Colloque Annuel du GdR CNRS HydroGEMM

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Mardi 05 novembre 2024

Comprehensive Overview from Earth cycle to experimental studies

Hydrogemm 2024
Raphaël Josse

Natural Hydrogen

What if everything was hidden in its Earth cycle ?

About me …

2023

Internship with Isabelle Moretti (ISTeP)

- Remote sensing
- Sources rock for natural hydrogen generation

2024

Graduated in MS.C Geology from Sorbonne University, France

Internship with Ema Frery (CSIRO)

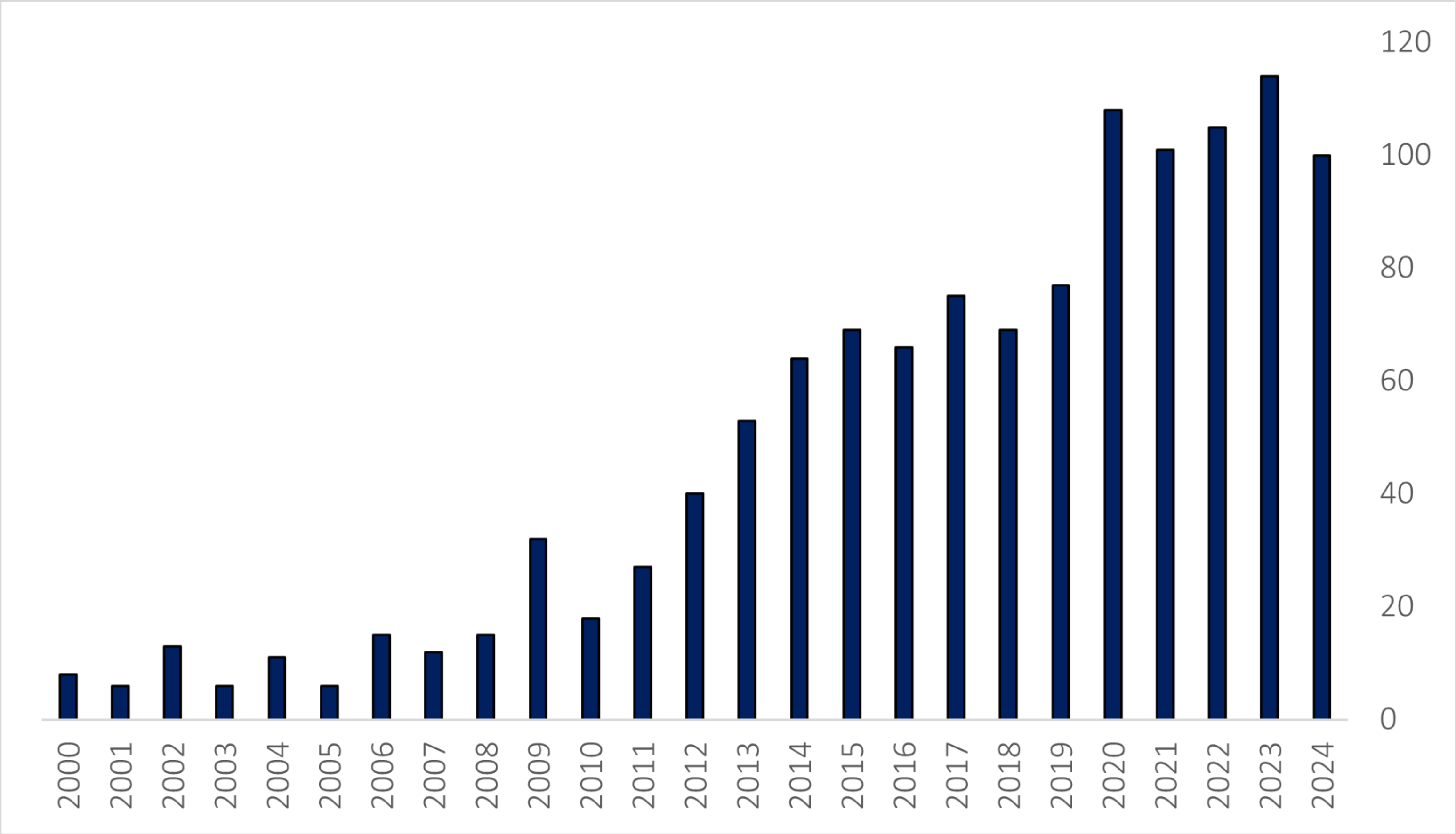
- Hydrogen cycle
- Long-term monitoring
- Artefacts measured on field

Now

Research Geologist Engineer at IFPEN

- Hydrogen exploration strategies
- Gas potentiel through expermientals studies

Scientifics papers related to **Natural hydrogen in Geology**



Source : WebOfScience, « natural hydrogen geology from 2000 to 2024 »

Scientifics papers related to Natural hydrogen Cycle in Geology ?

And the answer is …

Almost none

Need to create a more accurate H_2 cycle

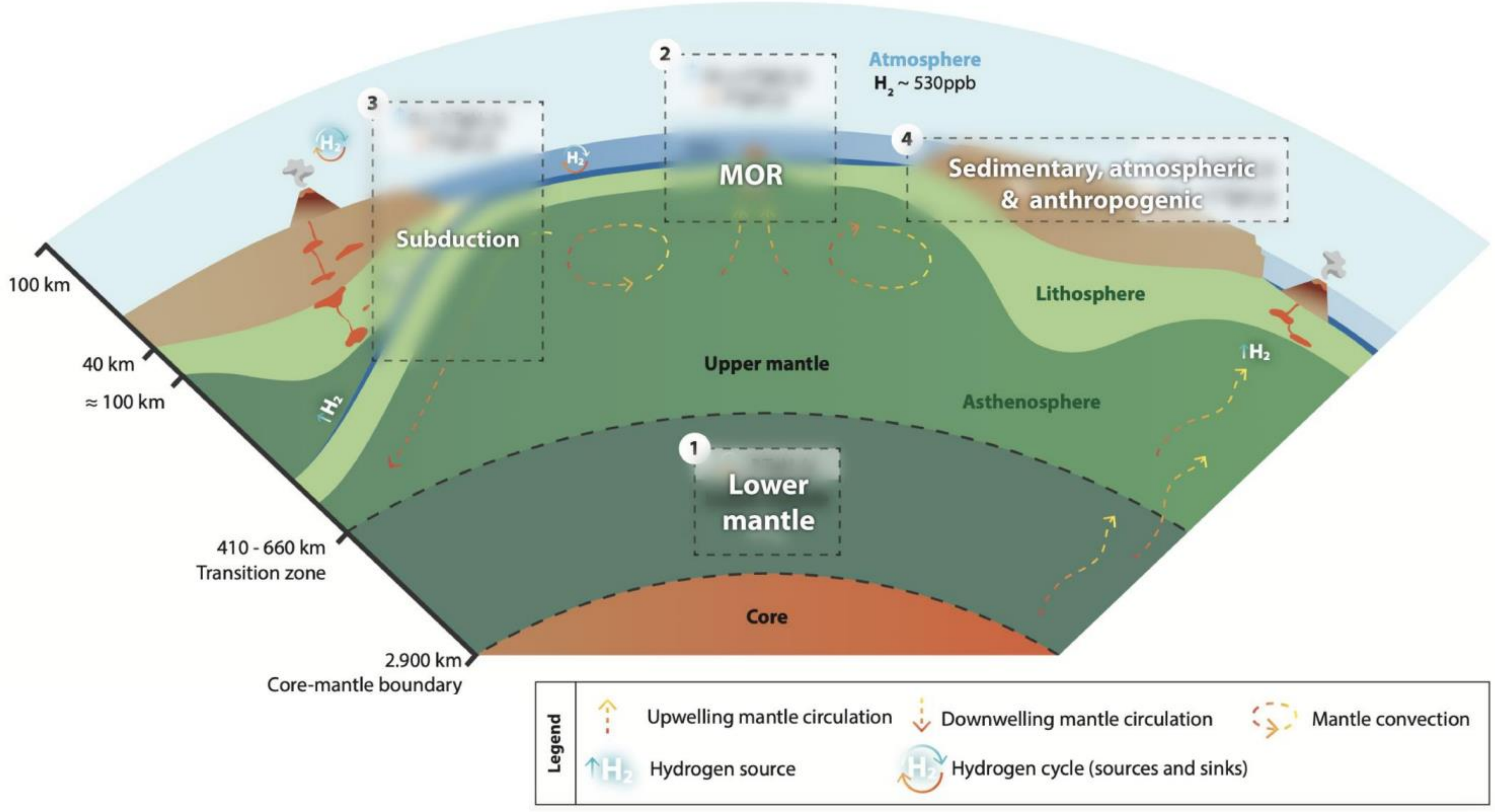
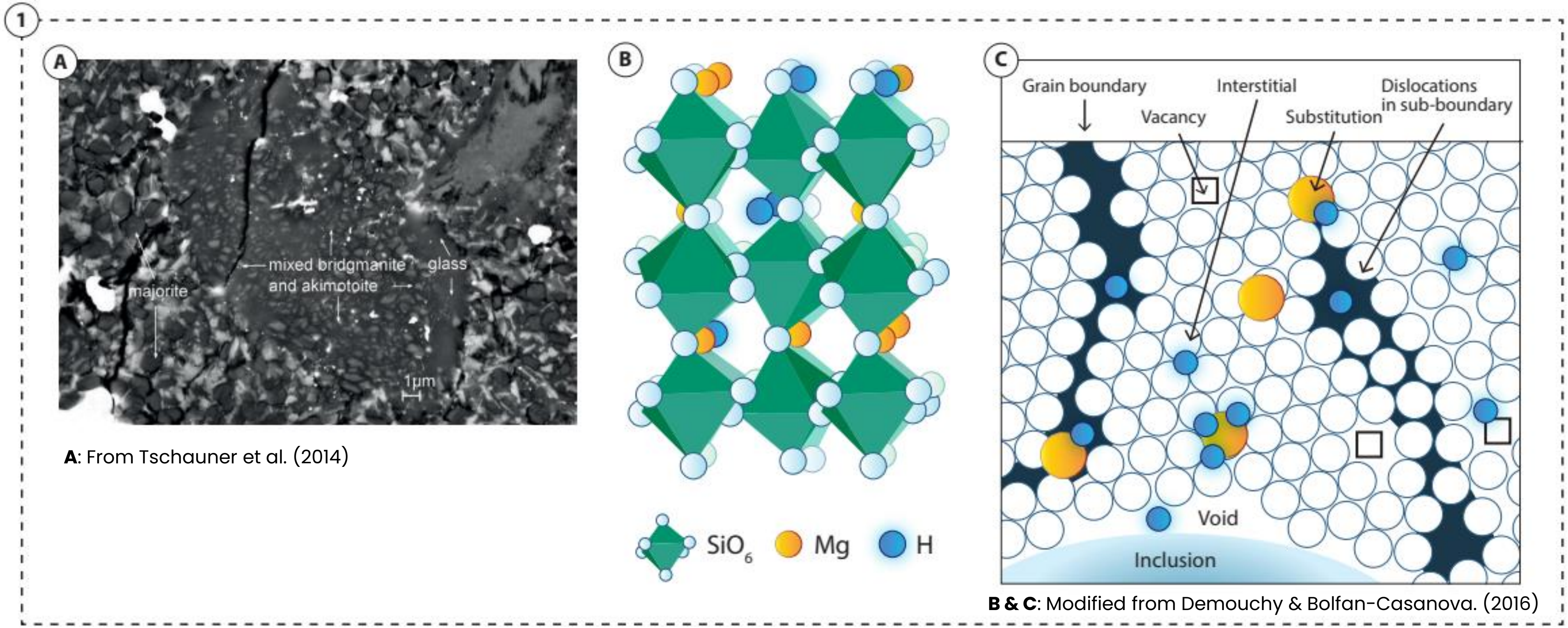


