- Solids accumulate at favored sites controlled by surface tension/nucleation phenomena (pore size, capillary pressure, bioclastic nuclei)
- CH_4 supersaturation can be maintained in fine-grained sediments
- Burial of pore water and solids decoupled due to compaction

Carbon & isotopic mass balance for coupled CH_4 and $MeCO_3$ production

$$2\ CH_2O + 2\ H_2O = 2\ CO_2 + 4\ H_2$$

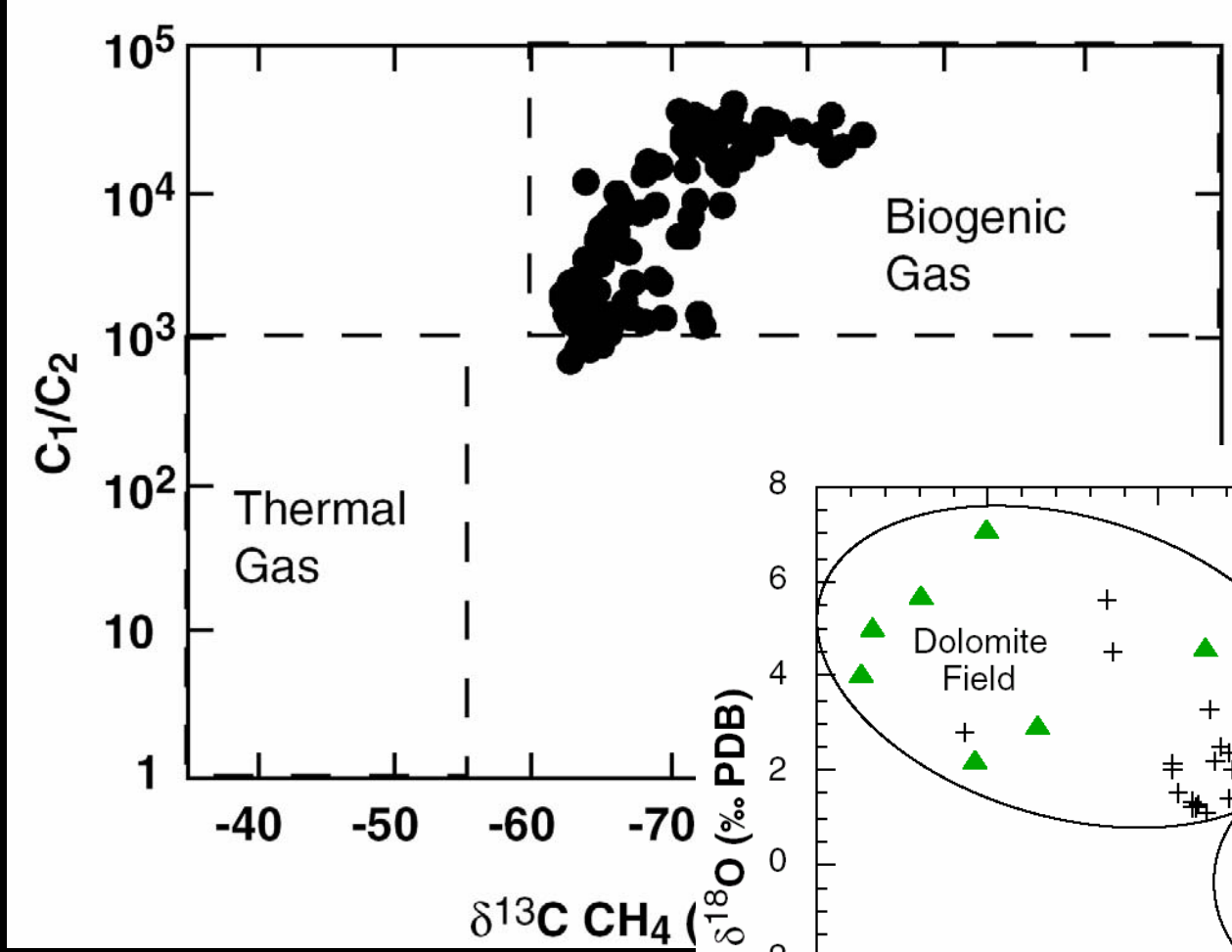
$$CO_2 + 4\ H_2 = CH_4 + 2\ H_2O$$

$$CO_2 + 2\ OH^- = CO_3^{--} + H_2O$$

