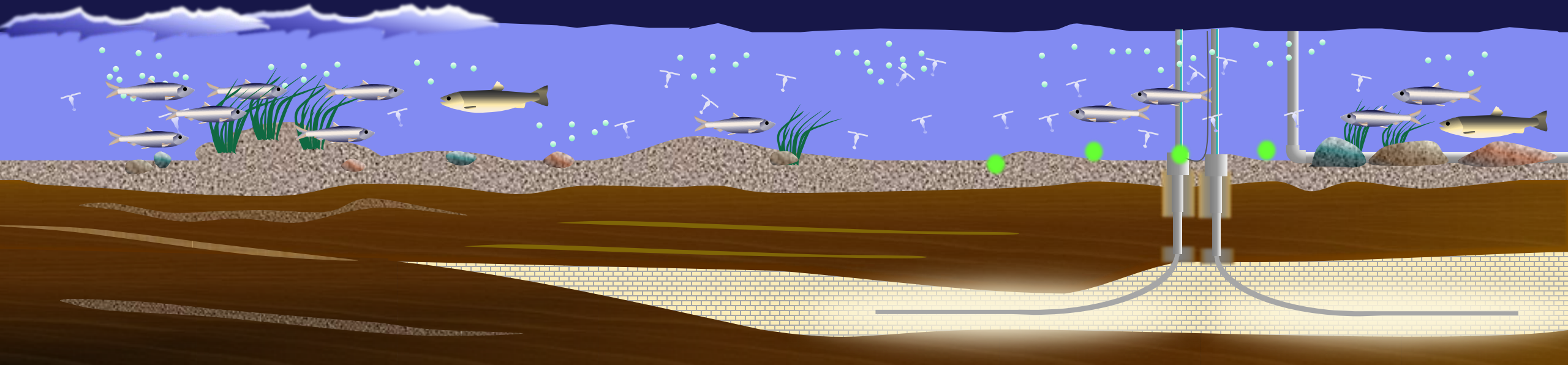


# Enabling compliance with EU Regulation on the Reduction of Methane Emissions

Innovative development of subsea methane sensors for leak detection and methane source determination

Hans Horikx, Charlotte Nørgaard Larsen, Hamid Nick, Paul Feng



Well leakage

Natural seepage

Quantification

Modelling of methane in water column and subsoil

Fossil methane

Biogenic methane

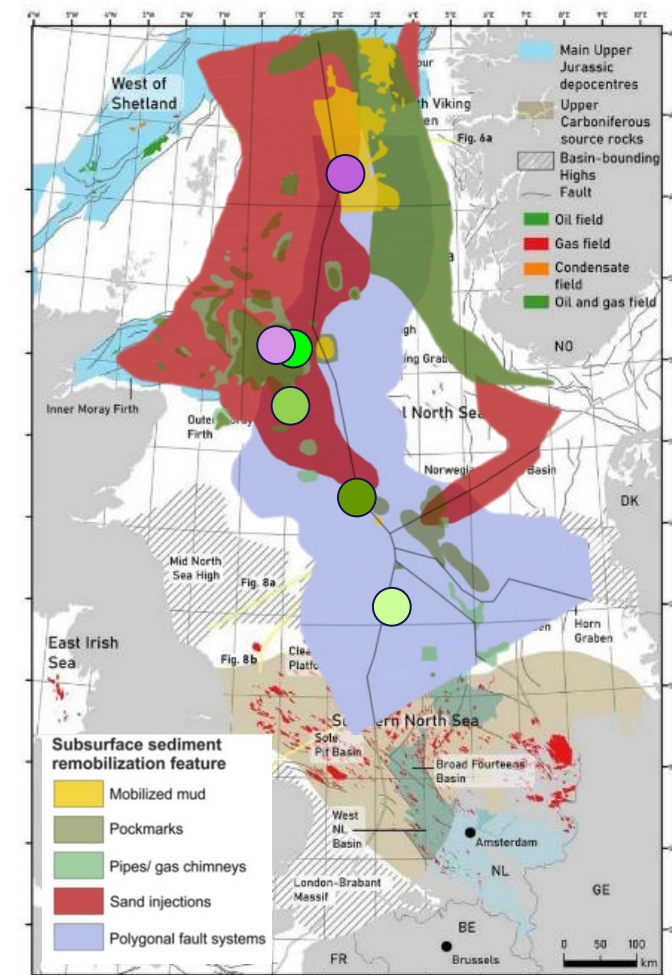
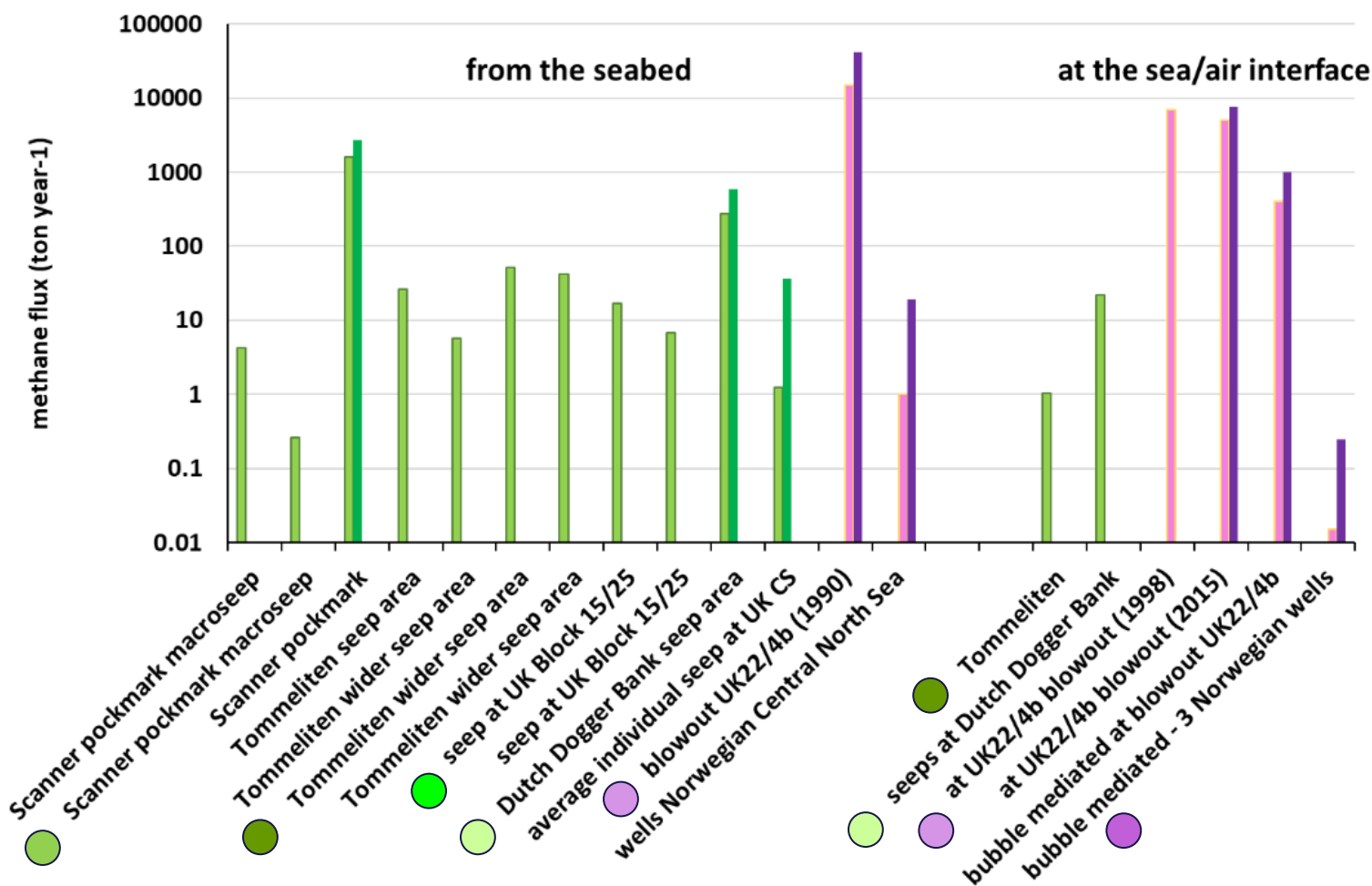
Pre-abandonment baselining