Figure 1: Main sketch of H_2 cycle on Earth

1 - H_2 in the Lower mantle



A: From Tschauner et al. (2014)

B & C: Modified from Demouchy & Bolfan-Casanova. (2016)

A – SEM image of bridgmanite

$(Mg,Fe)SiO_3$

B – 3D view of crystal structure $MgSiO_3$ Perovskite

C – 2D view of crystal structure $MgSiO_3$ Perovskite

Figure 2: H_2 reservoirs in the lower mantle, especially in a Mg-perovskite structure.

2 - H_2 in the MOR

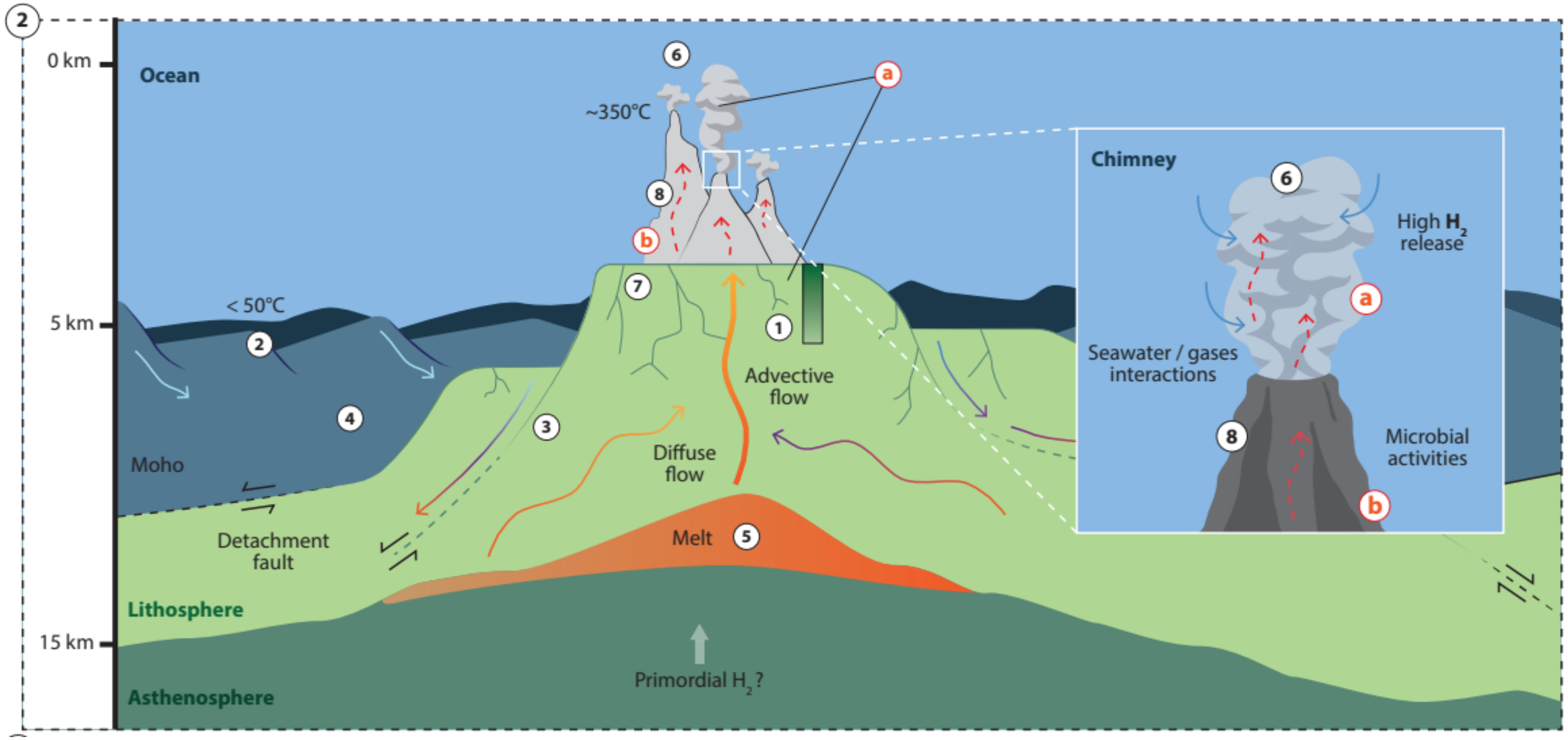


Figure 3: H_2 cycle associated with Mid-oceanic ridges in hydrothermal vents

Sources

Abiotic

(1) Serpentinization
$(Mg,Fe)_2SiO_4 + H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 + Fe_3O_4 + H_2$

(2) Oceanic crust weathering
$2FeO + 4H_2O \rightarrow 2Fe(OH)_3 + H_2$

(3) Rock fracturing
$Si\cdot + H_2O \rightarrow SiOH + H\cdot$
$H\cdot + H\cdot \rightarrow H_2$

(4) Water radiolysis
$H_2O + (\alpha, \beta, \gamma) \rightarrow H\cdot + OH\cdot + H^+ + OH^- + e^-$
$e^-_{(aq)} + H^+ \rightarrow H\cdot$
$H\cdot + H\cdot \rightarrow H_2$

(5) Magma crystallization
$3FeO_{(magma)} + H_2O_{(magma)} \rightarrow (FeO \cdot Fe_2O_3)_{(rock)} + H_2$

(6) Magma degassing
$CO + H_2O \leftrightarrow CO_2 + H_2$
$SO_2 + 2H_2O \leftrightarrow H_2SO_4 + H_2$
$H_2S + 2H_2O \leftrightarrow SO_2 + 3H_2$
$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$