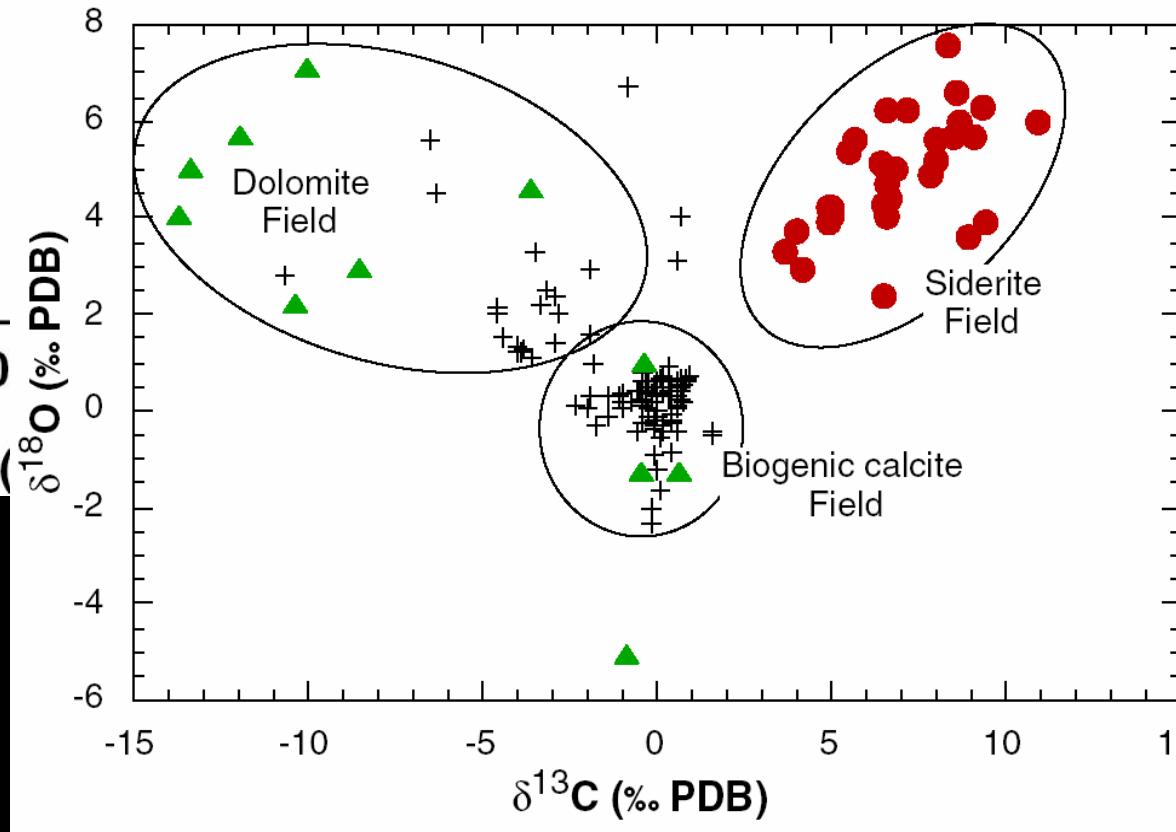
$$Me^{++} + CO_3^{--} = MeCO_3$$

$$\mathbf{2\ CH_2O + 2\ OH^- + Me^{++} = CH_4 + MeCO_3 + H_2O}$$

-22.5‰ -65‰ +20‰



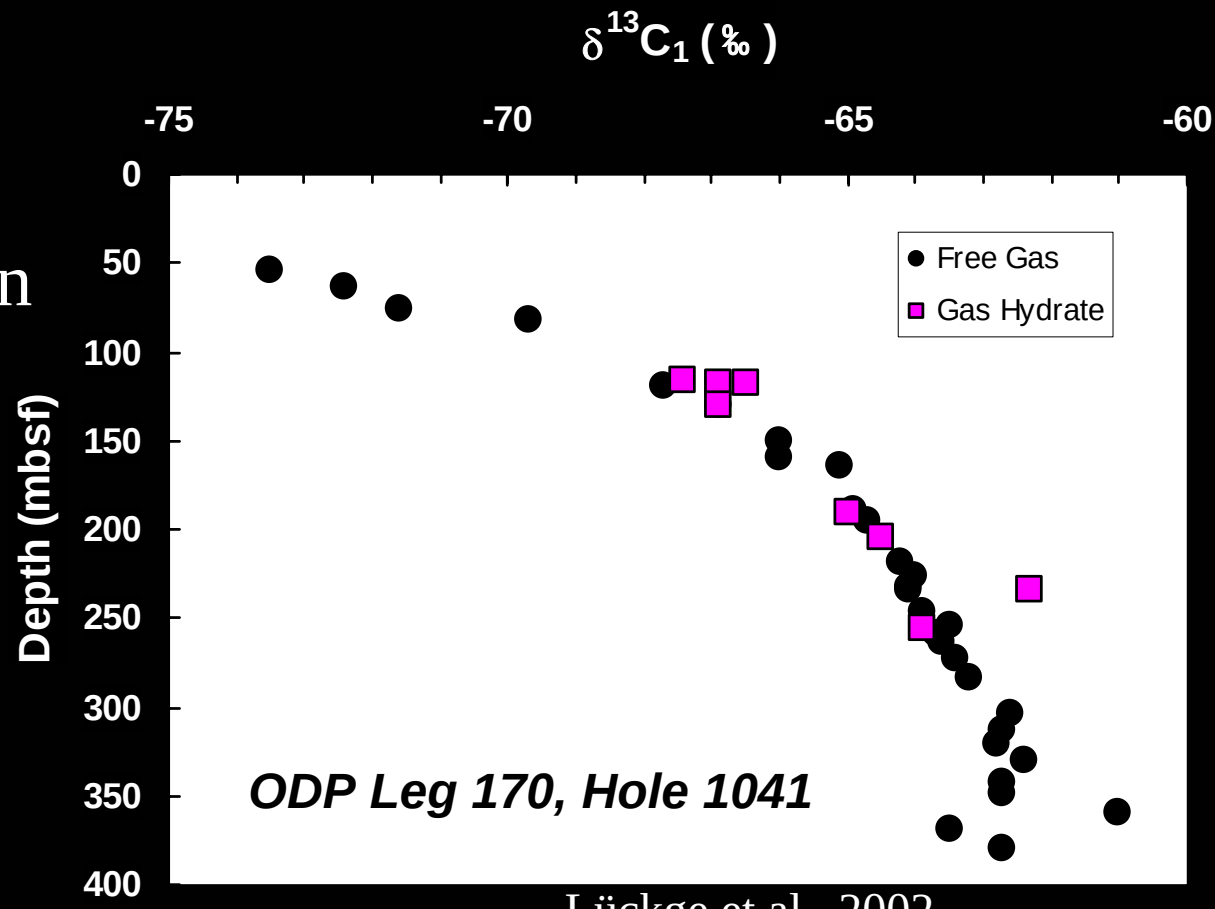
Paull et al., 2000 (164 SR)



