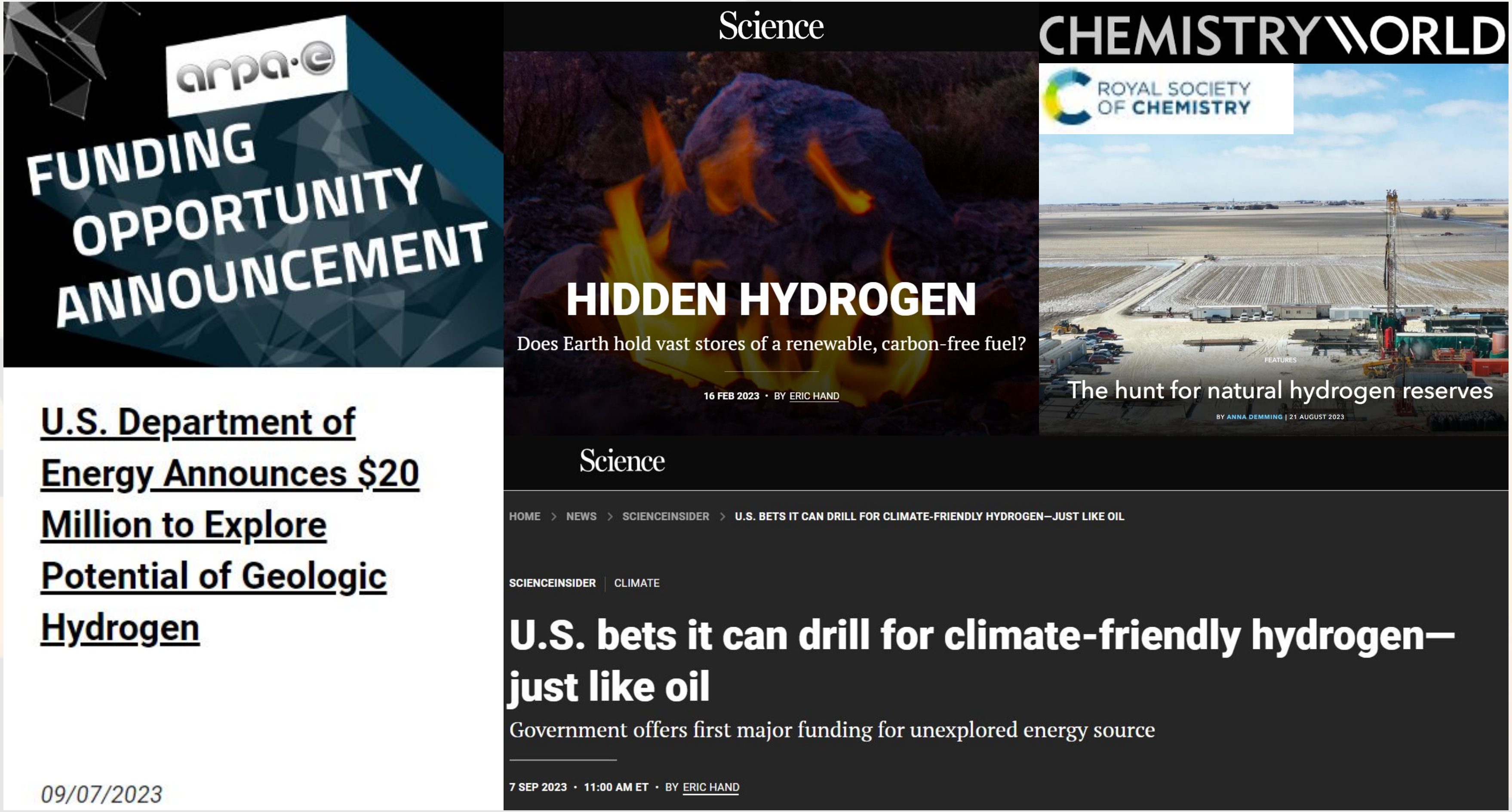
# WE NEED TO GO DEEPER

## STIMULATING ABIOGENIC PETROLEUM FORMATION IN THE SUBSURFACE FOR FUN AND PROFIT

arpa·e

september 13th, 2023

jonathan "jo" melville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FUNDING OPPORTUNITY ANNOUNCEMENT
U.S. Department of Energy Announces $20 Million to Explore Potential of Geologic Hydrogen
09/07/2023
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HIDDEN HYDROGEN
Does Earth hold vast stores of a renewable, carbon-free fuel?
16 FEB 2023 · BY ERIC HAND
CHEMISTRY WORLD
ROYAL SOCIETY OF CHEMISTRY
FEATURES
The hunt for natural hydrogen reserves
BY ANNA DEMMING | 21 AUGUST 2023
Science
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SCIENCEINSIDER | CLIMATE
U.S. bets it can drill for climate-friendly hydrogen—just like oil
Government offers first major funding for unexplored energy source
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THE FUTURE OF EVERYTHING

## Underground Hydrogen Could Supercharge Green Energy. First, Scientists Have to Find It.

It has the potential to power electrical grids, run factories, heat homes and propel vehicles when combined with a fuel cell


Forbes

TRANSPORTATION • DAILY COVER

## Forget Oil. New Wildcatters Are Drilling For Limitless 'Geologic' Hydrogen

The New York Times

OPINION

## A Gold Mine of Clean Energy May Be Hiding Under Our Feet

Feb. 27, 2023

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Energy | Industry Insight

## Startups race to strike hydrogen gold

By Paul Day

September 7, 2023 9:09 AM EDT · Updated 12 hours ago

Aa

The Washington Post

*Democracy Dies in Darkness*

ENERGY

## Natural Hydrogen Could Change the World, If We Understood It

Analysis by David Fickling | Bloomberg

July 31, 2023 at 4:21 p.m. EDT


SPICY TAKE:
This is what "mainstream" looks like.
Underground Hydrogen Could Supercharge Green Energy. First, Scientists Have to Find It.
The New York Times
A Gold Mine of Clean Energy May Be Hiding Under Our Feet
Startups race to strike hydrogen gold
By Paul Day
Natural Hydrogen Could Change the World, If We Understood It
Breakingviews
Technology

# PREFACE: yes, i am serious

**Geologic $H_2$:**

increasing attention & funding,
ongoing program development

**Dr. Emily Yedinak**
*ARPA-E Fellow*
*2021-2022*

**ARPA-E Fellows:**

high-risk, early stage
technology whitespacing

**Abiogenic Petroleum**

answers the question:

*"How might we follow up a successful GeoH$_2$ program?"*

# Fact: Abiogenic Hydrocarbons Exist

# Fact: Abiogenic Hydrocarbons Exist

**Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs**

**Methane-derived hydrocarbons produced under upper-mantle conditions**

**Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field**

**Generation of methane in the Earth's mantle: *In situ* high pressure–temperature measurements of carbonate reduction**


*Meteorit. Planet. Sci.* **2000**, *35*, 629.
*Nature* **2002**, *416*, 522.
*Proc. Natl. Acad. Sci.* **2004**, *101*, 14023.
*Chem. Geol.* **2006**, *226*, 328.
*Geophys. Res. Lett.* **2008**, *35*, 1.
*Science* **2008**, *319*, 604.
*Nat. Geosci.* **2009**, *2*, 566.
*Chem. Select* **2017**, *2*, 1336.

# So what?

## Leverage existing infrastructure

Hydrogen is leaky, embrittling, and not energy-dense.

We *know* how to drill, extract, store, and use oil & gas!

## Produce drop-in commodities

Liquid fuels are energy-dense and easy to use.

Short-chain olefins can make plastics carbon negative!

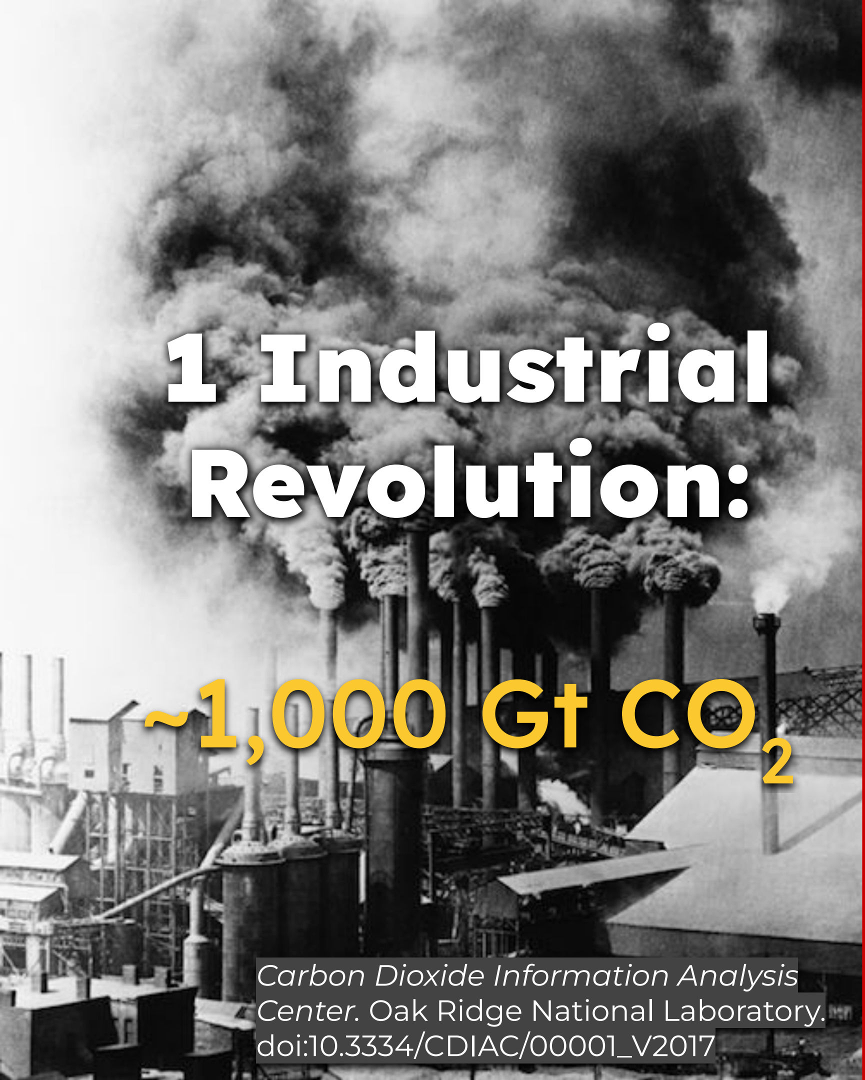
## Understand the geochemistry

30-60% of stimulated geo$H_2$ is lost as methane.