Continuous monitoring at abandoned sites

Targeted analyses to differentiate methane origins



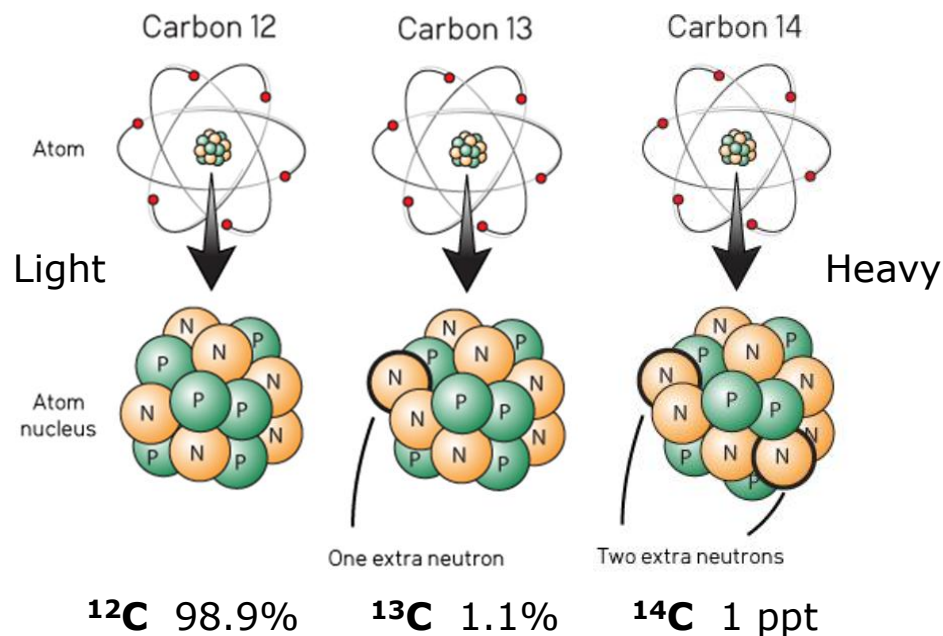
# Natural seeps and well seeps of methane in the North Sea



Methane fluxes from natural seeps (green) and associated with gas wells (pink/purple) both from the seabed and directly induced at the sea/air interface as measured in the **North Sea**.

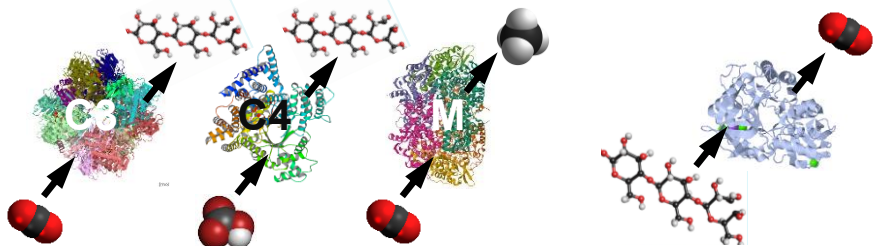
Literature review on natural seepage and human-induced leakage of methane at the North Sea and Gulf of Mexico - Griffioen TNO 2023