(7) Pyritization and sulphur interactions
$FeS + H_2S \rightarrow FeS_2 + H_2$
$H_2S + 2H_2O \leftrightarrow SO_2 + 3H_2$

Biotic

(8) Nitrogen fixation
$N_2 + 8H^+ + 16ATP + 8e^- \rightarrow 2NH_3 + 16ADP + H_2$

Sinks

Abiotic

(a) *Aerobic*
Hydrogen oxidation
$2H_2 + 2O_2 \rightarrow 2H_2O$
$5H_2 + 2NO_3^- \rightarrow N_2 + 4H_2O + 2OH^-$

Anaerobic
Sulfate reduction
$4H_2 + 2H^+ + SO_4^{2-} \rightarrow H_2S + 4H_2O$

Nitrate reduction
$H_2 + NO_3^- \rightarrow NO_2^- + H_2O$

Carbone reduction
$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

Biotic

(b) Microbial consumption
$2H^+ + 2e^- \leftrightarrow H_2$

Legend

Fluid / rock interactions

- Cold seawater infiltration
- High fluid modification
- Hot hydrothermal fluid rise
- Hydrothermal plume
- Basalts / Lavas
- Gabbroic rocks
- Peridotite
- Serpentinization gradient (+ / -)

3 - H_2 in Subduction

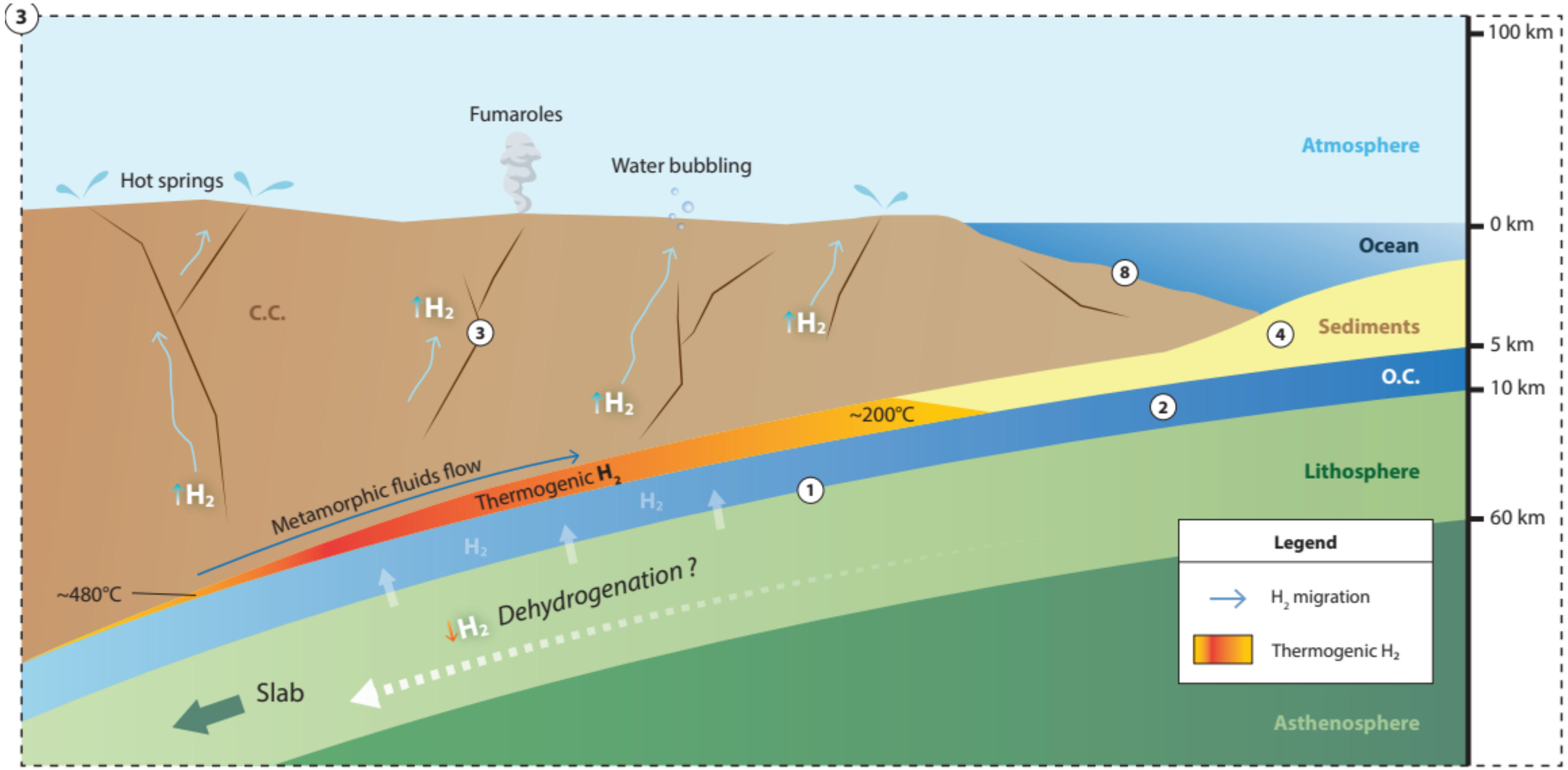
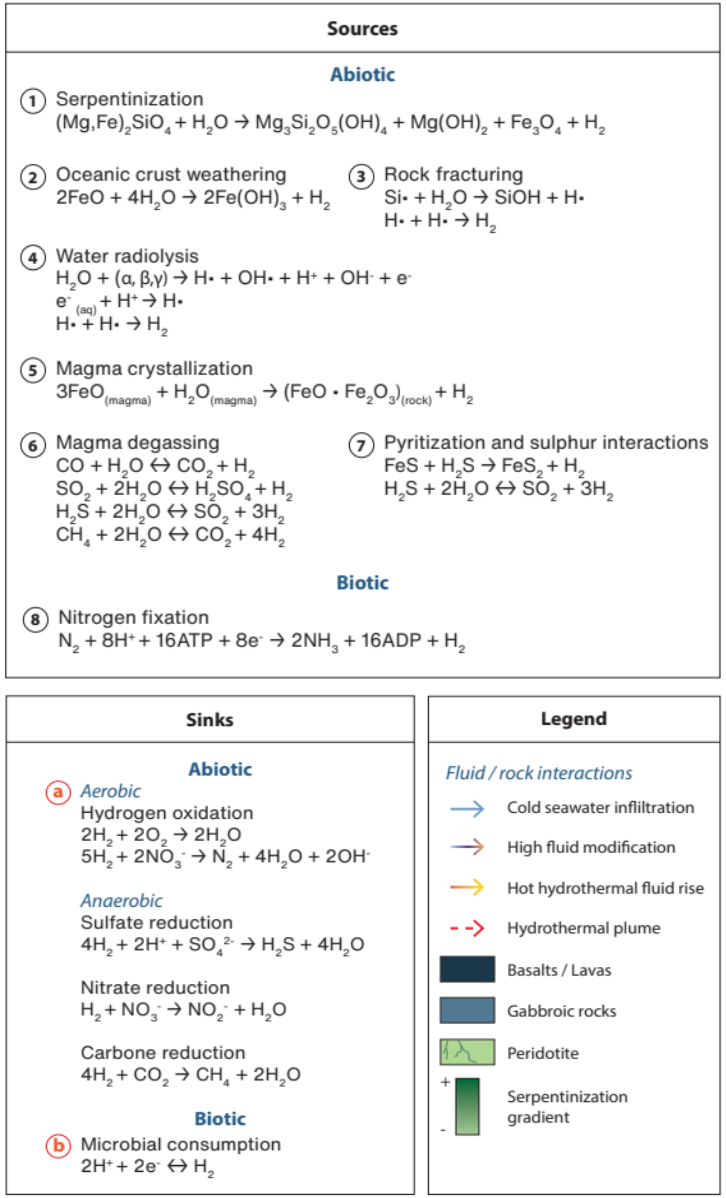