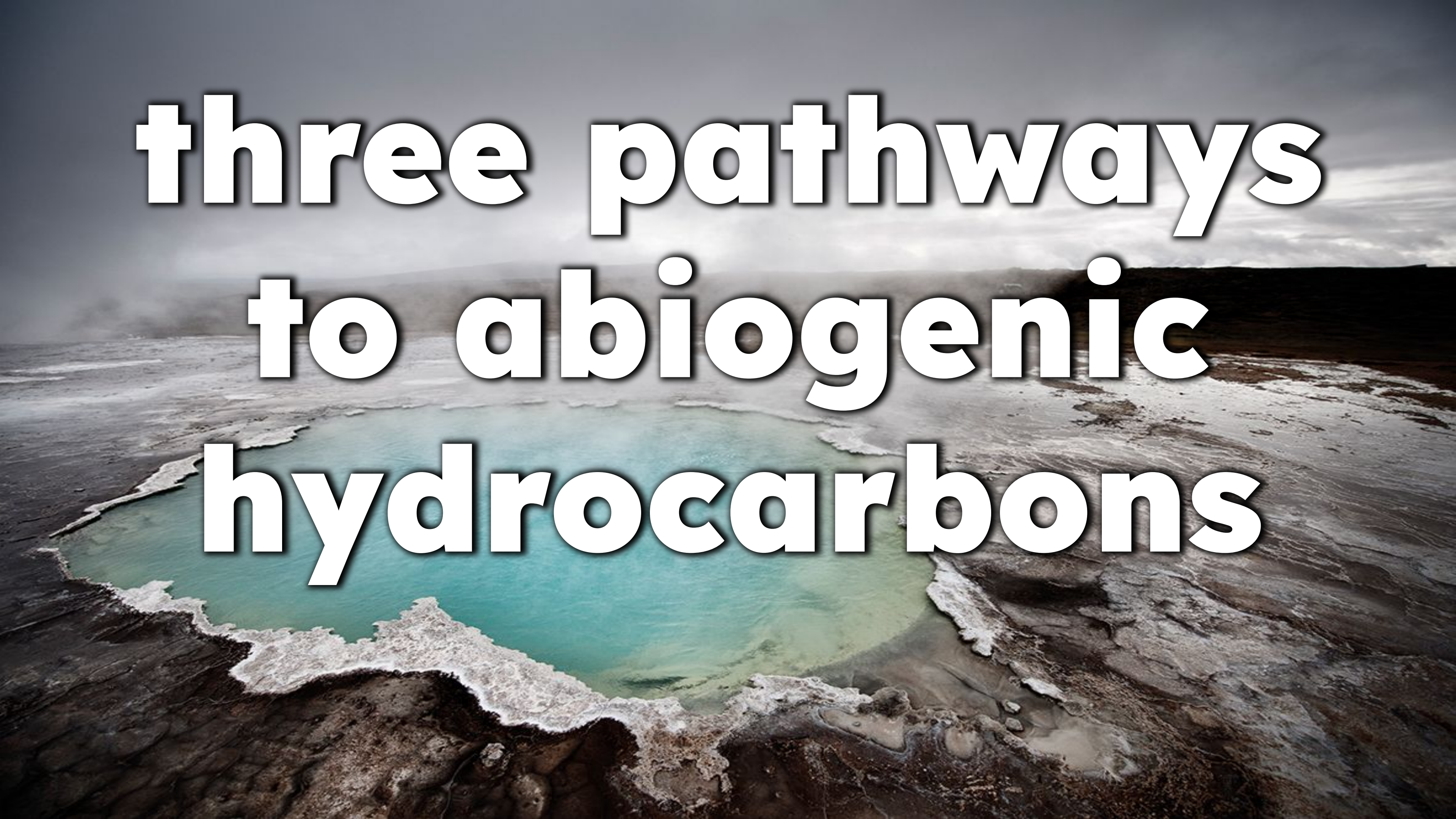
CCS injections are *already* producing geomethane!

If it works…

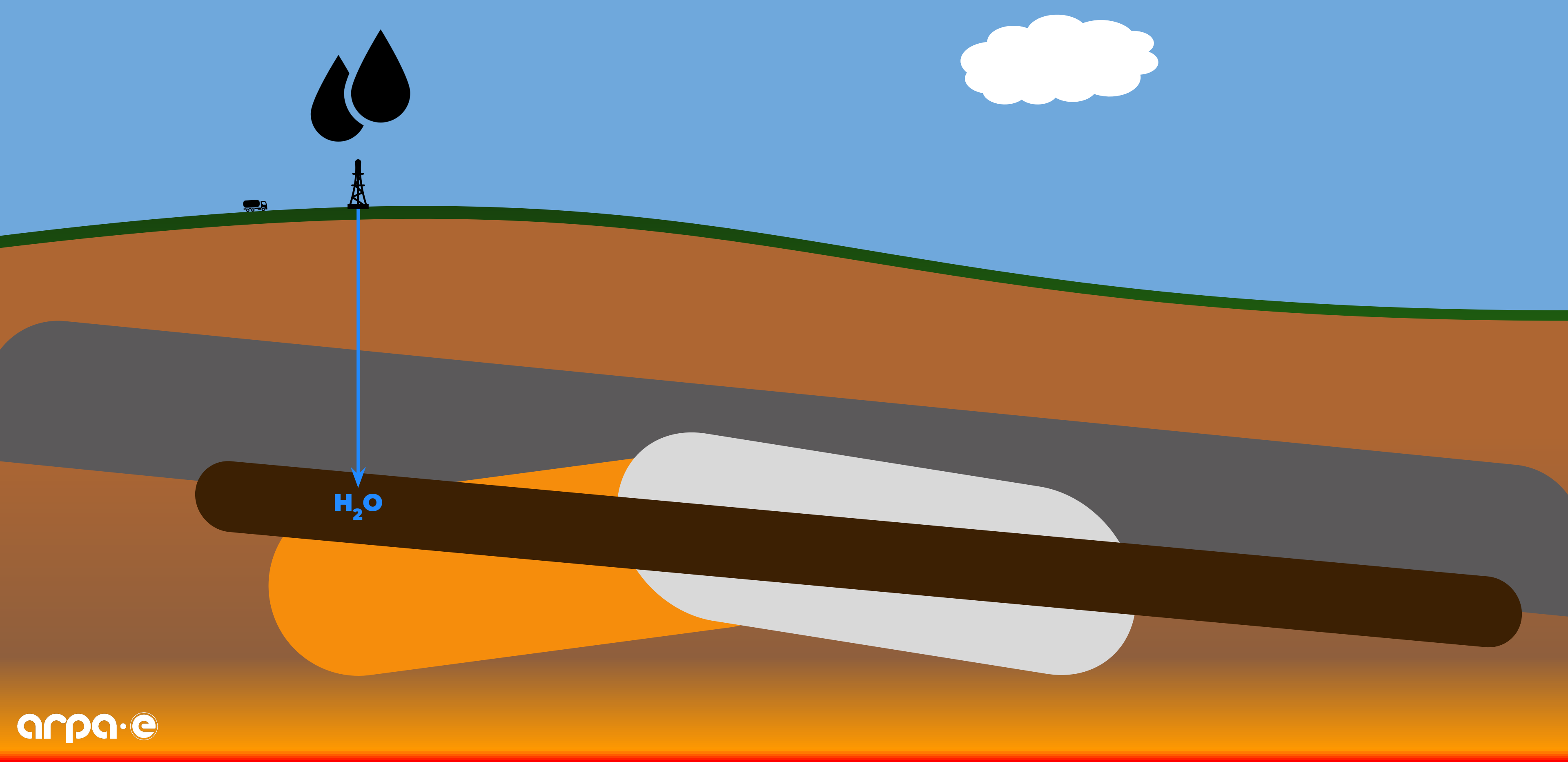
*…will it matter?*


1 Industrial Revolution:
~1,000 Gt $CO_2$
Carbon Dioxide Information Analysis Center. Oak Ridge National Laboratory.
doi:10.3334/CDIAC/00001_V2017


$GeoH_2$ drawdown potential:
~10,000 Industrial Revolutions


three pathways
to abiogenic
hydrocarbons

# 1. Inject water

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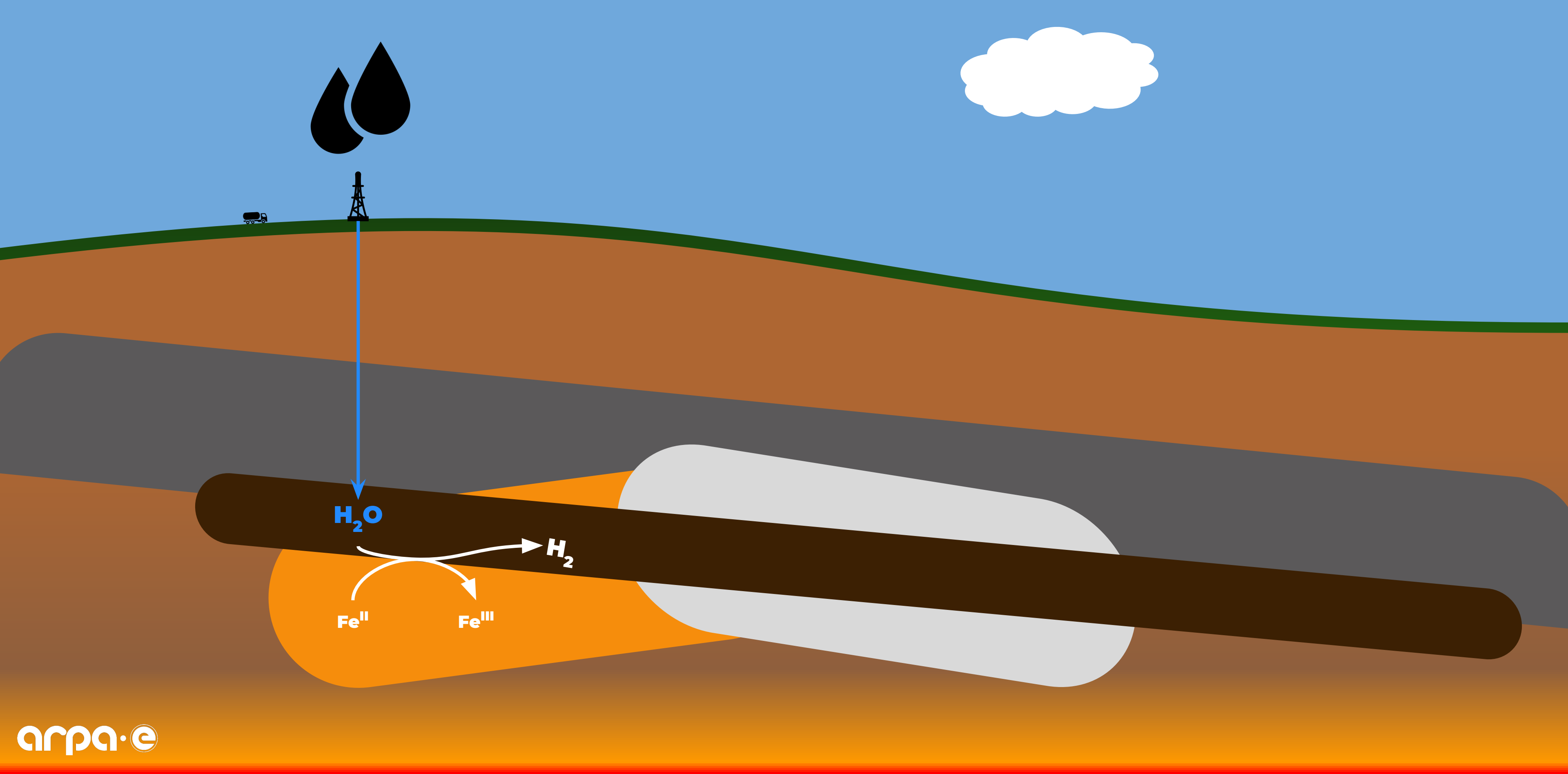