# Carbon isotopes can be used to determine source origin

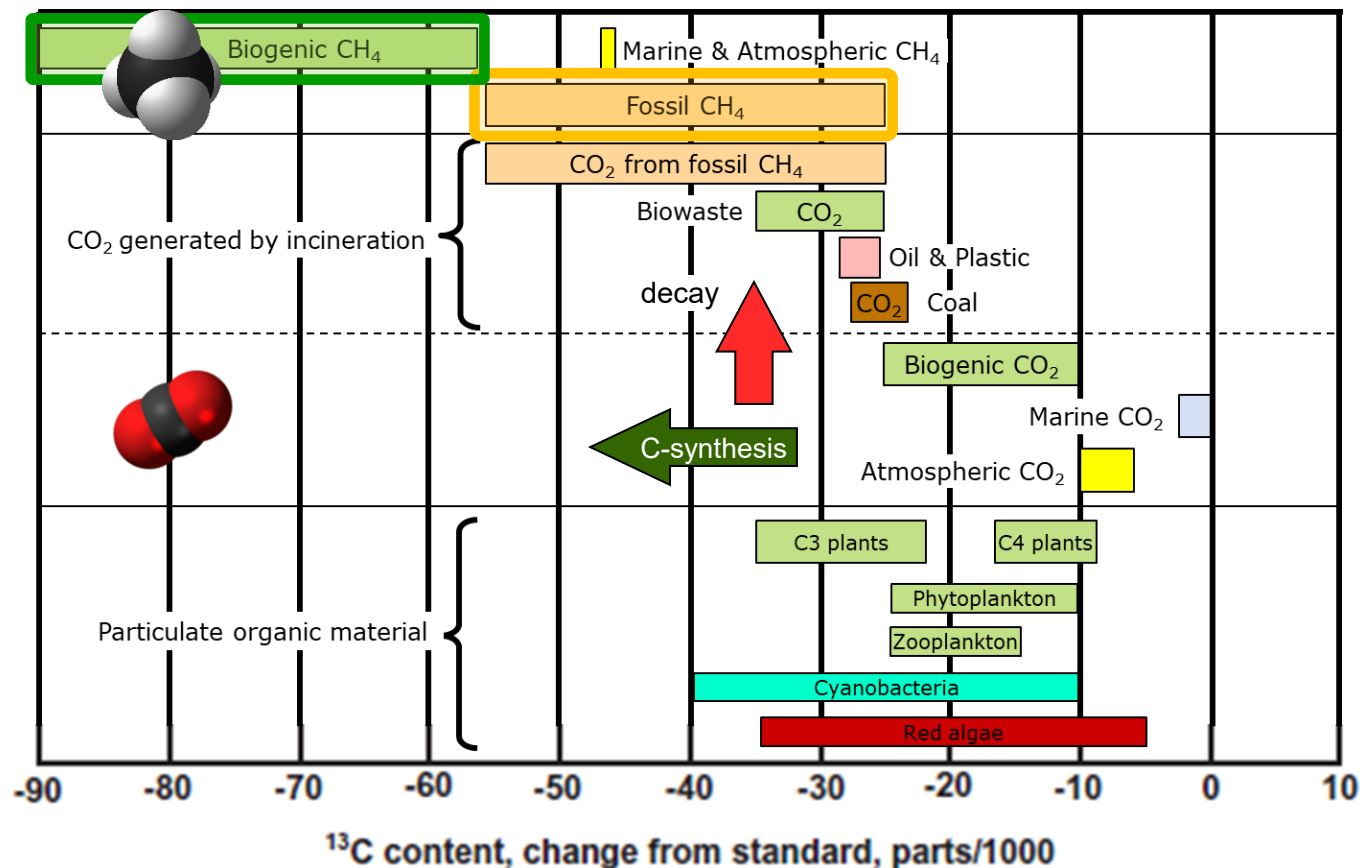


## Kinetic isotope fractionation

- Strong preference for light isotope during synthesis
- No isotope effect during decay



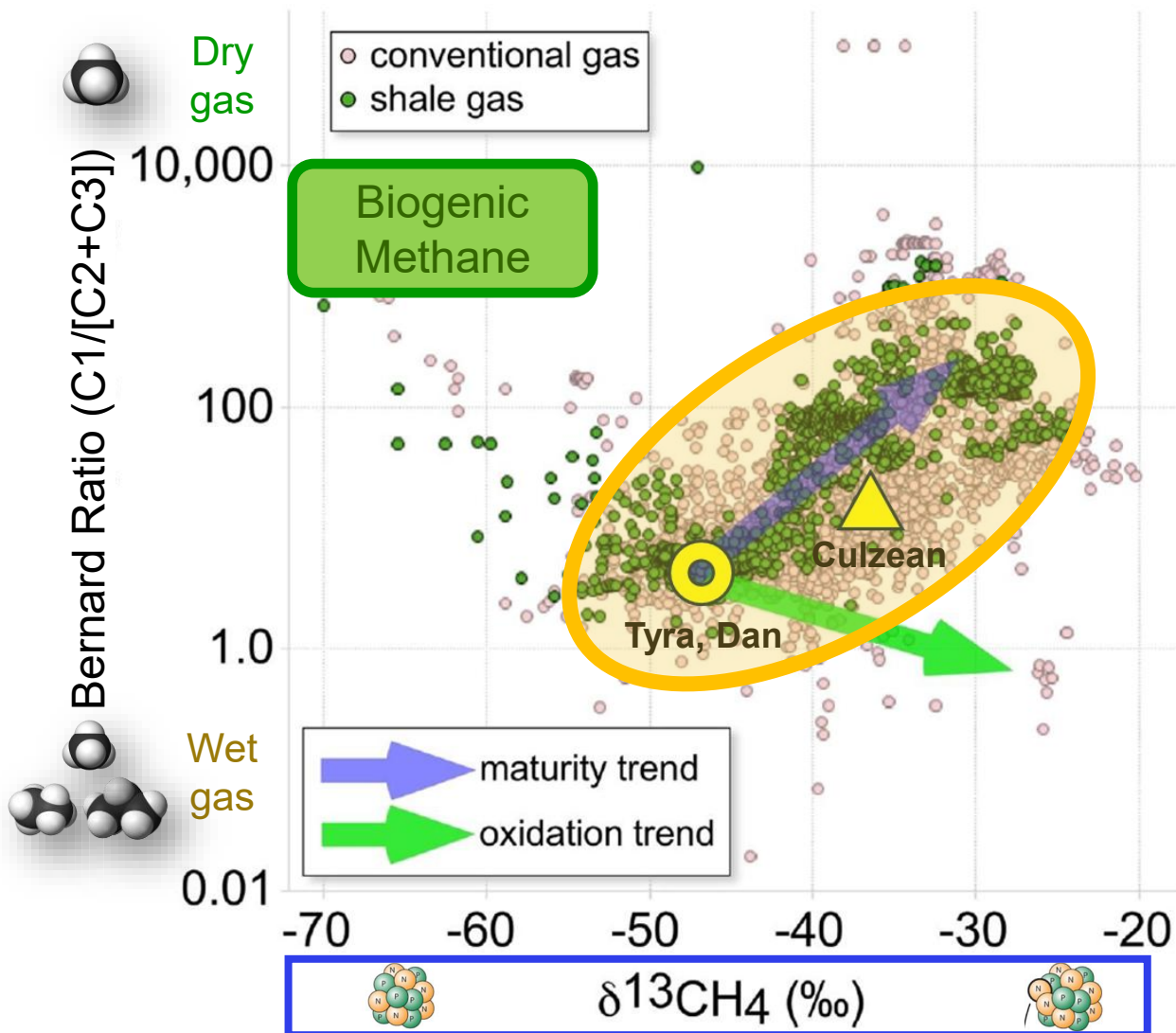
## $\delta^{13}\text{C}$ isotope ratios of $\text{CH}_4$ and $\text{CO}_2$ in seawater