Figure 4: H_2 cycle associated with Subduction



4 - H_2 in Sedimentary, Atmospheric and Anthropogenic

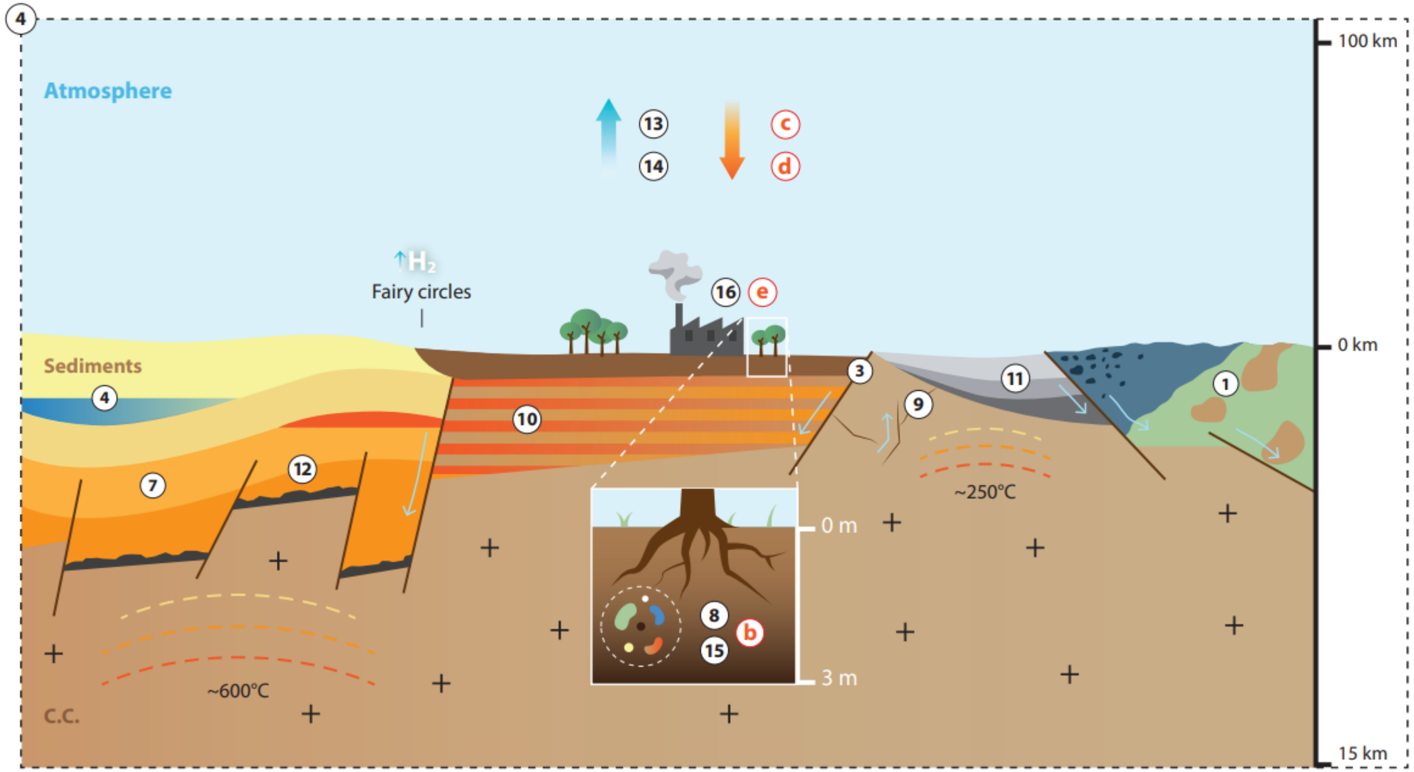


Figure 5: H_2 cycle H2 cycle associated with sedimentary, atmospheric and anthropogenic contexts.

Sources

Abiotic

(1) Serpentinization
$(Mg,Fe)_2SiO_4 + H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 + Fe_3O_4 + H_2$

(3) Rock fracturing
$Si\cdot + H_2O \rightarrow SiOH + H\cdot$
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$H_2O + (\alpha, \beta, \gamma) \rightarrow H\cdot + OH\cdot + H^+ + OH^- + e^-$
$e^-_{(aq)} + H^+ \rightarrow H\cdot$
$H\cdot + H\cdot \rightarrow H_2$

(7) Pyritization and sulphur interactions
$FeS + H_2S \rightarrow FeS_2 + H_2$
$H_2S + 2H_2O \leftrightarrow SO_2 + 3H_2$

(9) Hydration of biotite
$KFe_3^{2+}(AlSi_3)O_{10}(OH)_2 + 2H_2O \rightarrow Fe_2^{3+}O_3 + Fe_3O(OH) + H_2$

(10) BIF weathering
$2Fe^{2+}O + H_2O \rightarrow Fe^{3+}2O_3 + H_2$

(11) Siderite weathering
$3FeCO_3 + H_2O \rightarrow Fe_3O_4 + 3CO_2 + H_2$

(12) Pyrolysis of shales/coals

Atmospheric

(13) CH_4 photochemical oxidation
$CH_4 + OH \rightarrow CH_3 + H_2O$

(14) VOC photochemical oxidation
$HCHO + h\nu \rightarrow H_2 + CO$

Biotic

(8) Nitrogen fixation
$N_2 + 8H^+ + 16ATP + 8e^- \rightarrow 2NH_3 + 16ADP + H_2$

(15) Biological production

Anthropogenic

(16) Anthropogenic hydrogen emissions

Sinks

Abiotic

(c) OH oxidation
$H_2 + OH \rightarrow H_2O + H^+$

(d) Planetary air leaks

Biotic

(b) Microbial consumption
$2H^+ + 2e^- \leftrightarrow H_2$

Anthropogenic

(e) FTT reaction
$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$

Legend

- Water infiltration
- Geothermal gradient
- Microbial life
- Banded-Iron Formations (BIF)
- Siderite rocks

Ophiolite complex

- Basalts / Lavas
- Gabbroic rocks
- Chromite
- Peridotite

Conclusion

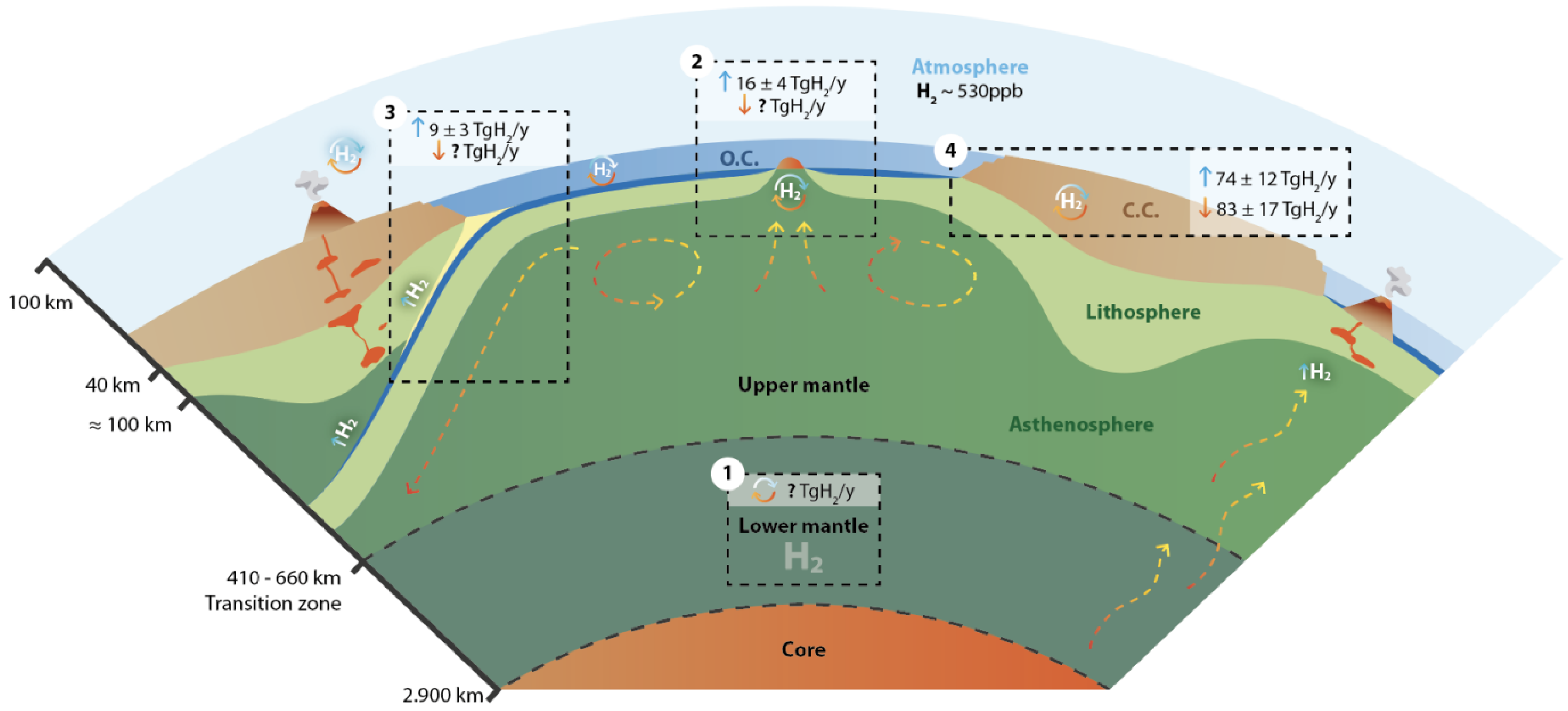

Figure 6: Final H_2 cycle with total flux

Gaps:

- Volume on each compartment
- Interactions between each domain
- Processes overlooked

What's **next** ?