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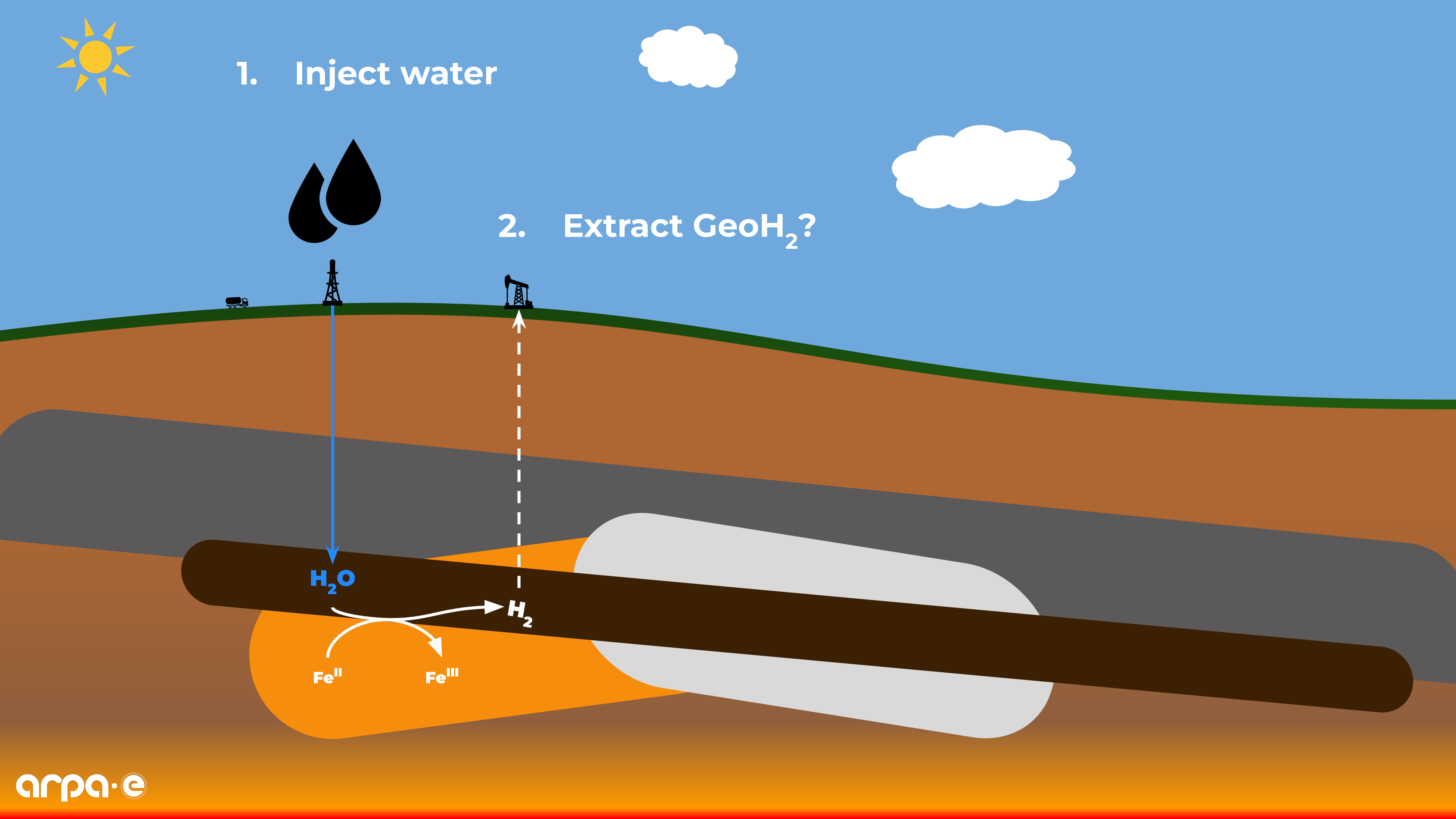
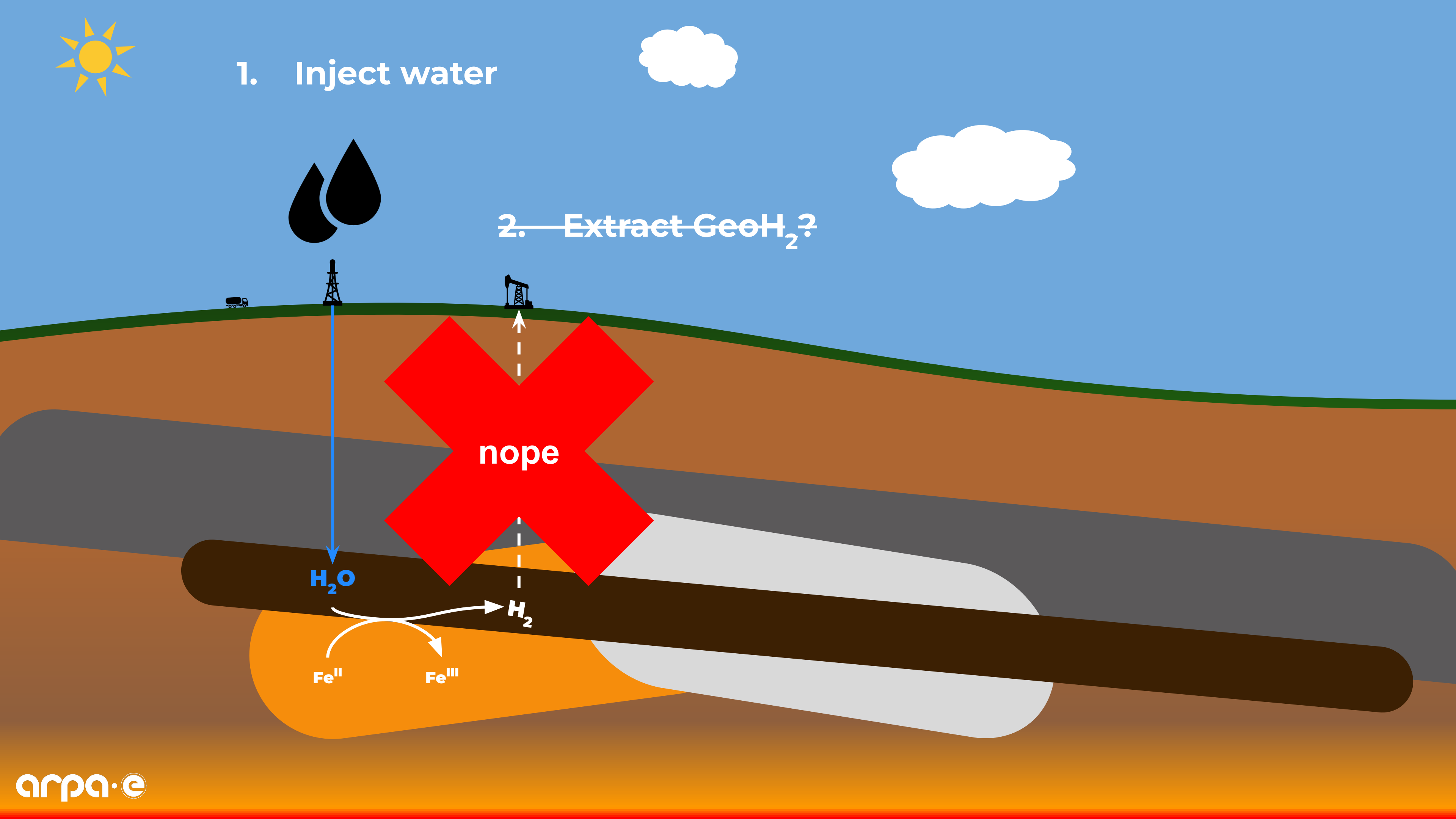