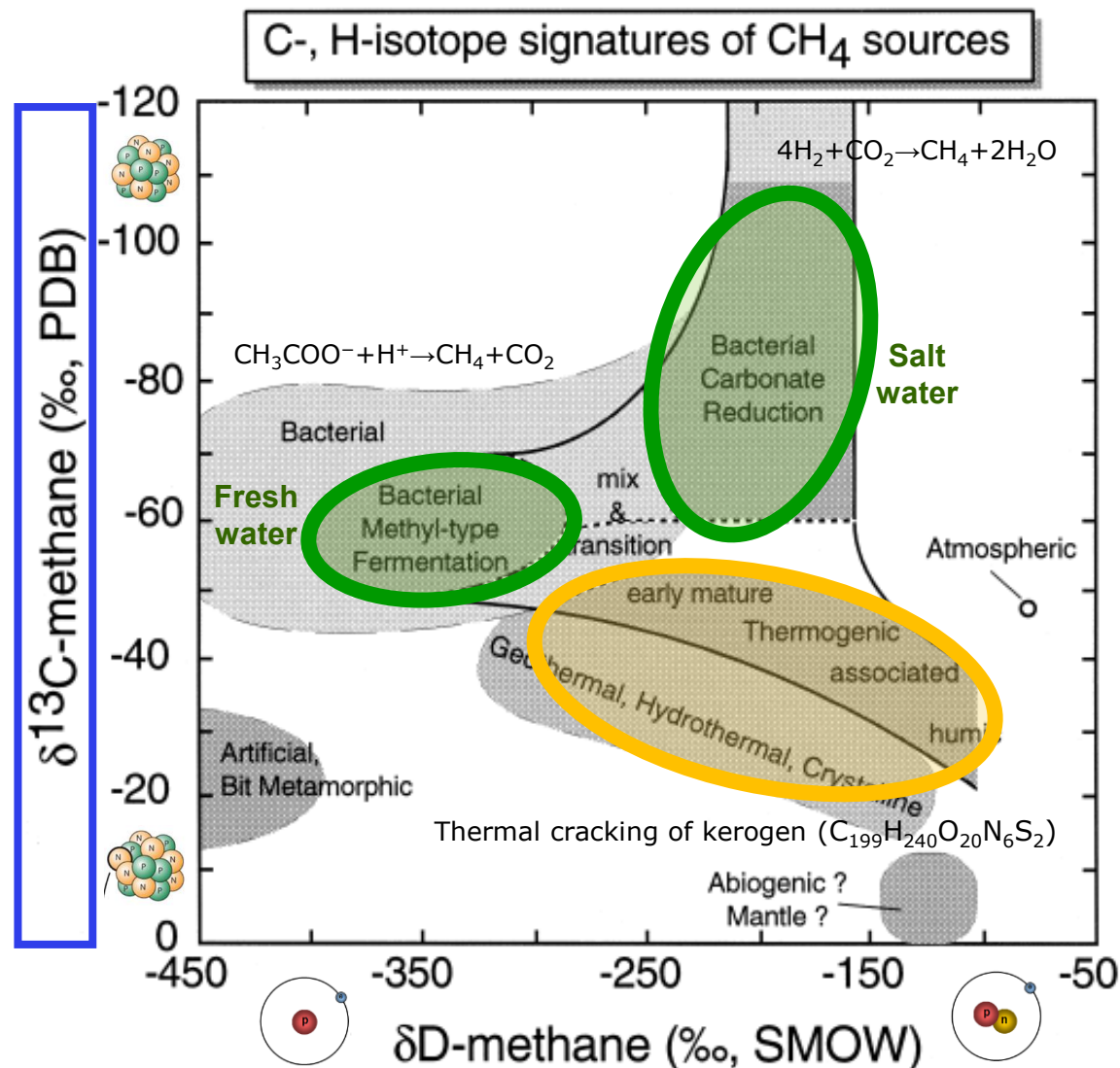
### Sources:

- Stable Carbon Isotopes of Phytoplankton as a Tool to Monitor Anthropogenic  $\text{CO}_2$  Submarine leakages - Relitti 2020
- The Carbon-Isotope Record of the Sub-Sea-floor Biosphere - Meister 2019
- The DIC carbon isotope evolutions during  $\text{CO}_2$  bubbling: Implications for ocean acidification laboratory culture - Zhang 2022

# Isotope differences of **biogenic** and **fossil-based** methane



Response by Michael Lewan to Howarth 2019 paper (from Milkow 2020)