Create and Calibrate H_2 sensors

for hydrogen exploration

Let's play with experiments with H_2 injections

- **1st step:** Use right sensors

Semiconductor Gas Sensors (**SGX**)

- Silicium layers

Metal Oxide Sensors (**MOX**)

- Zinc or copper layers

! MADE BY CSIRO !

↑ H_2 = ↑ Electrical resistivity

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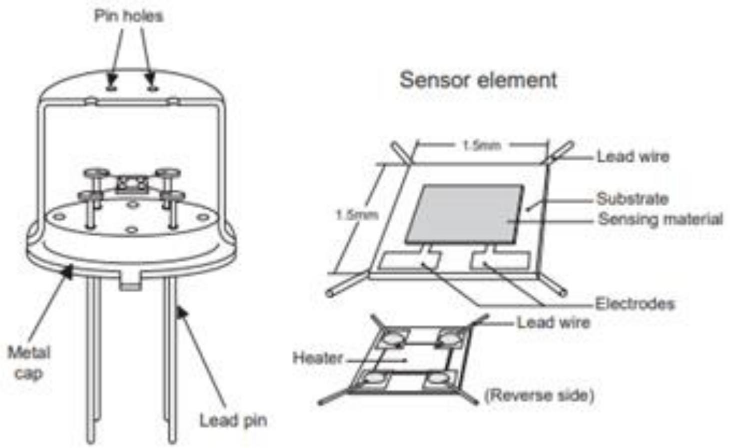
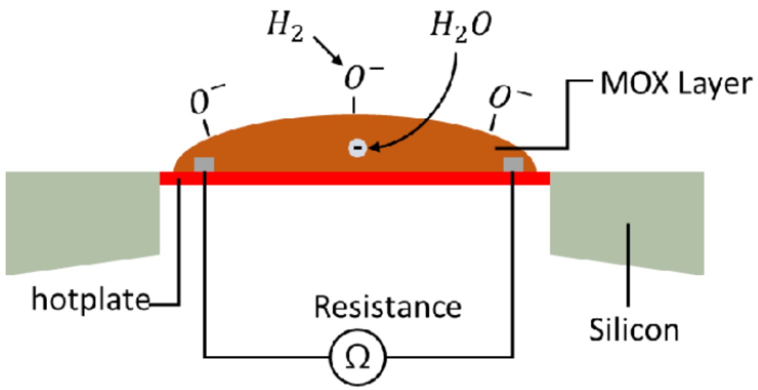
Sensors and Transmitters. (n.d.). A brief introduction to MOS sensors and their applications