1. Inject water
2. Extract $GeoH_2$?
$H_2O$
$H_2$
$Fe^{II}$
$Fe^{III}$
arpa·e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nope
$H_2O$
$H_2$
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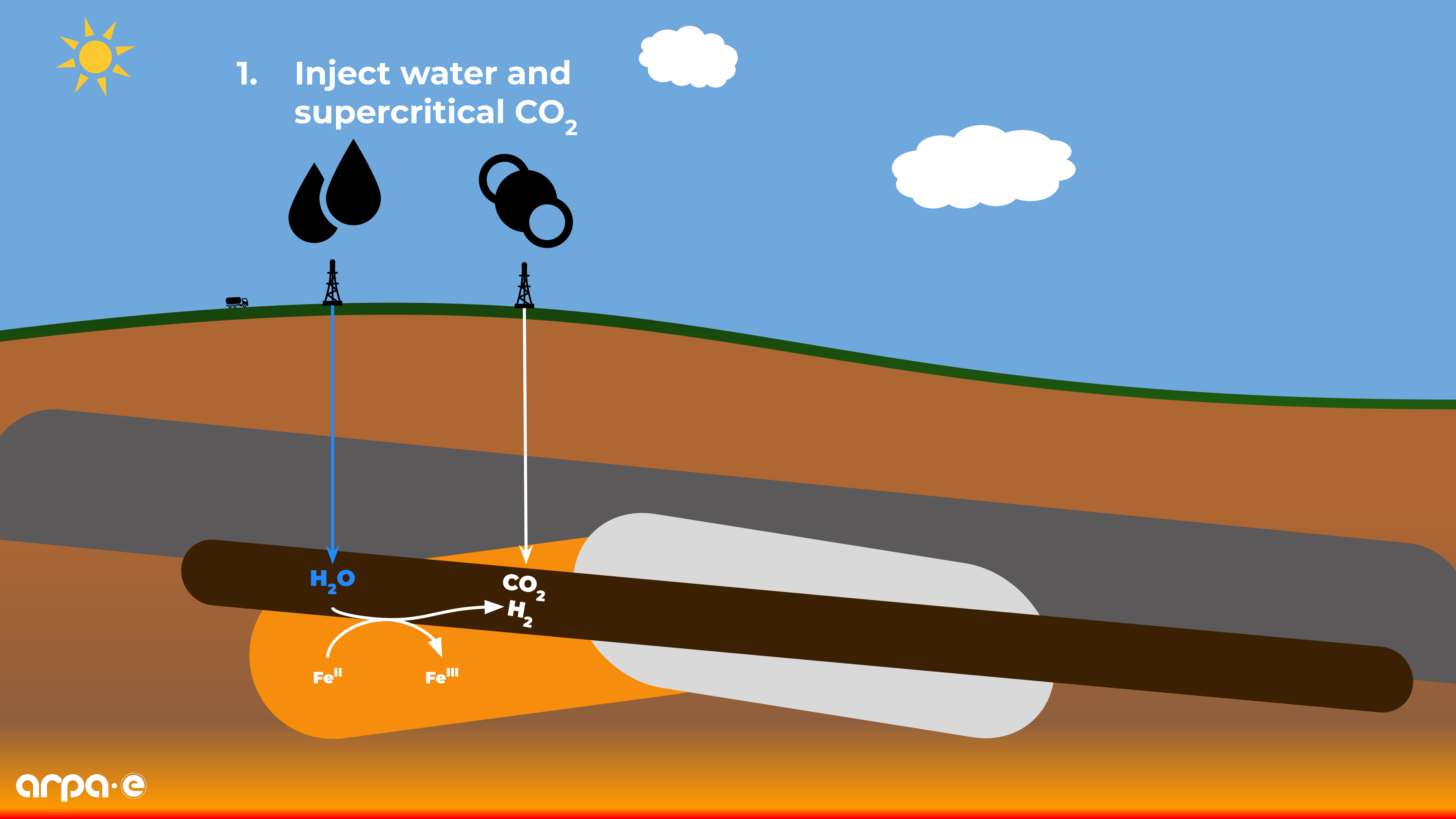
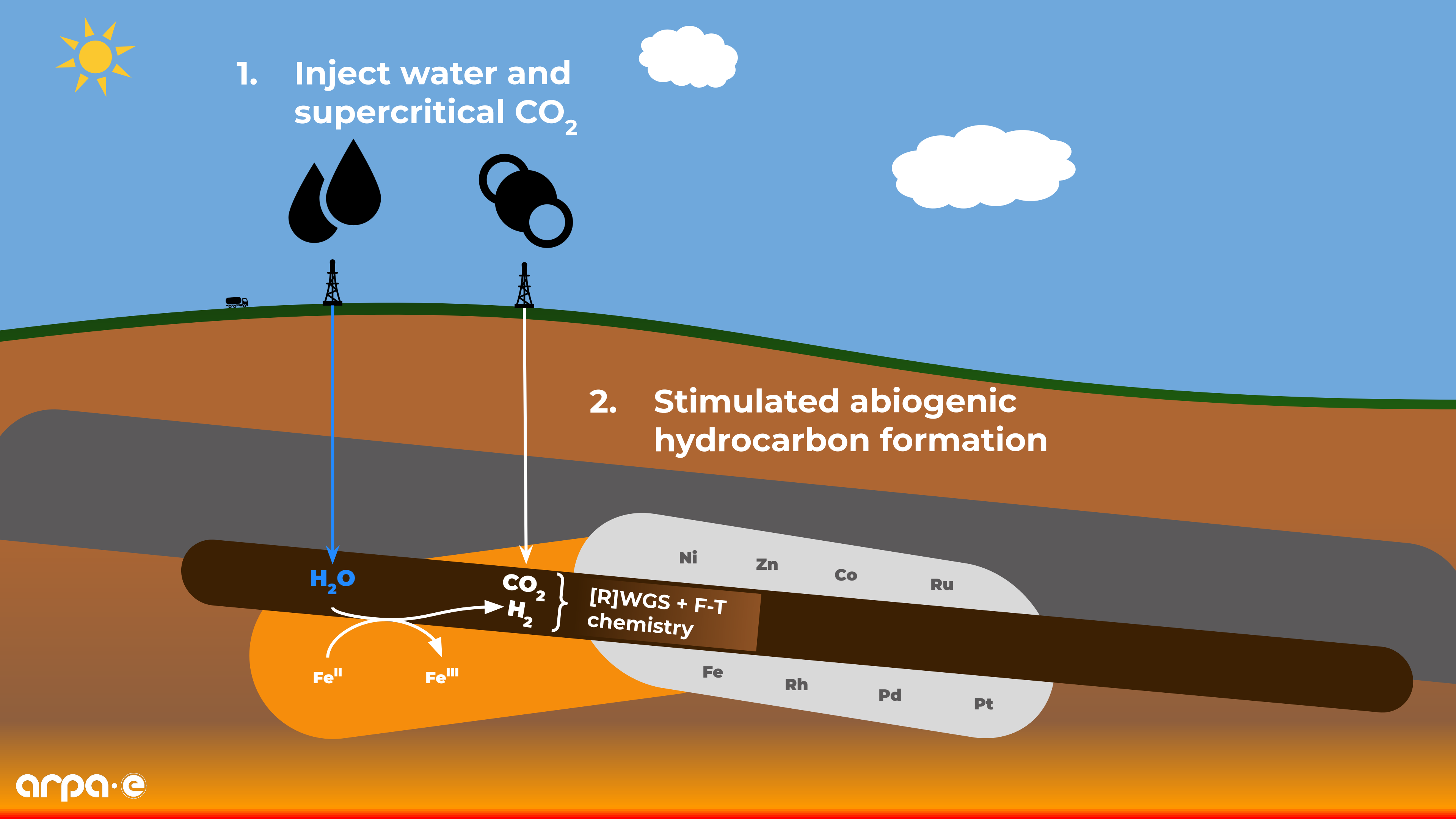
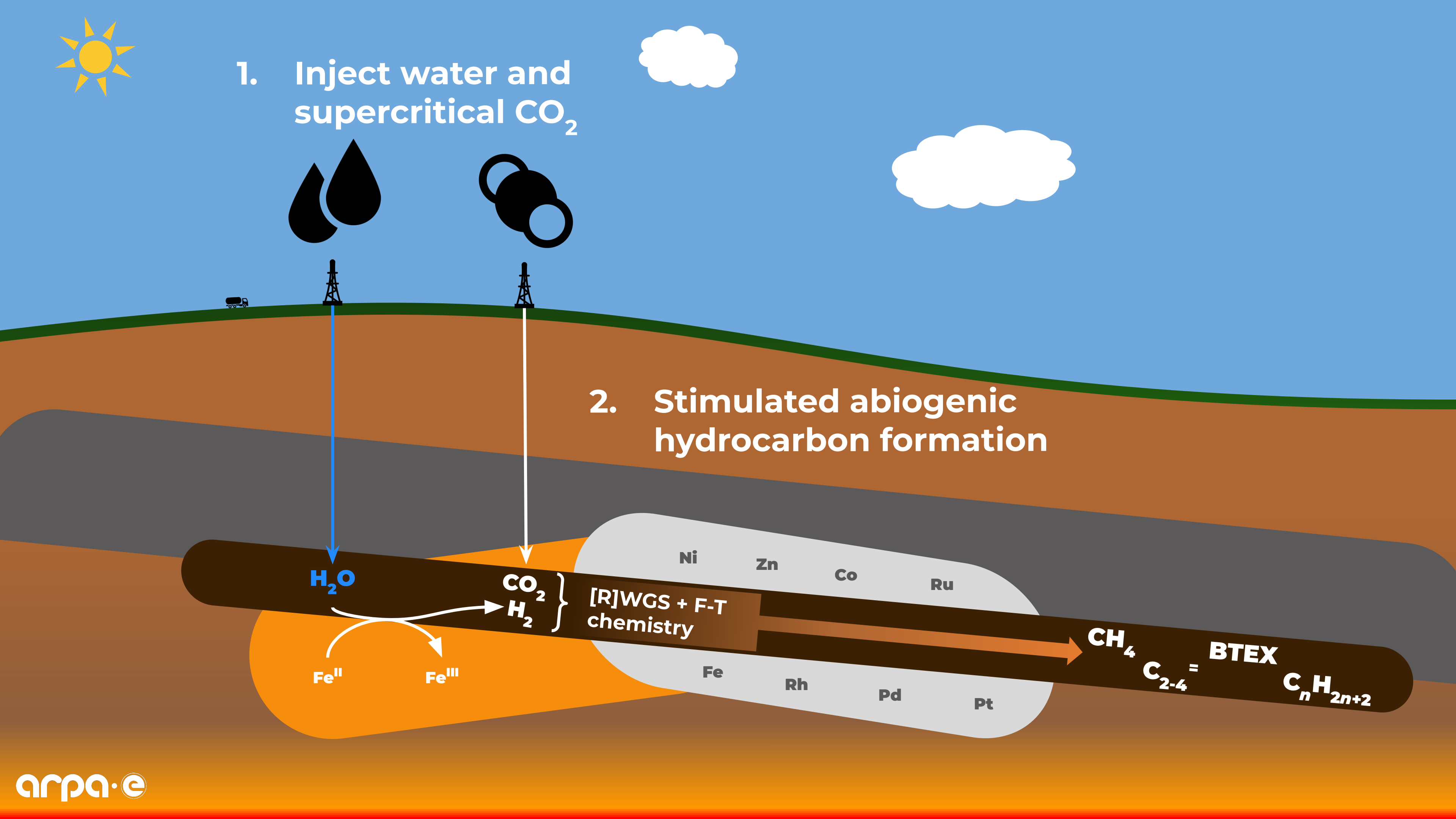