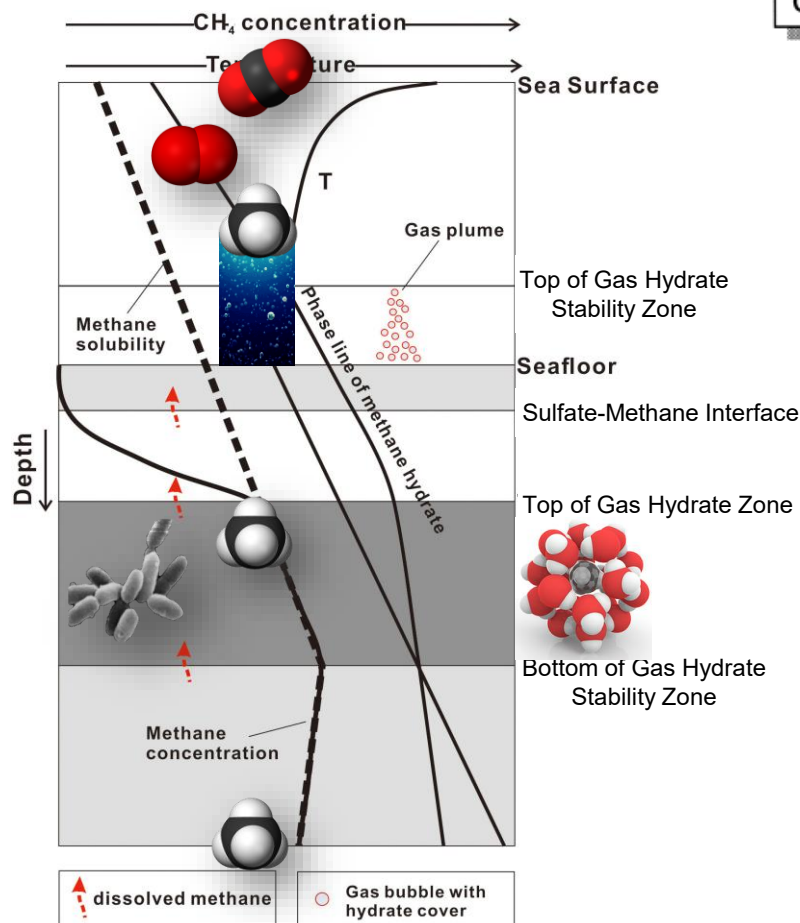


Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane - Whiticar 1999

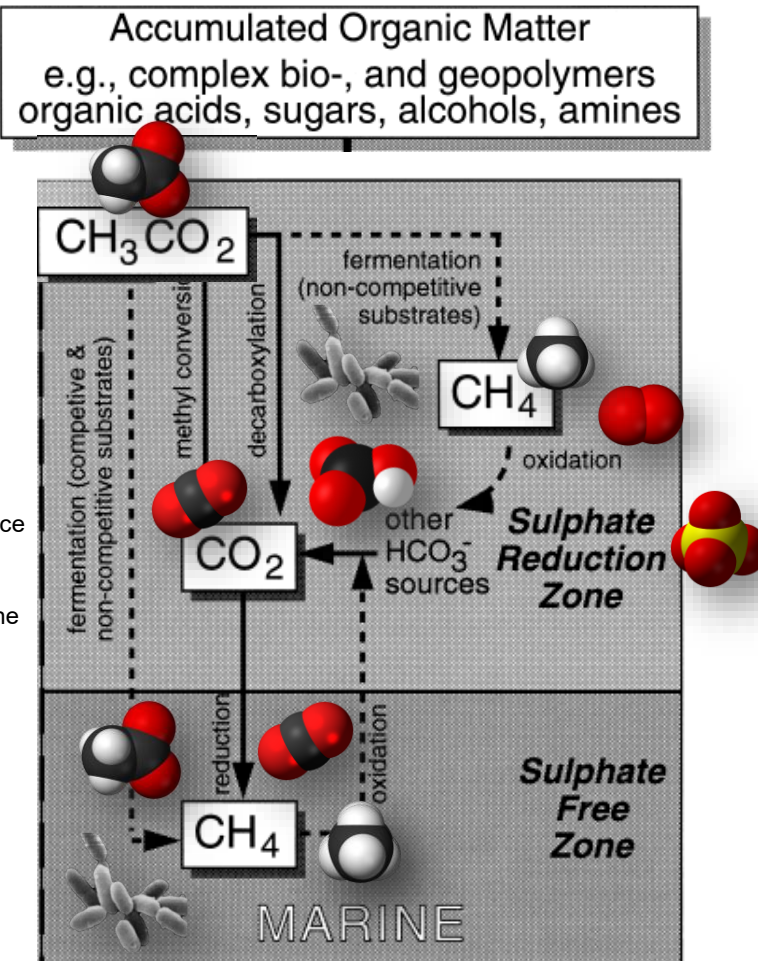


# Modelling biogenic methane chemistry & isotopes

## Methane migration pathways

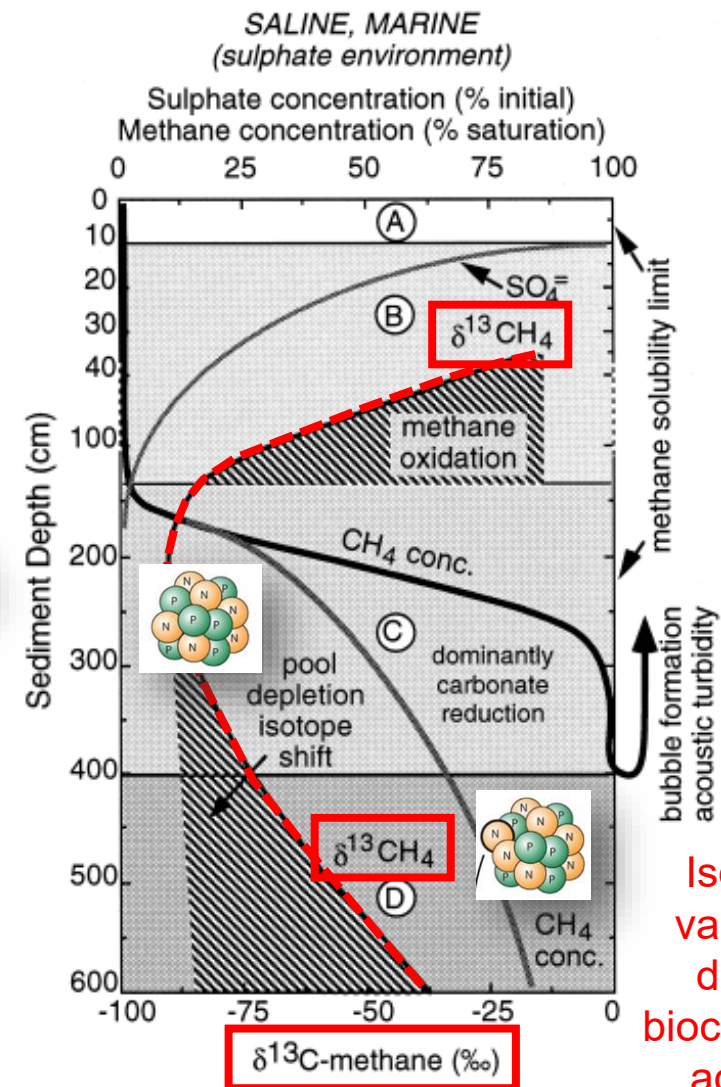