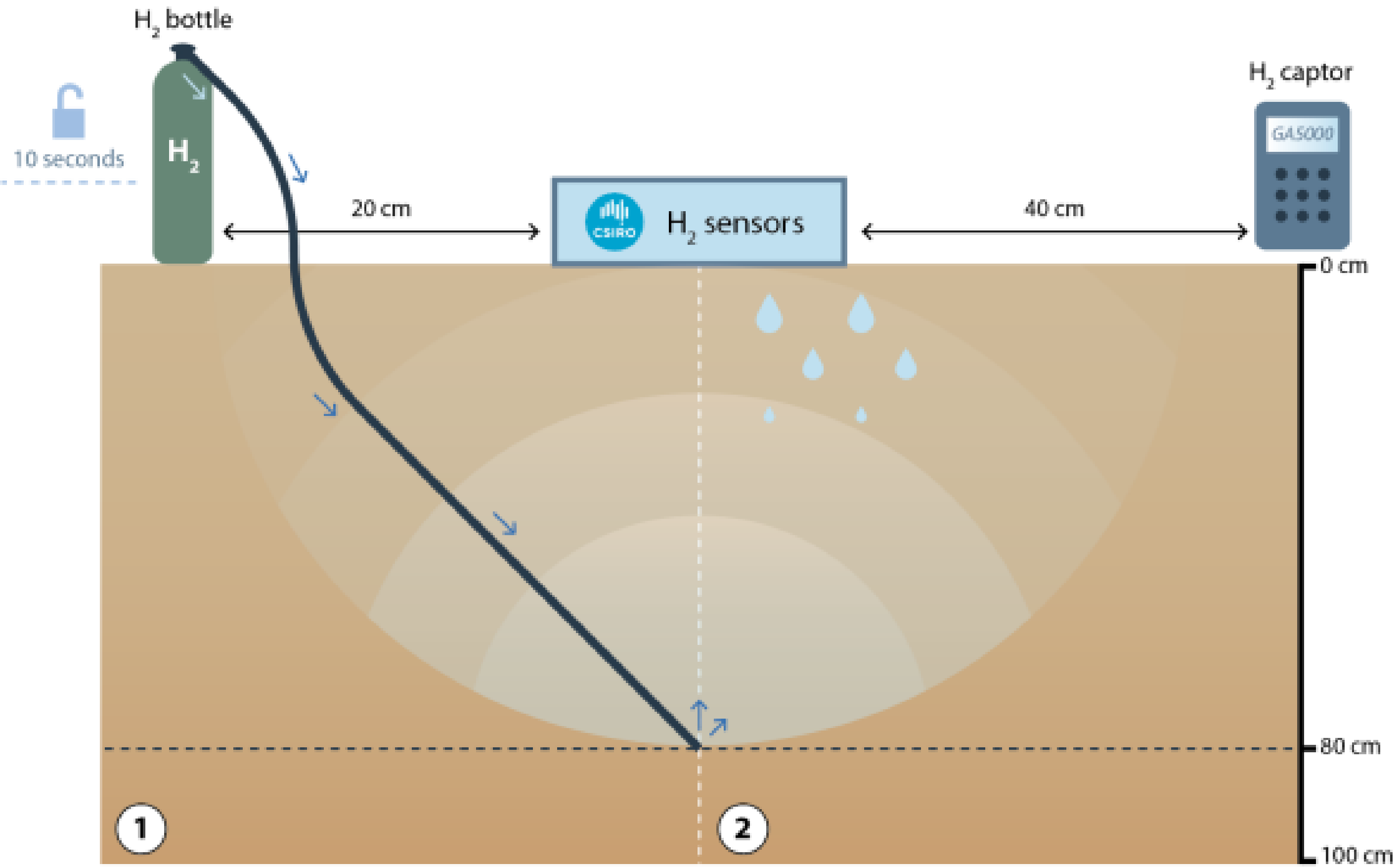




Protocol for H_2 injections

- 2nd step: Create ("valuable") protocol

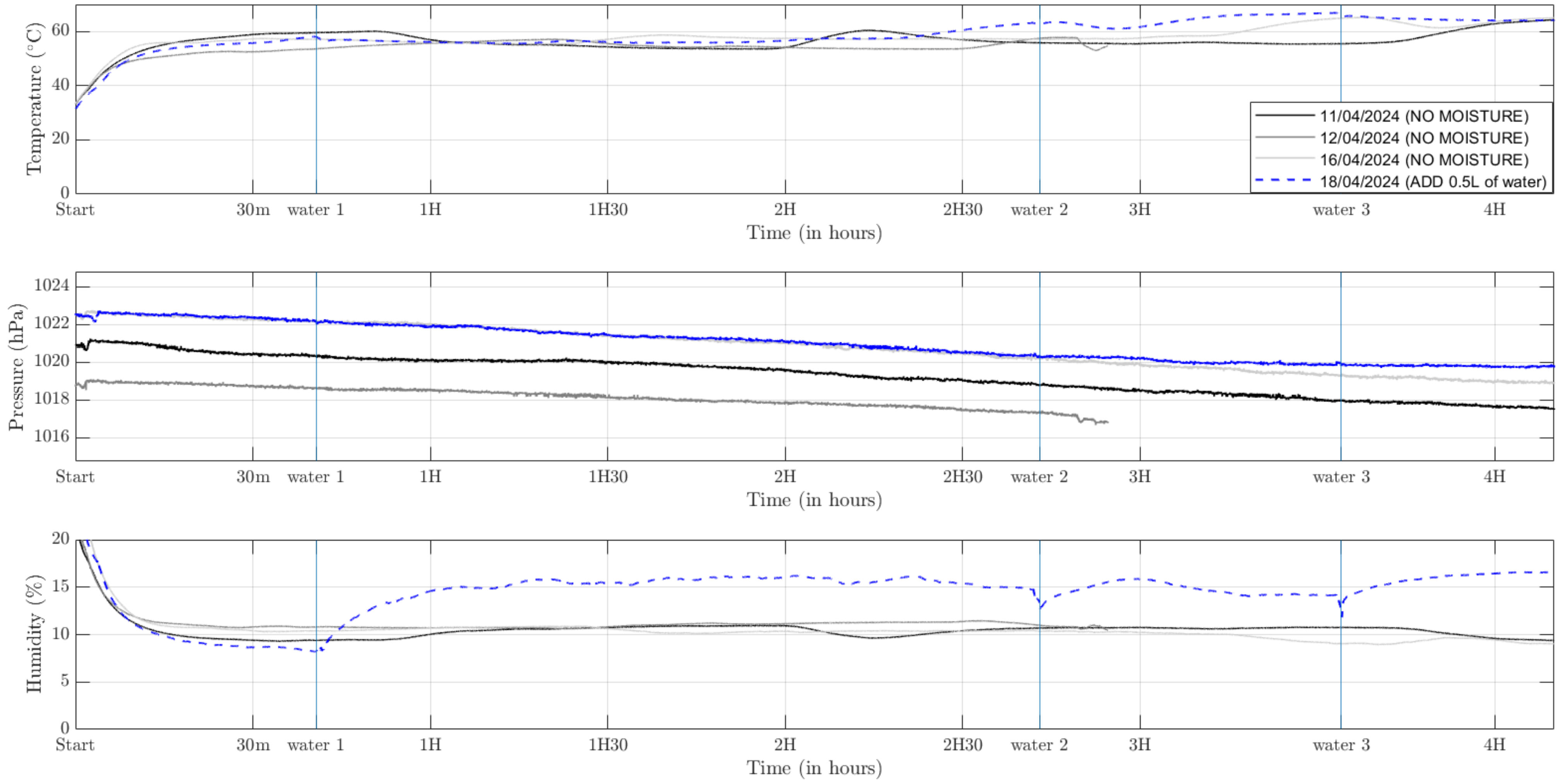
Protocol sketch



Picture

Before H_2 injections

- 1st step: Check environmental parameters

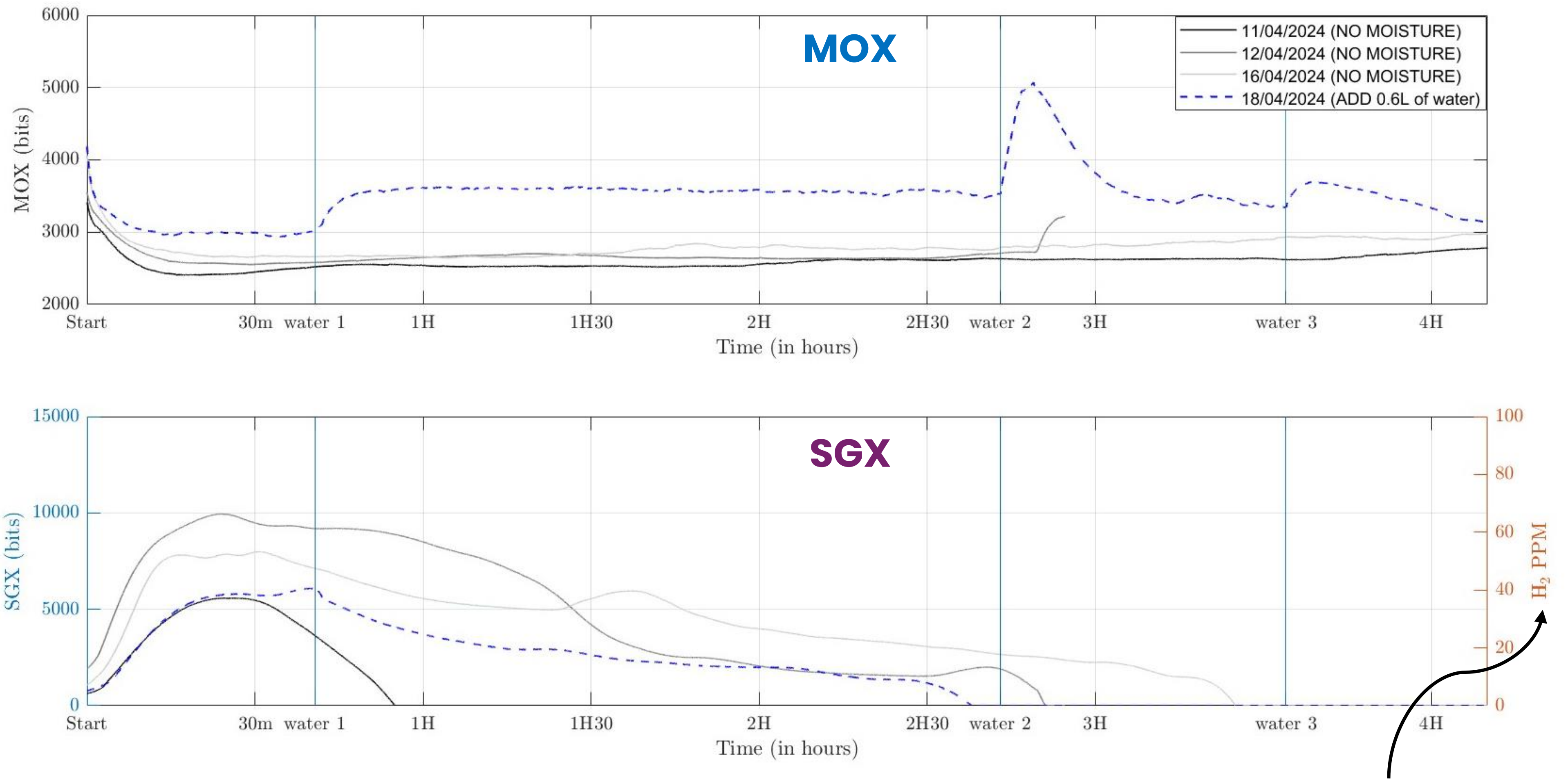


Essential for :

- Impact of water injection on each parameter
- Disfunctions

Before H_2 injections

- **2nd step:** Check H_2 sensors



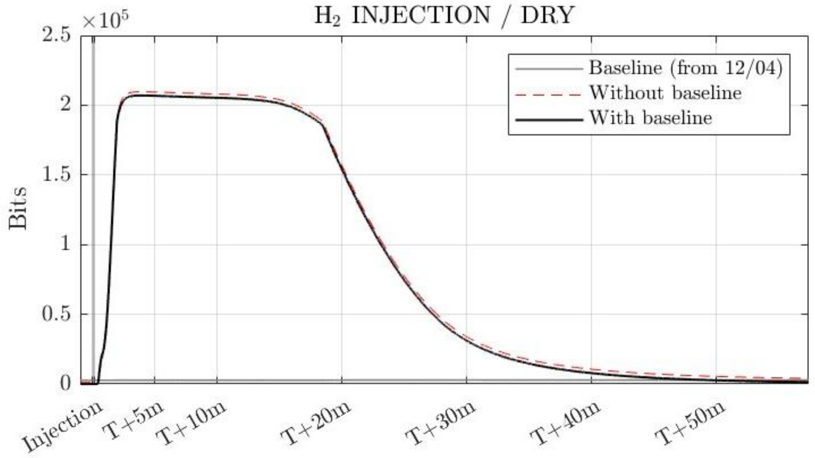
H_2 (ppm) = 6.51* Sensor SGX (bits)/1000

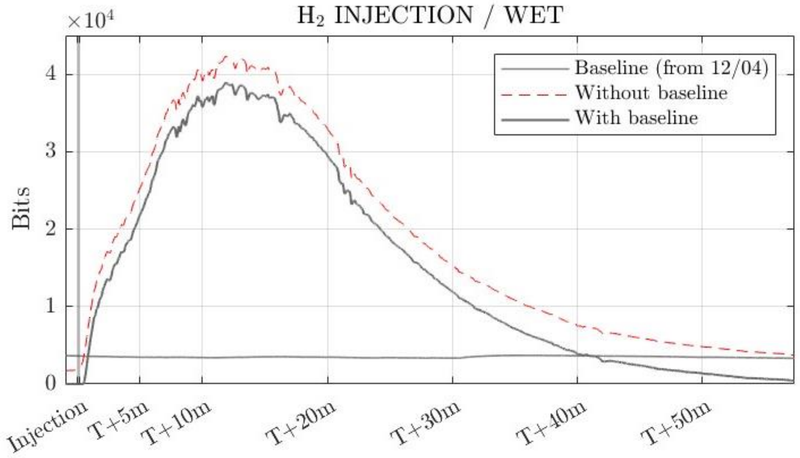
Essential for :