1. Inject water and supercritical $CO_2$
$H_2O$
$CO_2$
$H_2$
$Fe^{II}$
$Fe^{III}$
arpa·e



1. Inject water and supercritical $CO_2$
2. Stimulated abiogenic hydrocarbon formation
$H_2O$
$CO_2$
$H_2$
[R]WGS + F-T chemistry
$Fe^{II}$
$Fe^{III}$
Ni
Zn
Co
Ru
Fe
Rh
Pd
Pt
arpa·e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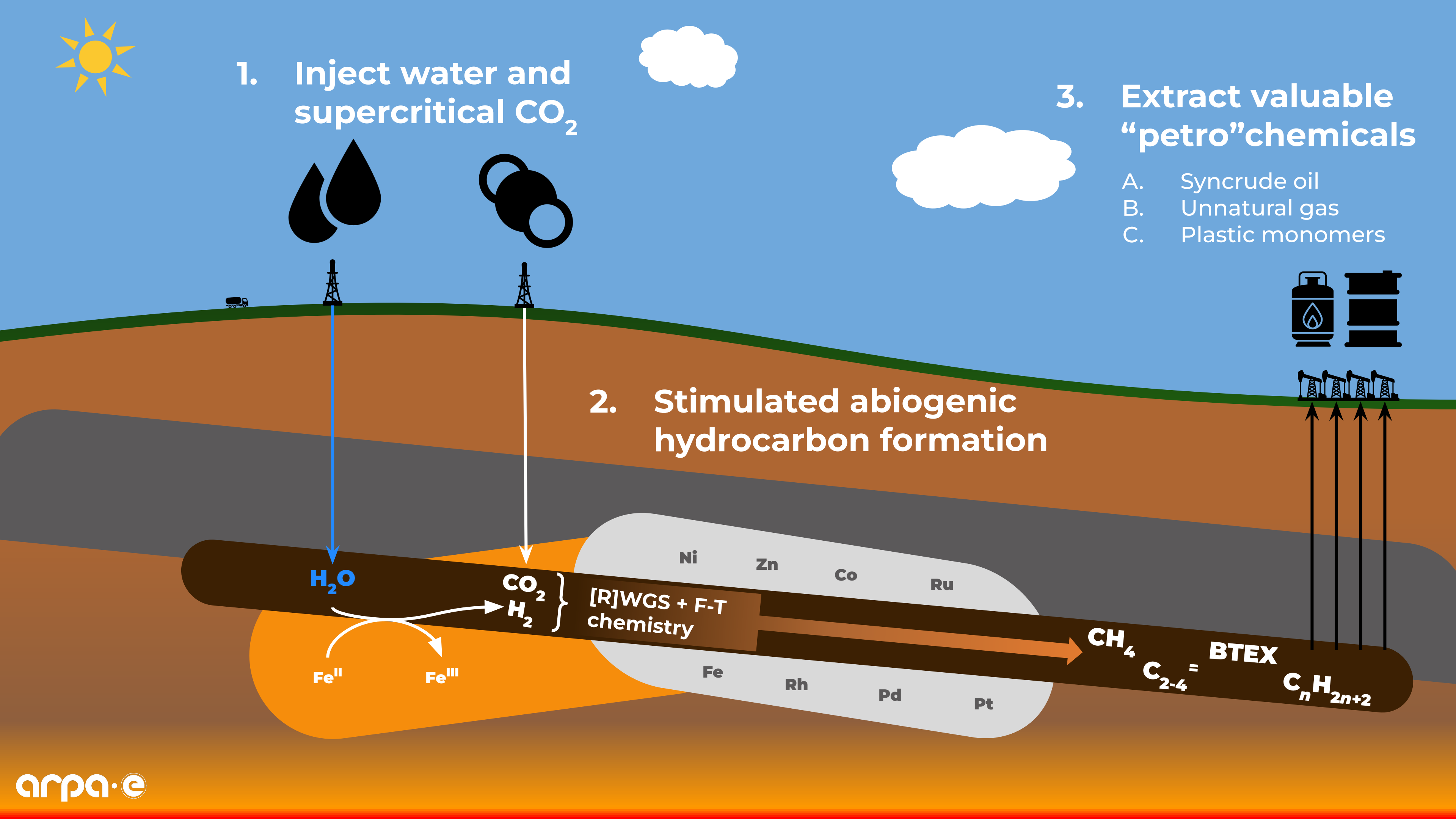

1. Inject water and supercritical $CO_2$
2. Stimulated abiogenic hydrocarbon formation
3. Extract valuable "petro"chemicals
A. Syncrude oil
B. Unnatural gas
C. Plastic monomers
$H_2O$
$CO_2$
$H_2$
[R]WGS + F-T chemistry
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$Fe^{III}$
Ni
Zn
Co
Ru
Fe
Rh
Pd
Pt
$CH_4$
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BTEX
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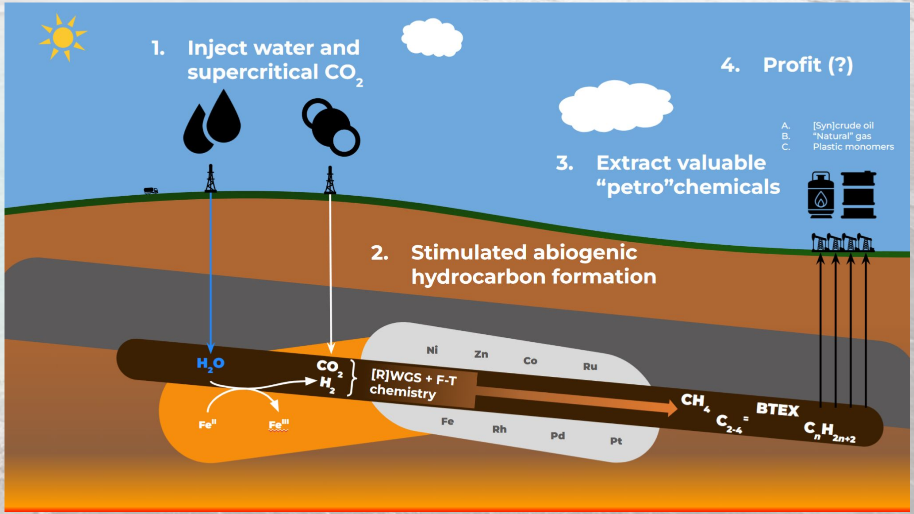
arpa·e

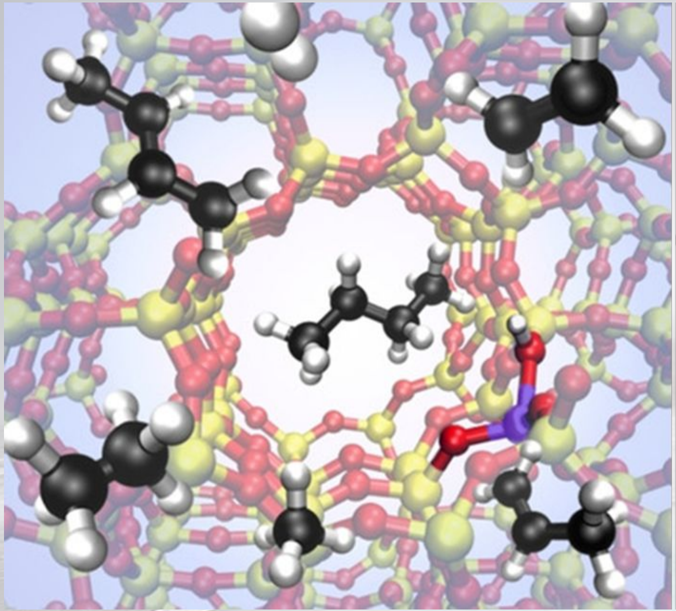
# abiogenic hydrocarbons, three ways

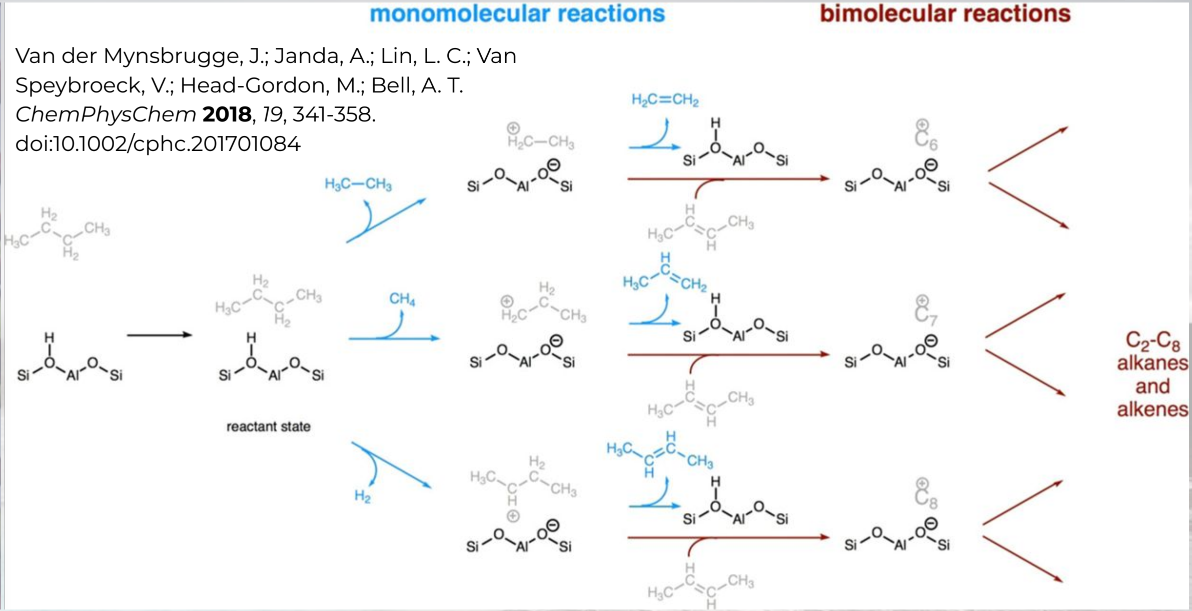
1. Natural F-T georeactors
    a. medium T+P, moderate depth
    b. strong siting limitation



# Fischer-Tropsch Georeactors

- Industrial [R]WGS + F-T rxn conditions:
  - T: 200-500 °C
  - P: 20-50 bar (2-5 MPa)
  - Catalysts: Fe, Cu, Zn, Co, Ni, Ru, Rh, Pt, Pd
- Can we identify natural F-T georeactors?
  - Can we coinject catalyst mixtures to make our own?