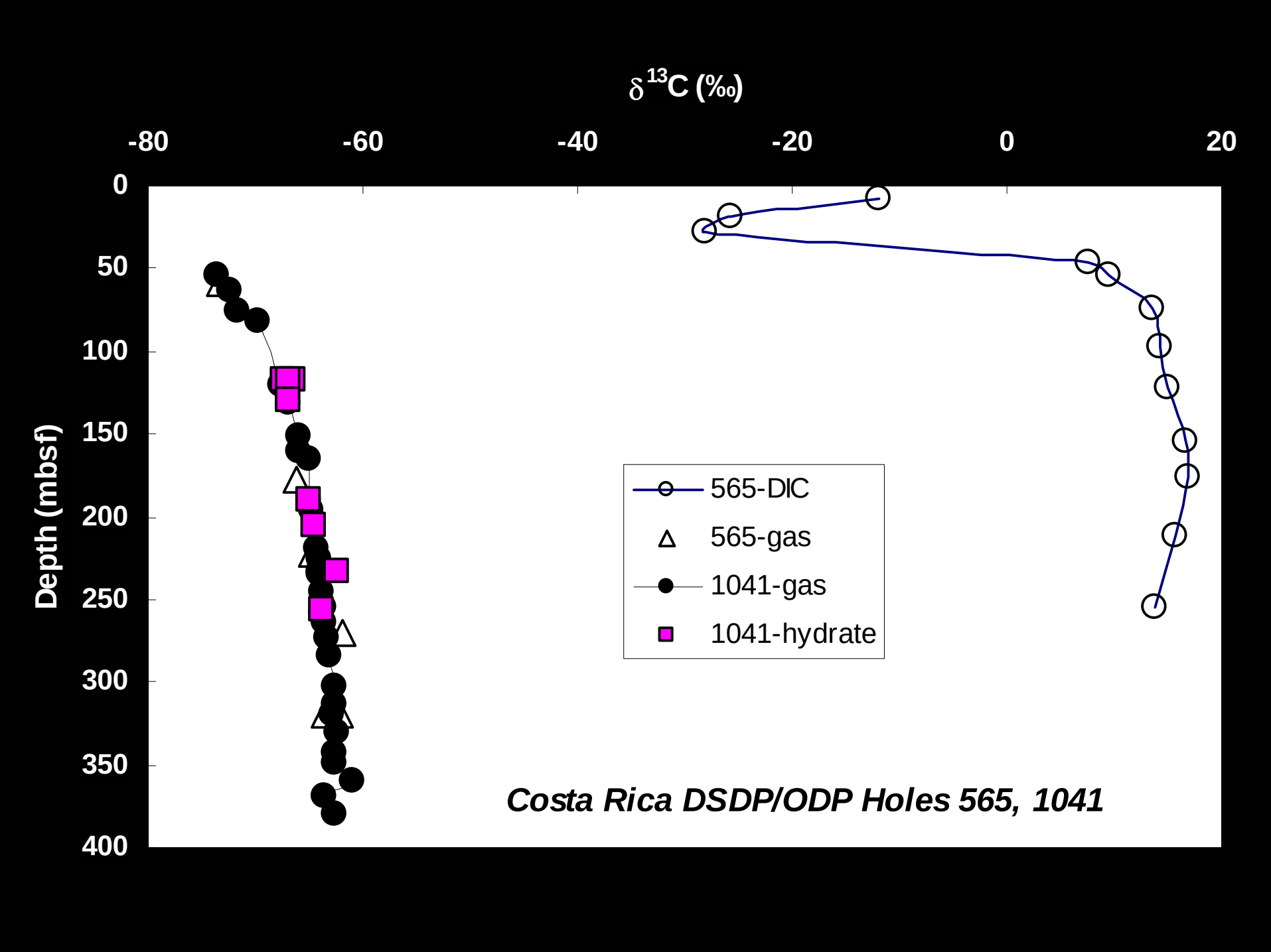
Rodriguez et al., 2000 (164 SR)

Locally generated hydrates have variable $\delta^{13}C_1$, but same as gas from adjacent cores

- Reaction gradient from ^{12}C-depletion in substrate CO_2
- Transported gas unrelated to shallow microbial process



Lückge et al., 2002
M. Kastner, pers. commun.


δ13C (‰)
-80
-60
-40
-20
0
20
0
50
100
150
200
250
300
350
400
Depth (mbsf)
565-DIC
565-gas
1041-gas
1041-hydrate
Costa Rica DSDP/ODP Holes 565, 1041

Conclusions--I

- CH_4 is limiting factor for gas hydrate formation (0.1% TOC converted to CH_4 at $\phi = 0.5$ yields 217 mM).
- Most microbial CH_4 generated at relatively shallow depths (50-500m), but can be buried and remobilized.
- Migrating thermogenic gas forms hydrates near sea floor, requires gas-dominated (dry) pathways through HSZ.

Conclusions--II

- Free gas required (by phase rule) if hydrate present at base of HSZ.
- Free gas limited to residual saturation levels (5-10%) at hydrostatic pressure in water-dominated system.
- Gas accumulations capped by marine gas hydrates in water-dominated systems probably subeconomic.