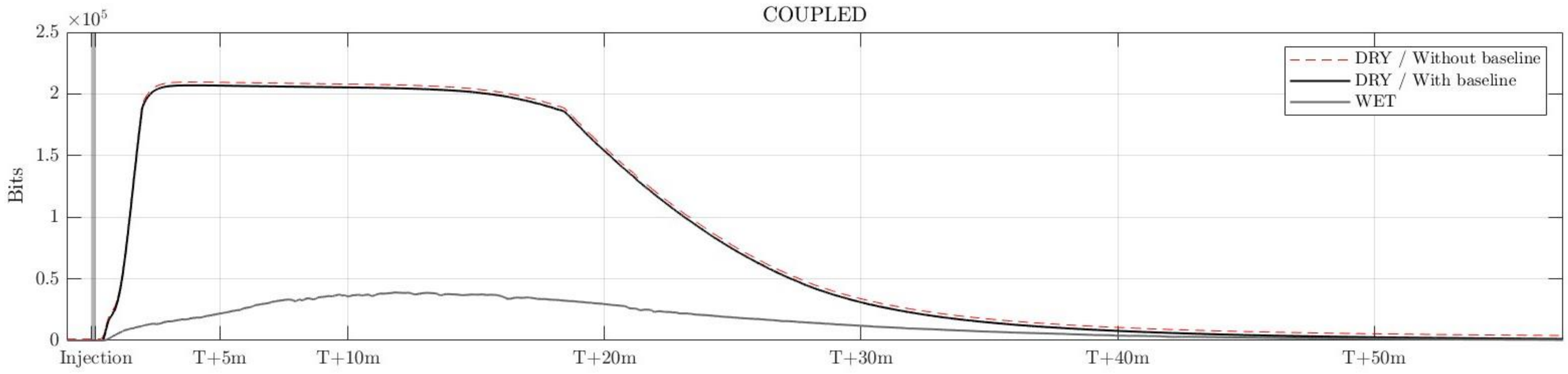
- Sensor time calibration
- Sensor baseline
- Impact of water injection

H_2 injections

MOX







Results

Sensor

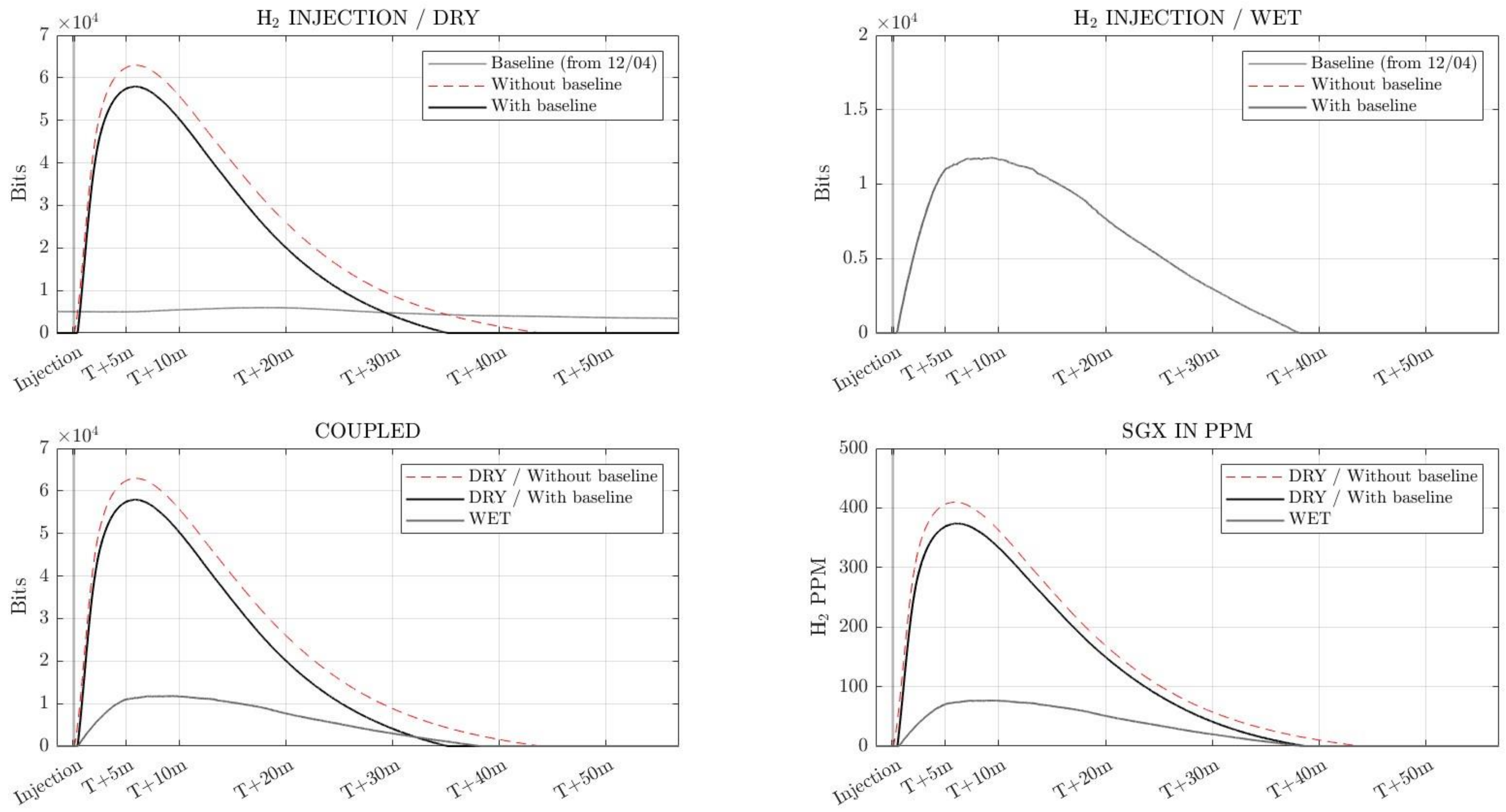
- **Fast response**
- **Sensor saturated for 20 min.**
- **Peak variabilites**