Van der Mynsbrugge, J.; Janda, A.; Lin, L. C.; Van Speybroeck, V.; Head-Gordon, M.; Bell, A. T. *ChemPhysChem* **2018**, *19*, 341-358. doi:10.1002/cphc.201701084

# Target mineral bodies:

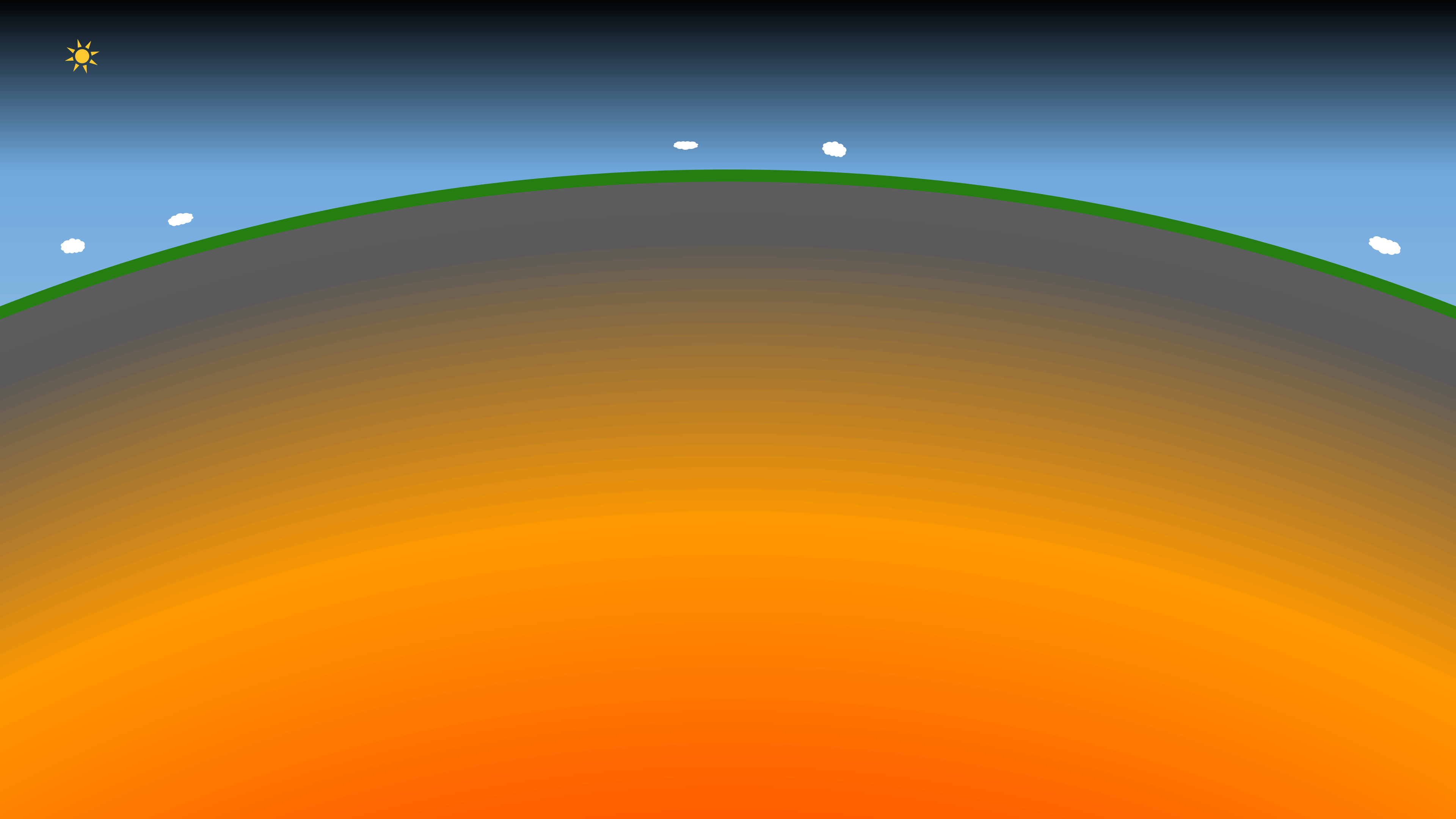
- Serpentinizable
- PGM-rich
- Ophiolitic

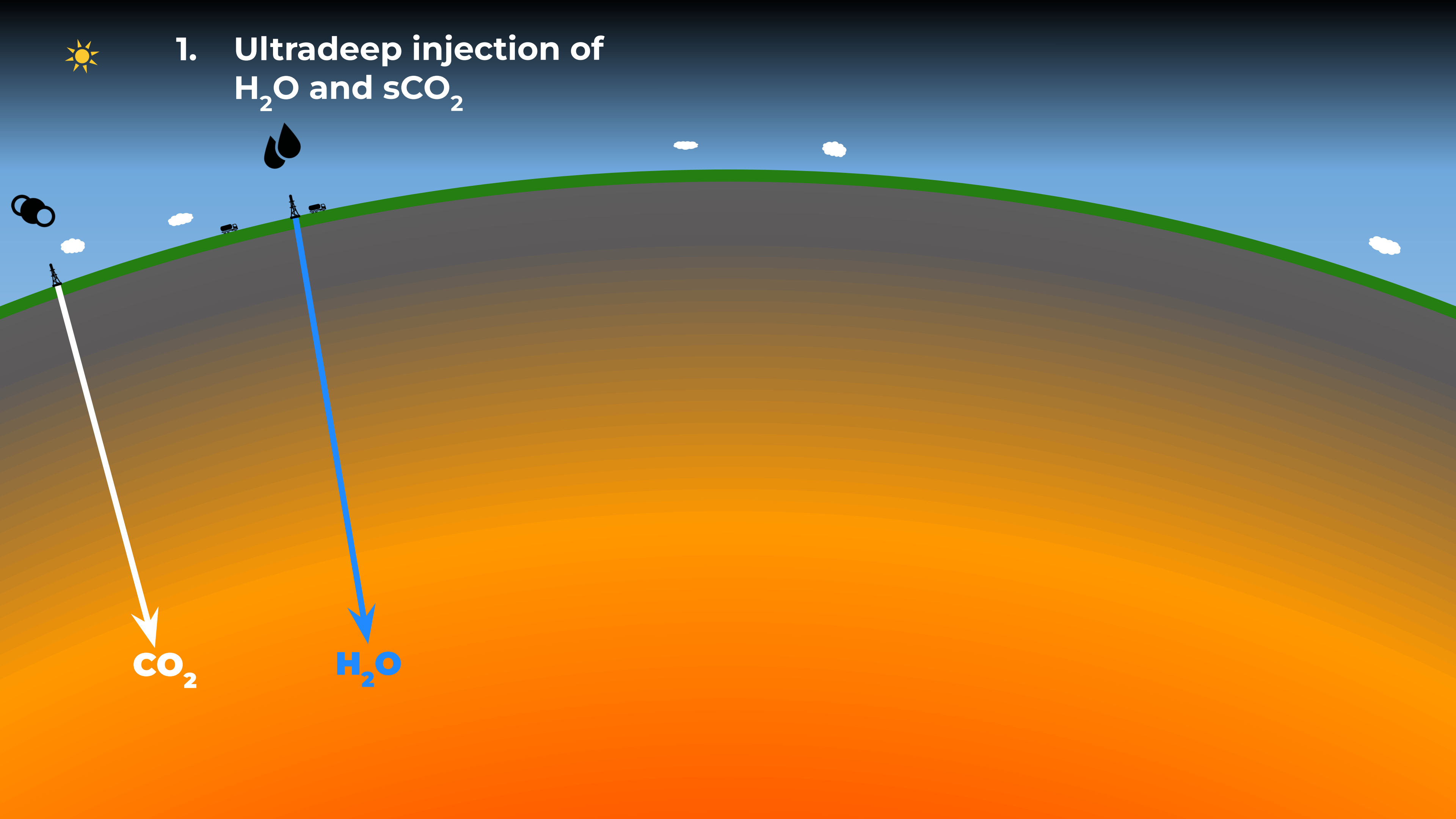
} *Ultramafic igneous formations:*

- Basalts
- Olivine
- Peridotite
- Kimberlite

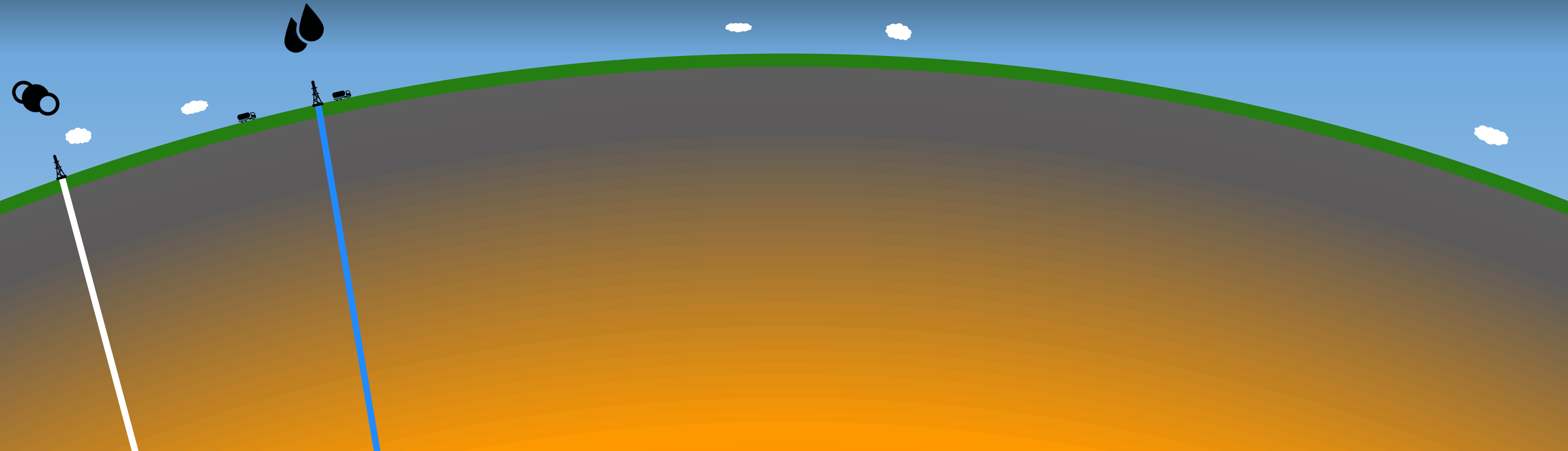
Low-molecular-weight hydrocarbons in natural hydrothermal fluids have been attributed to **abiogenic production by Fischer-Tropsch** type (FTT) reactions, although clear evidence for such a process has been elusive. Here, we present concentration, and stable and radiocarbon isotope, data from hydrocarbons dissolved in hydrogen-rich fluids venting at the **ultramafic-hosted** Lost City Hydrothermal Field. A distinct “inverse” trend in the stable carbon and hydrogen isotopic composition of **C1 to C4 hydrocarbons** is compatible with FTT genesis. Radiocarbon evidence rules out seawater bicarbonate as the carbon source for FTT reactions, suggesting that a mantle-derived inorganic carbon source is leached from the host rocks. Our findings illustrate that the **abiotic synthesis of hydrocarbons in nature may occur in the presence of ultramafic rocks, water, and moderate amounts of heat**.

Proskurowski, G.; Lilley, M. D.; Seewald, J. S.; Früh-Green, G. L.; Olson, E. J.; Lupton, J. E.; Sylva, S. P.; Kelley, D. S. *Science* **2008**, *319*, 604.