Mechanisms for upward migration of methane in marine sediments - Liu 2022



## Methane generation biochemistry pathways (saline environment)

Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane - Whiticar 1999

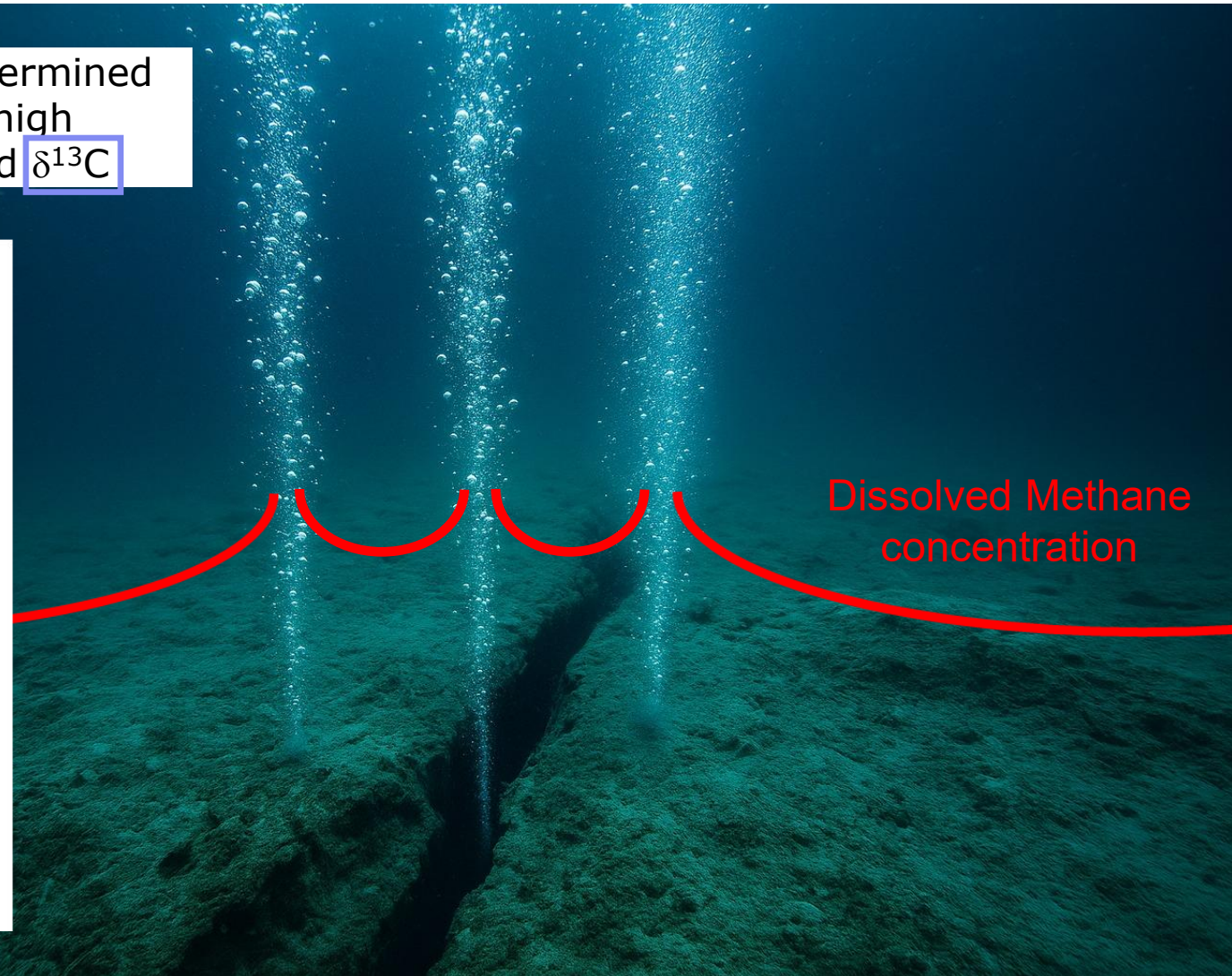
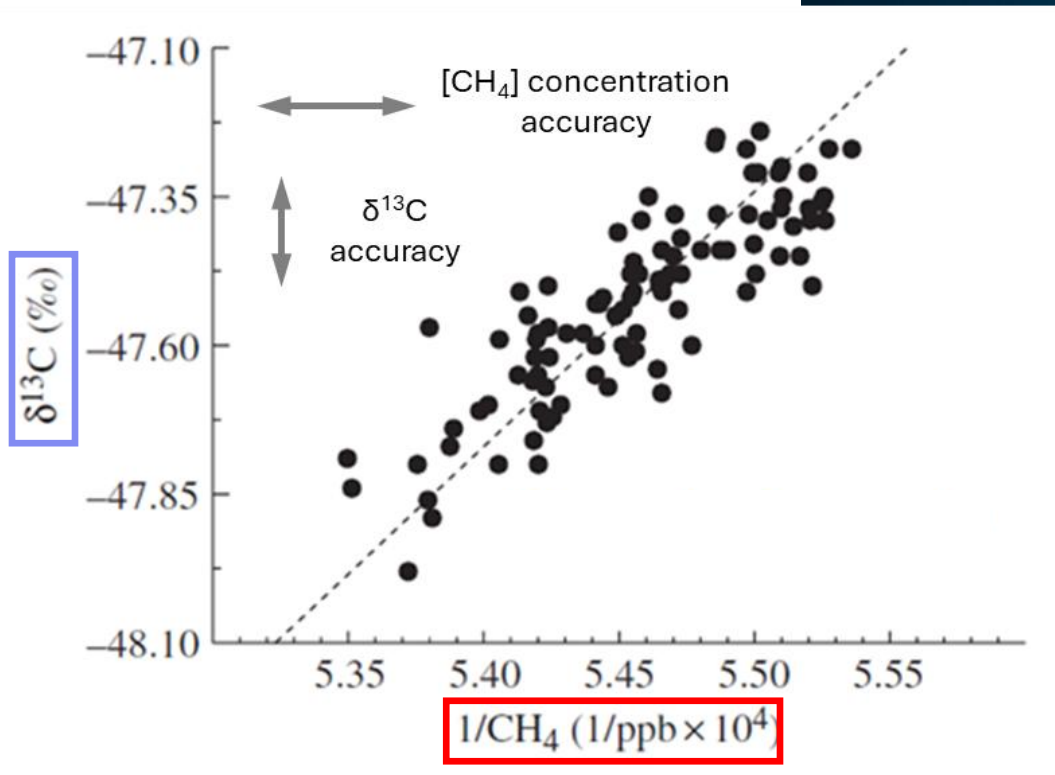