H_2

- No H_2 recorded after 50 min.
- High impact on H_2 with wet soil

H_2 injections

SGX



Results

Sensor

- **Fast response**
- **Not saturated**
- **No peak deformation**

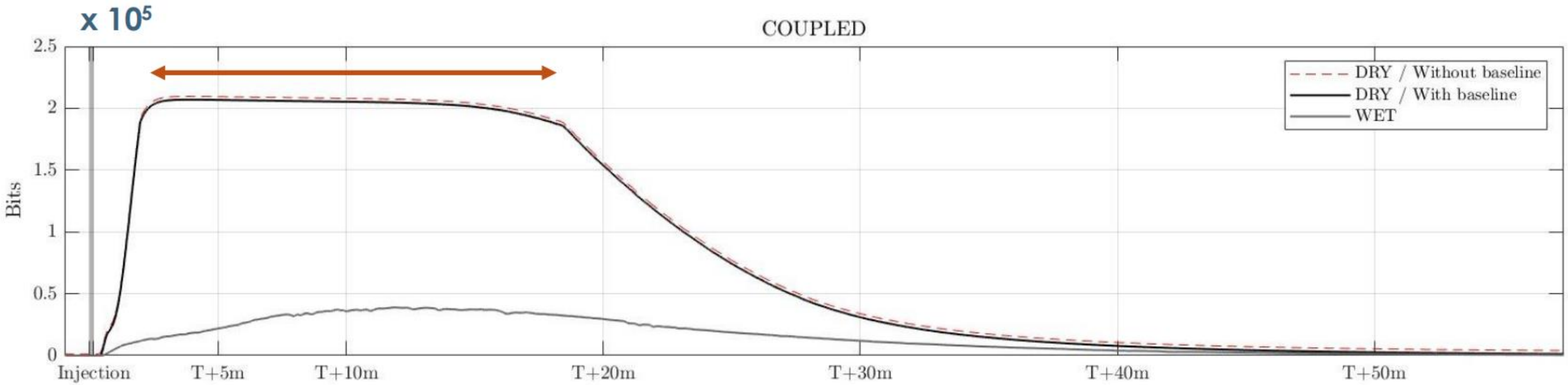
H_2

- No H_2 recorded after 40 min.
- High impact on H_2 with wet soil

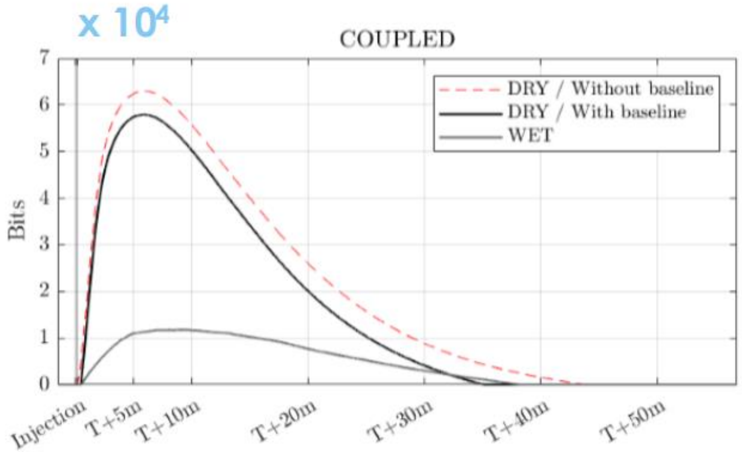
Conclusions and discussions

- (1) -

MOX



SGX

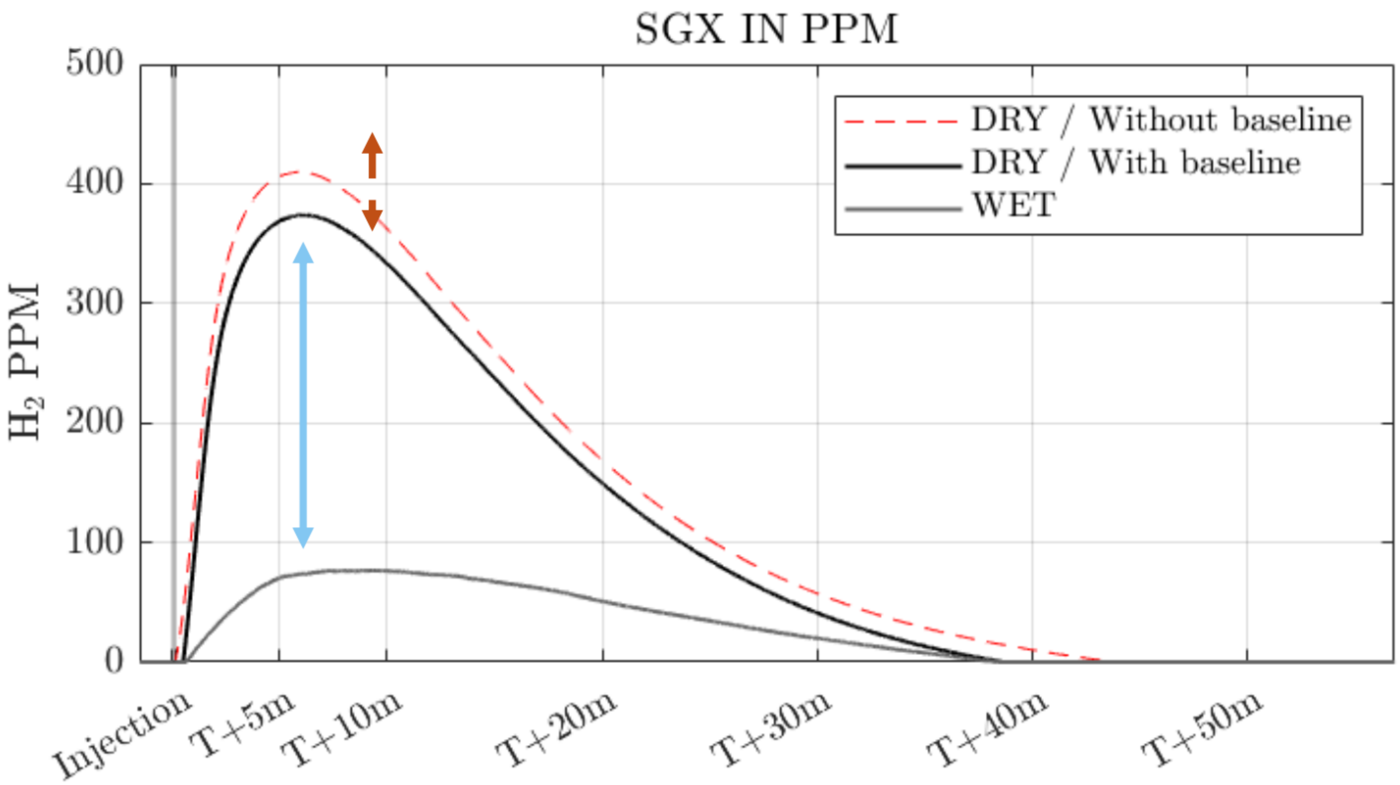


- **MOX** is **saturated** for 15 minutes !

- **MOX** = 2×10^5 bits and **SGX** = 6.5×10^4 bits

Conclusions and discussions

- (2) -

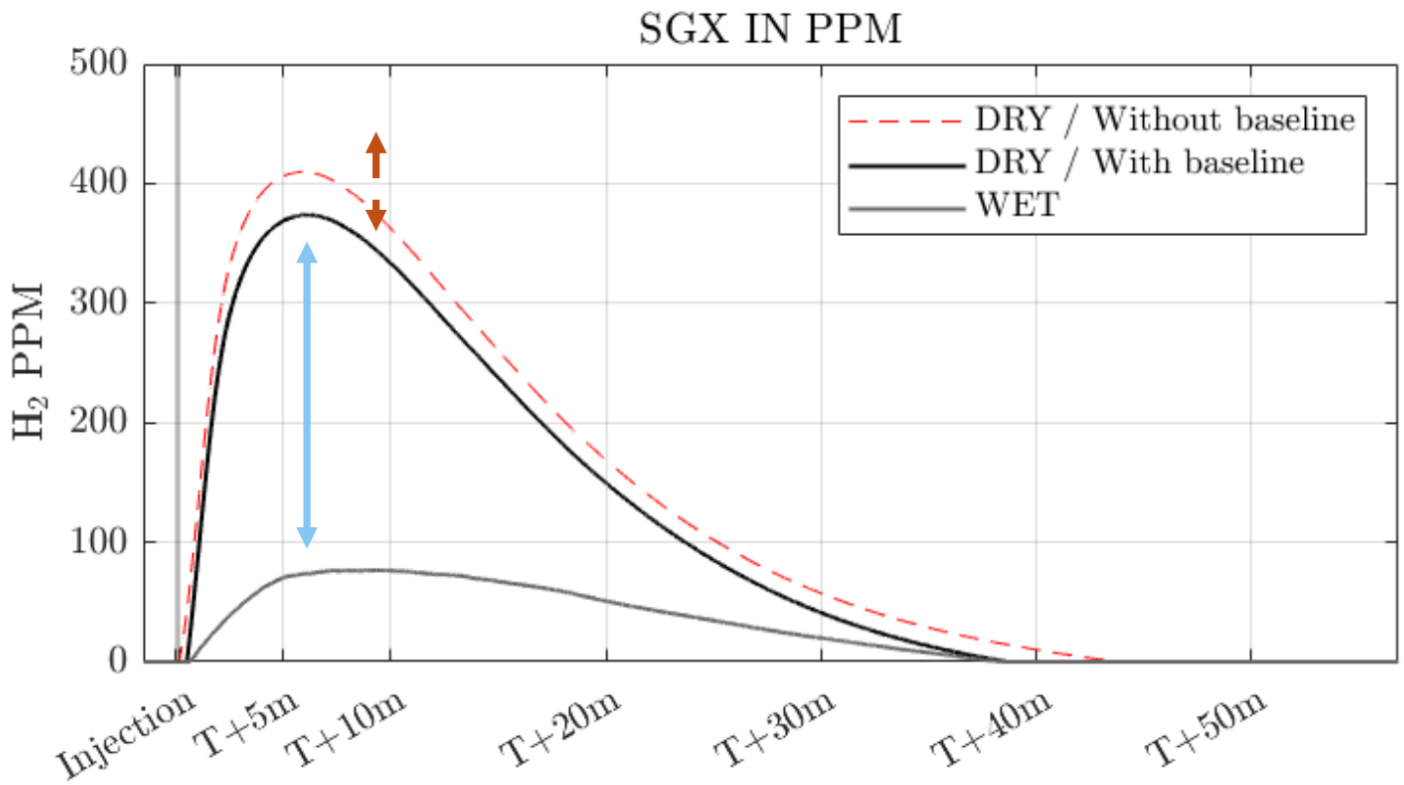


(a) False positive … or negative

- Anomaly of H_2 up to 65 ppm without baseline (DRY)

Conclusions and discussions

- (3) -



(b) H_2 concentration received

- High variability between dry and wet soil (80% not recorded)

Why ?

- H_2 dissolved in the water ?
- New fluid pathways ?
- Micriobial life ?

Thank you for listening!

Raphaël Josse