1.
Ultradeep injection of
$H_2O$ and $sCO_2$
$CO_2$
$H_2O$

## 1. Ultradeep injection of $H_2O$ and $sCO_2$



## 2. Noncatalytic upper-mantle abiogenic hydrocarbon formation

$$n\ CO_2 + (2n+1)\ H_2O + n\ CaO + (9n+3)\ FeO \rightarrow n\ Ca(OH)_2 + (3n+1)\ Fe_3O_4 + C_nH_{2n+2}$$

Proskurowski, G.; Lilley, M. D.; Seewald, J. S.; Früh-Green, G. L.; Olson, E. J.; Lupton, J. E.; Sylva, S. P.; Kelley, D. S. *Science* **2008**, *319*, 604.
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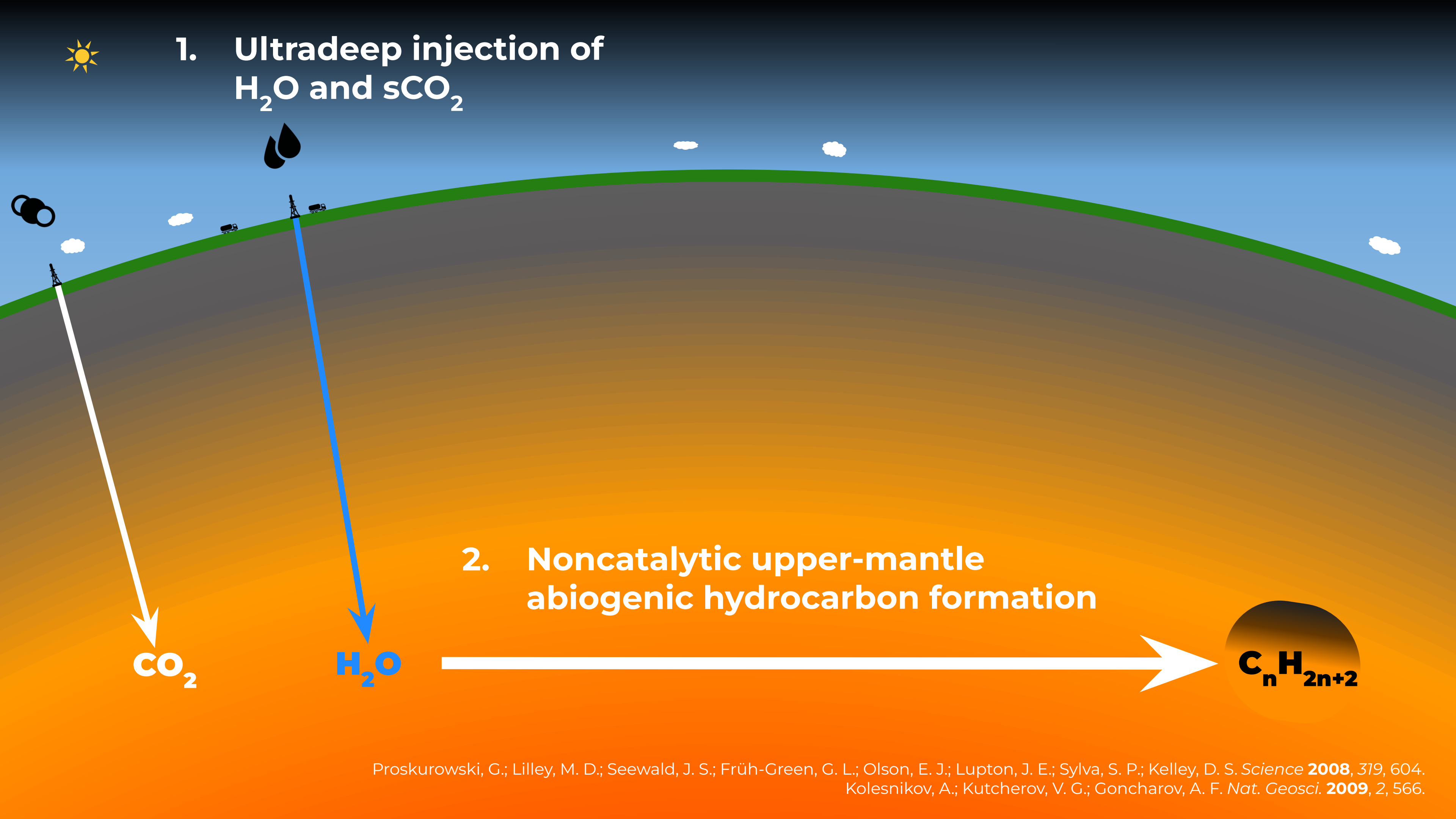
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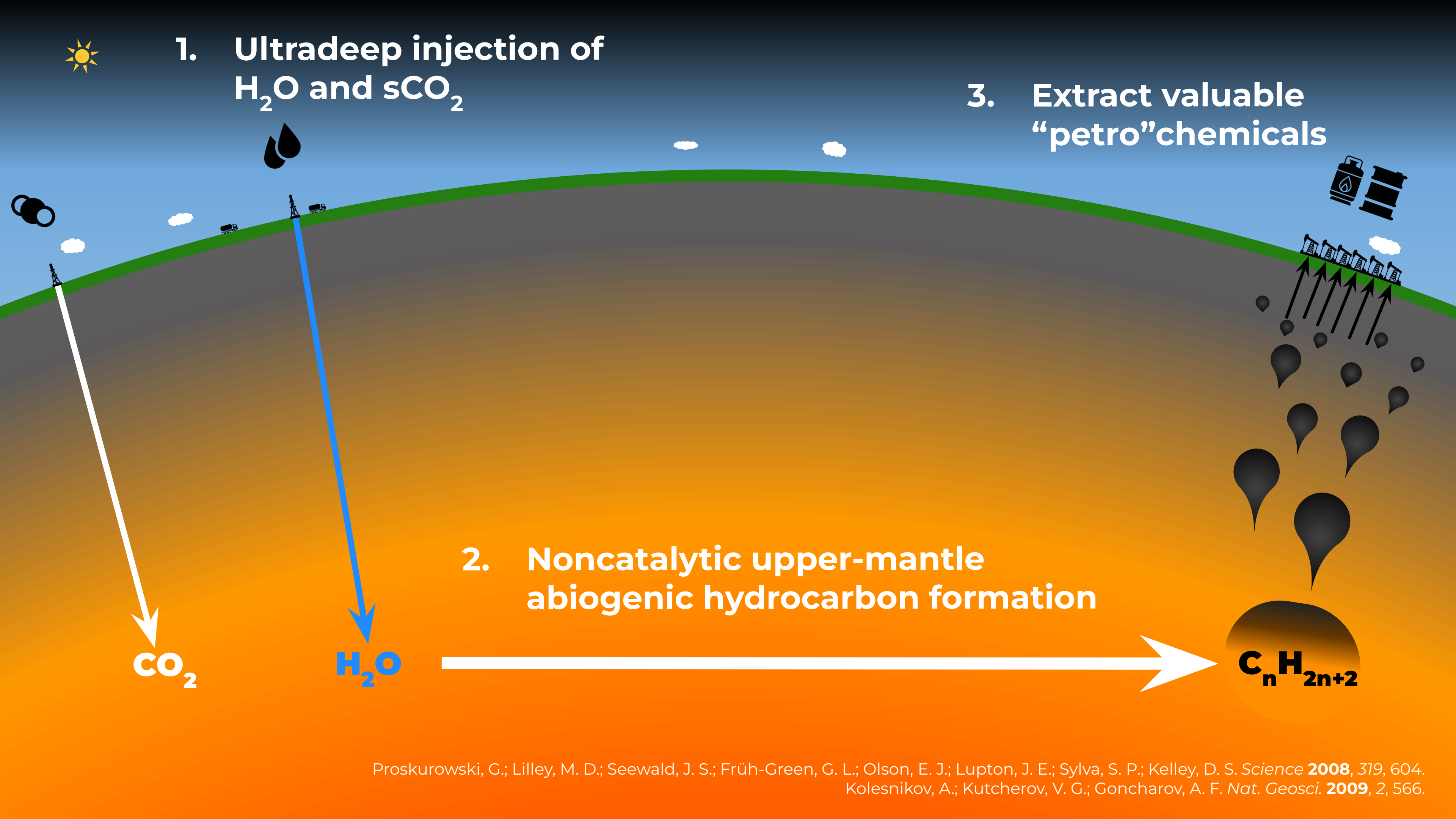
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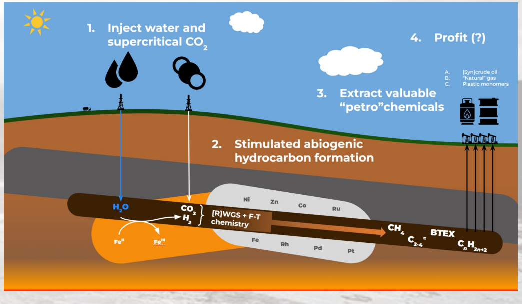
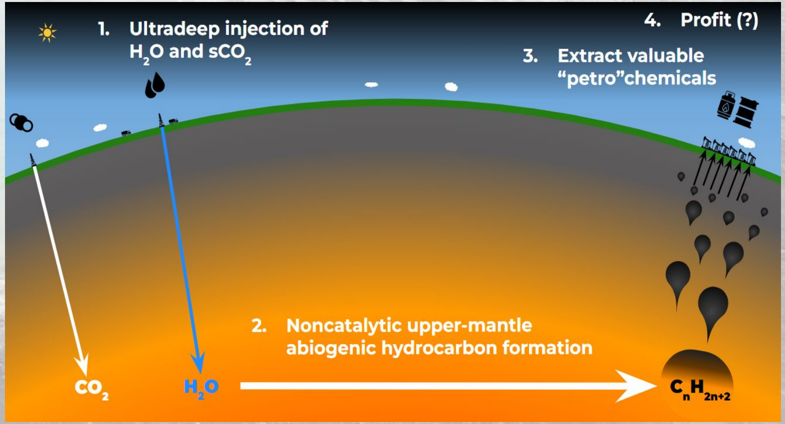
# abiogenic hydrocarbons, three ways

1. Natural F-T georeactors
   a. medium T+P, moderate depth
   b. strong siting limitation
2. Upper-mantle non-catalytic
   a. extreme T+P, extreme depth
   b. massive potential