Isotope variation due to biochemical activity



# Determining $^{13}\text{C}/^{12}\text{C}$ Carbon isotope ratio of methane seep

The  $\delta^{13}\text{C}$  isotope ratio of the  $\text{CH}_4$  influx can be determined via a Keeling crossplot (below), which requires a high measurement accuracy of  $[\text{CH}_4]$  concentration and  $\delta^{13}\text{C}$



# Accuracy comparison of various sensor techniques

New technology aims at real-time underwater

- $[\text{CH}_4]$  measurement accuracy of 10 ppb
- $\delta^{13}\text{C}$  measurement accuracy of 0.1‰

Required accuracy:

$\delta^{13}\text{C}$	0.1 ‰
$[\text{CH}_4]$	10 ppb

Underwater sensors

Kleint & Hartmann CRDS accuracy:

$\delta^{13}\text{C}$	0.8 ‰
$[\text{CH}_4]$	20 ppb

Wankel deep sea (ABB) accuracy:

$\delta^{13}\text{C}$	1.2 ‰
$[\text{CH}_4]$	90 ppb

$\delta^{13}\text{C}$  accuracy

$[\text{CH}_4]$  concentration accuracy

Mass spectrometer accuracy:

$\delta^{13}\text{C}$	0.06 ‰
$[\text{CH}_4]$ concentration	1 ppb
$[\text{CH}_4]$ + sampling error	20 ppb

Atmospheric sensors

Picarro CRDS accuracy:

$\delta^{13}\text{C}$ (HDR mode)	0.4 ‰
$[\text{CH}_4]$ concentration	10 ppb
$[\text{CH}_4]$ + sampling error	20 ppb
$\delta^{13}\text{C}$ (HP mode)	0.8 ‰
$[\text{CH}_4]$ concentration	1 ppb
$[\text{CH}_4]$ + sampling error	11 ppb

Note that for comparison reasons all methane concentrations and concentration errors are quoted in ppb, which is a standard unit for methane concentration in air. The most widely used unit for methane concentration in water is nmol/l, and the Keeling crossplot method for methane dissolved in water can also be made using concentrations in nmol/l. For comparison: the average atmospheric  $\text{CH}_4$  concentration of ca. 1850 ppb corresponds with a seawater  $\text{CH}_4$  concentration of ca. 3 nmol/l at equilibrium conditions.



# Greenhouse Gas detection using Infra Red absorption

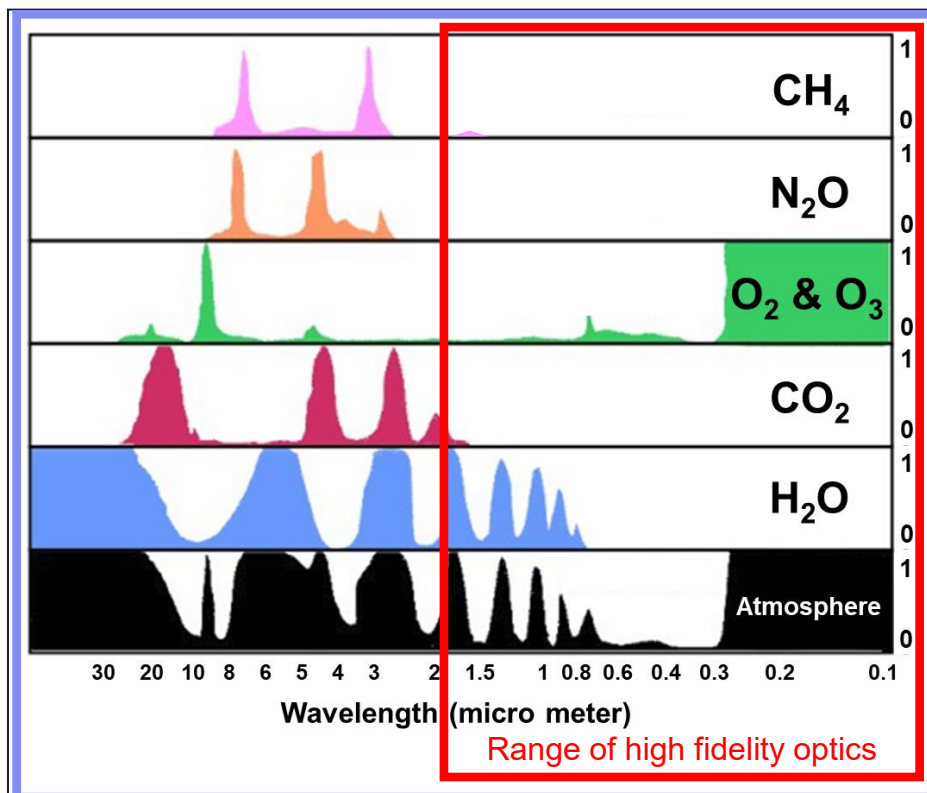


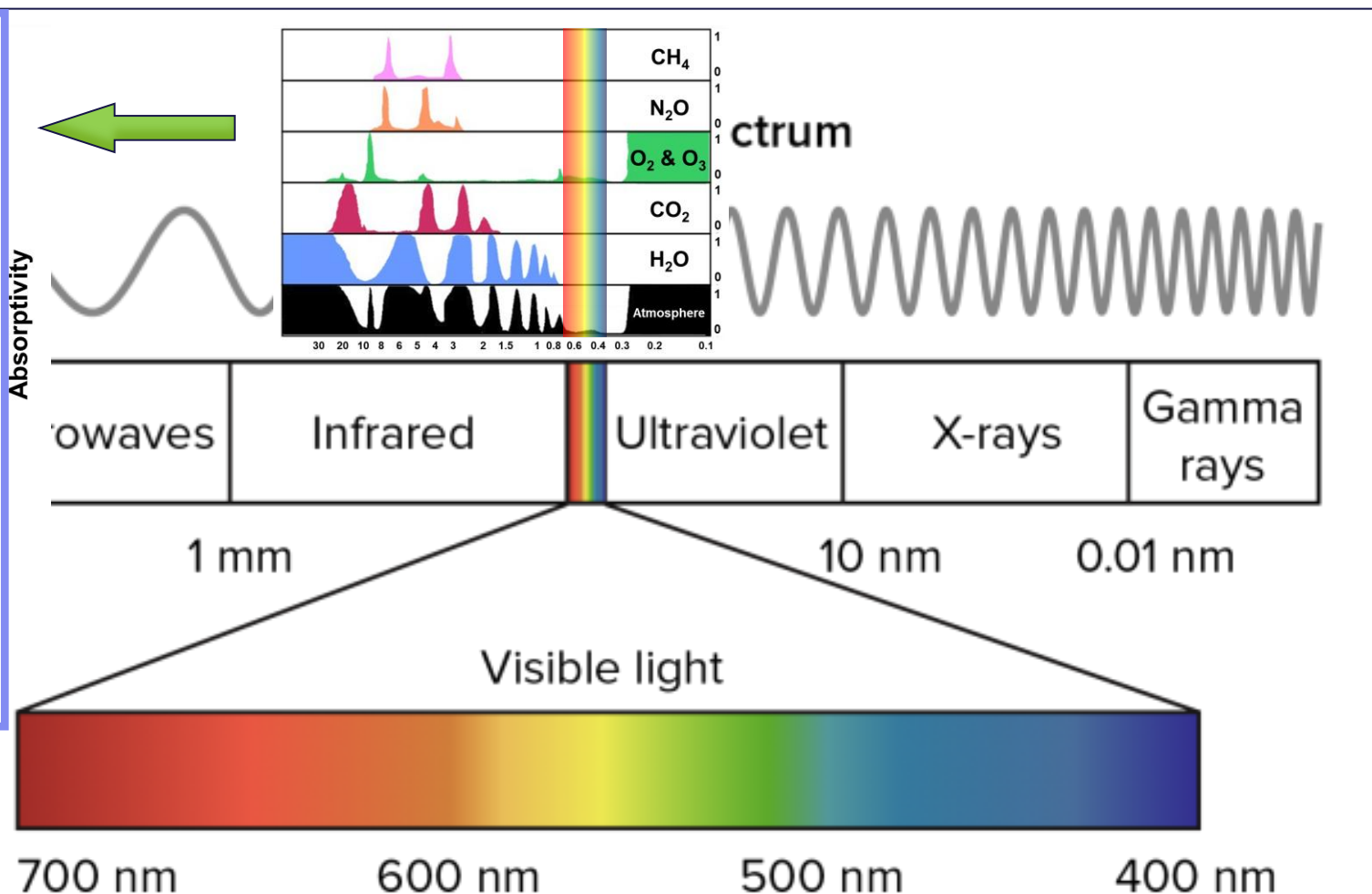
Photo Acoustic Spectroscopy

Optical Spectroscopy

Harmonic oscillator model for molecular vibrations

$$\text{Frequency } \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$k$  = bond strength  
 $\mu$  = reduced mass



Mass of <sup>13</sup>CH<sub>4</sub> > Mass of <sup>12</sup>CH<sub>4</sub> → Frequency of <sup>13</sup>CH<sub>4</sub> < Frequency of <sup>12</sup>CH<sub>4</sub>

# Monitoring opportunity and Project objective

Based on these observations DTU-Offshore and NxPAS ApS have secured EUDP funding of a project to exploit the opportunity that these natural isotope differences provide to distinguish biogenic methane from fossil methane, and build an analyzer that works under water.

## CH<sub>4</sub>IsotopMonitor - CIM



EUDP description:

- The North Sea region's closed oil and gas fields pose a potential leakage risk that requires monitoring.
- The CIM project develops a technology that can distinguish between methane from natural sources and leaks from oil and gas fields.
- The project also includes a simulator for the correct interpretation of data from the seabed.

Timeline: 2026-2028

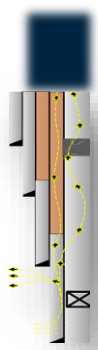
Partners:





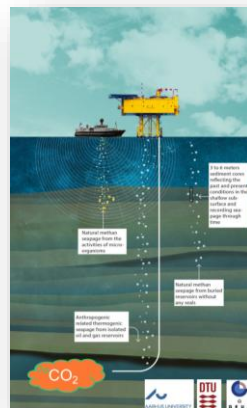
# Suggested Framework for Compliance with EU regulations

## Planning phase



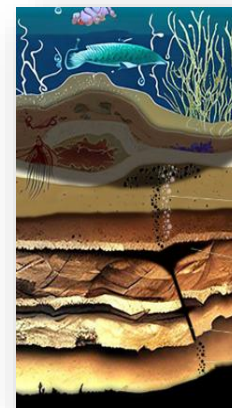
### Model Leak path scenarios

- Wells
- Sediment breach
- Faults & fractures
- Pockmarks
- Aquifers



### Develop Environmental Baseline

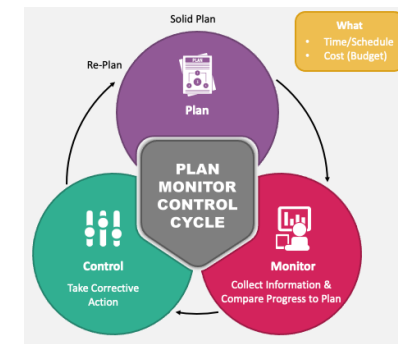
- Modelling
- Data acquisition



### Understand leakage composition (chemical and isotopes)

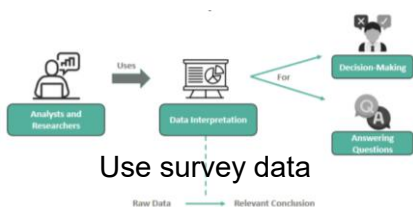
- Modelling
- Data acquisition

### Design Monitoring plan



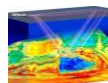
## Operational phase

### Monitoring and Interpretation of data



### Understand origins of detected methane

- Seismic
- Isotopic sensors (fossil vs biogenic)
- Environmental baseline
- Decision making



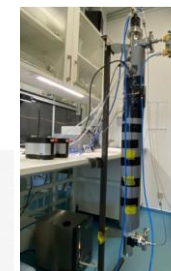
### Remediating actions – when/how



Well intervention



Or: e.g. CH<sub>4</sub> scrubbing in water column using UV



DTU