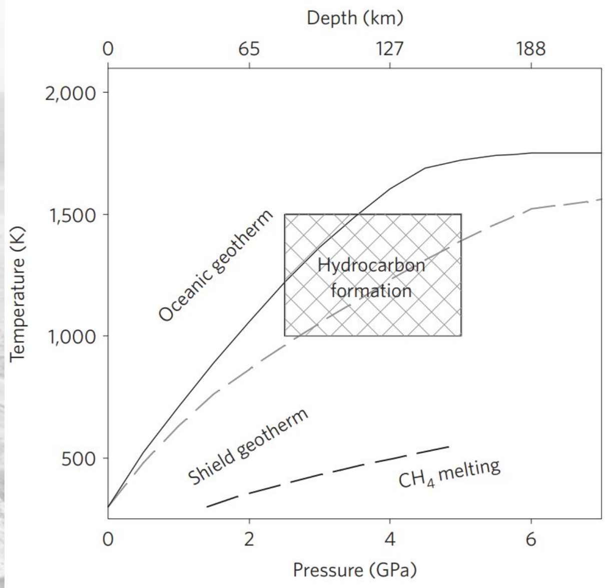



# Can we drill deep enough?

- Noncatalytic abiogenesis:
  - T > 1000 K
  - P > 2 GPa

# Can we drill deep enough? (probably not)

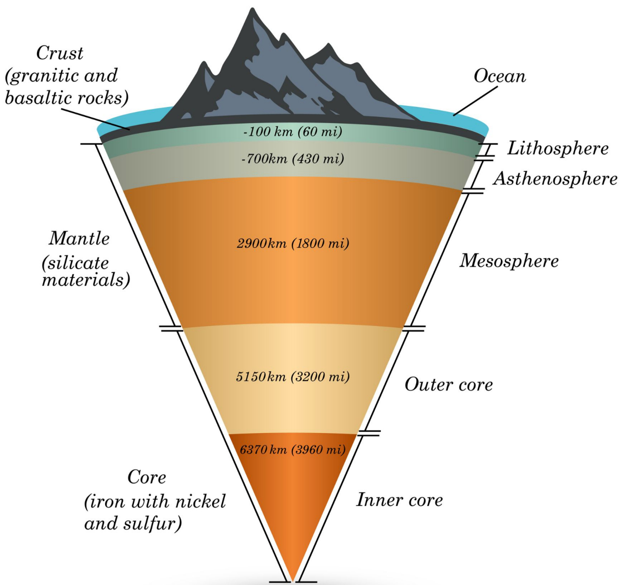
- Noncatalytic abiogenesis:
  - T > 1000 K
  - P > 2 GPa
- Approx. drill depth: 70-150 km

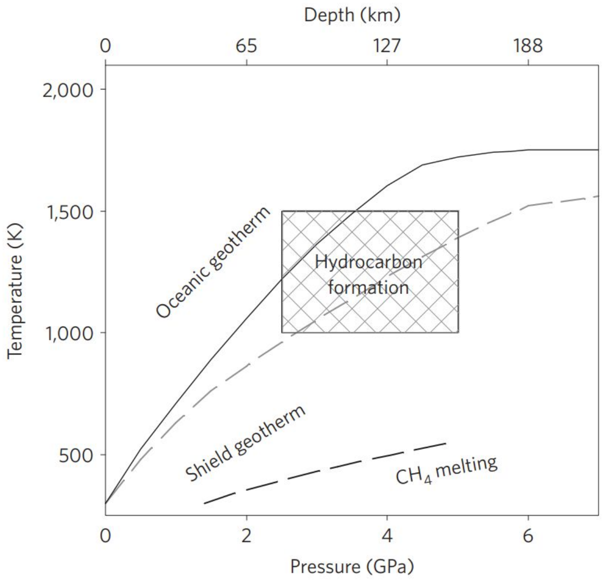



Kolesnikov, A.; Kutcherov, V. G.; Goncharov, A. F. *Nat. Geosci.* **2009**, *2*, 566.

# Can we drill deep enough? (probably not)

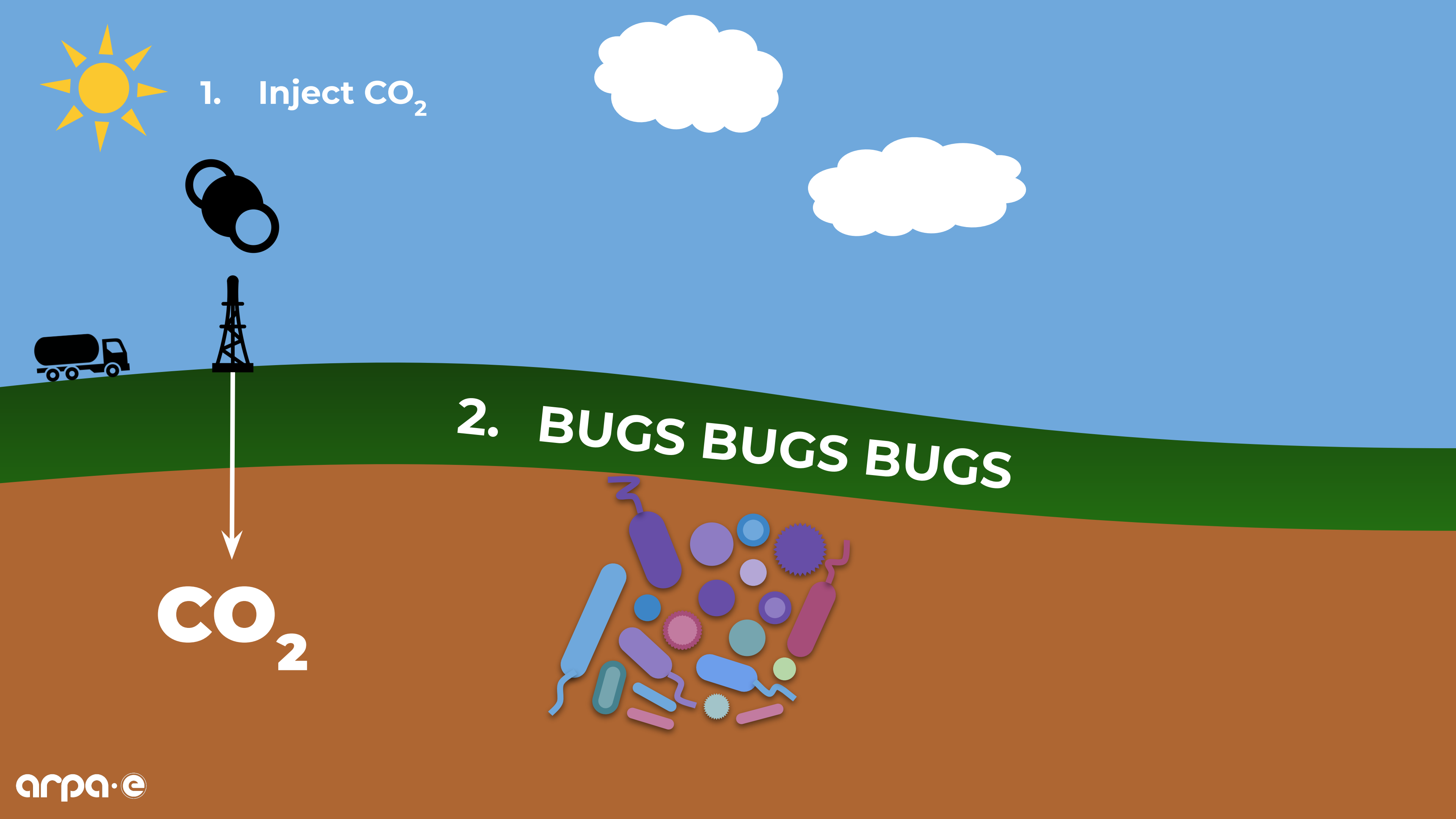
- Noncatalytic abiogenesis:
  - T > 1000 K
  - P > 2 GPa
- Approx. drill depth: 70-150 km (upper mantle)



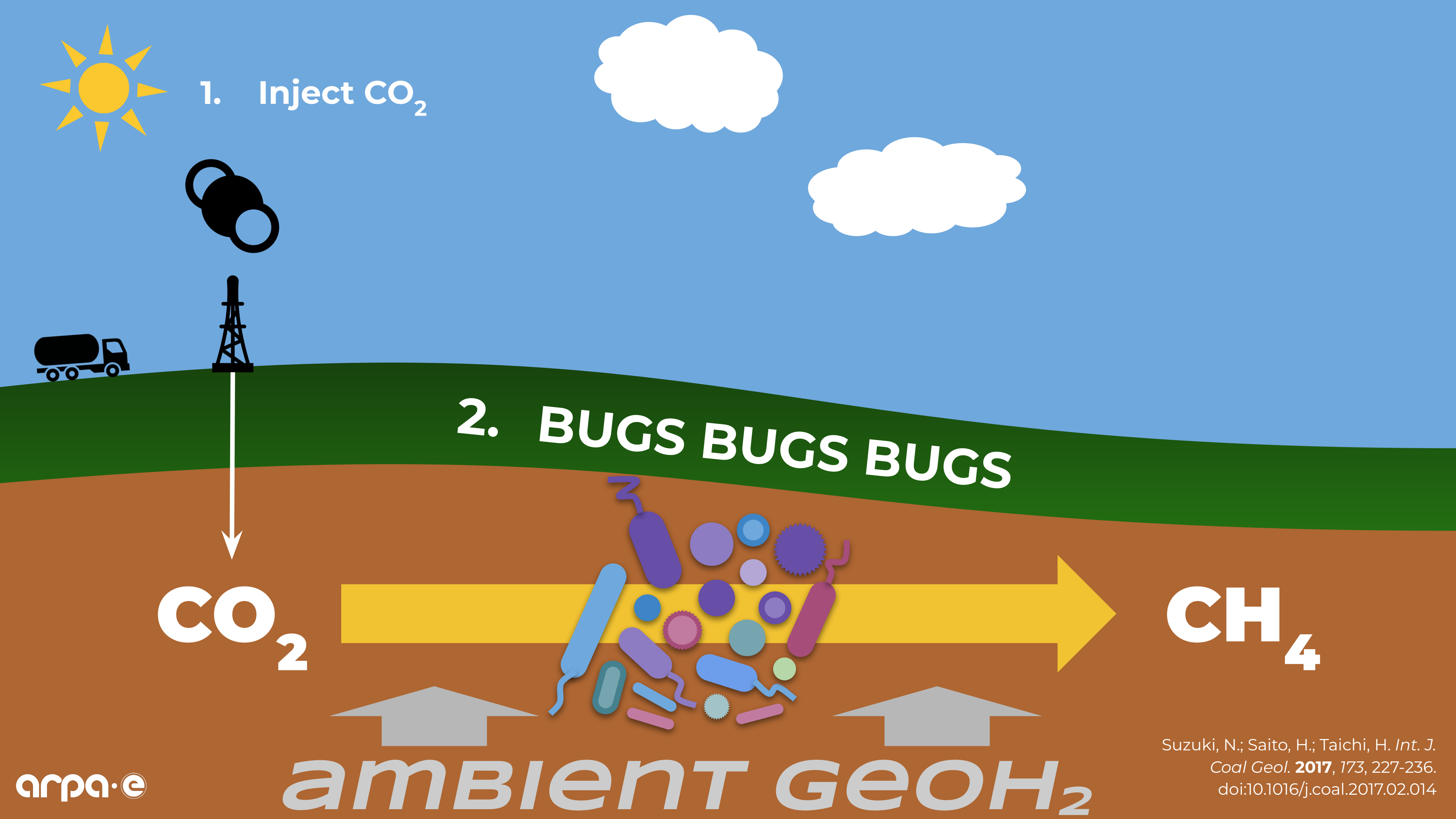




Kolesnikov, A.; Kutcherov, V. G.; Goncharov, A. F. *Nat. Geosci.* **2009**, *2*, 566.

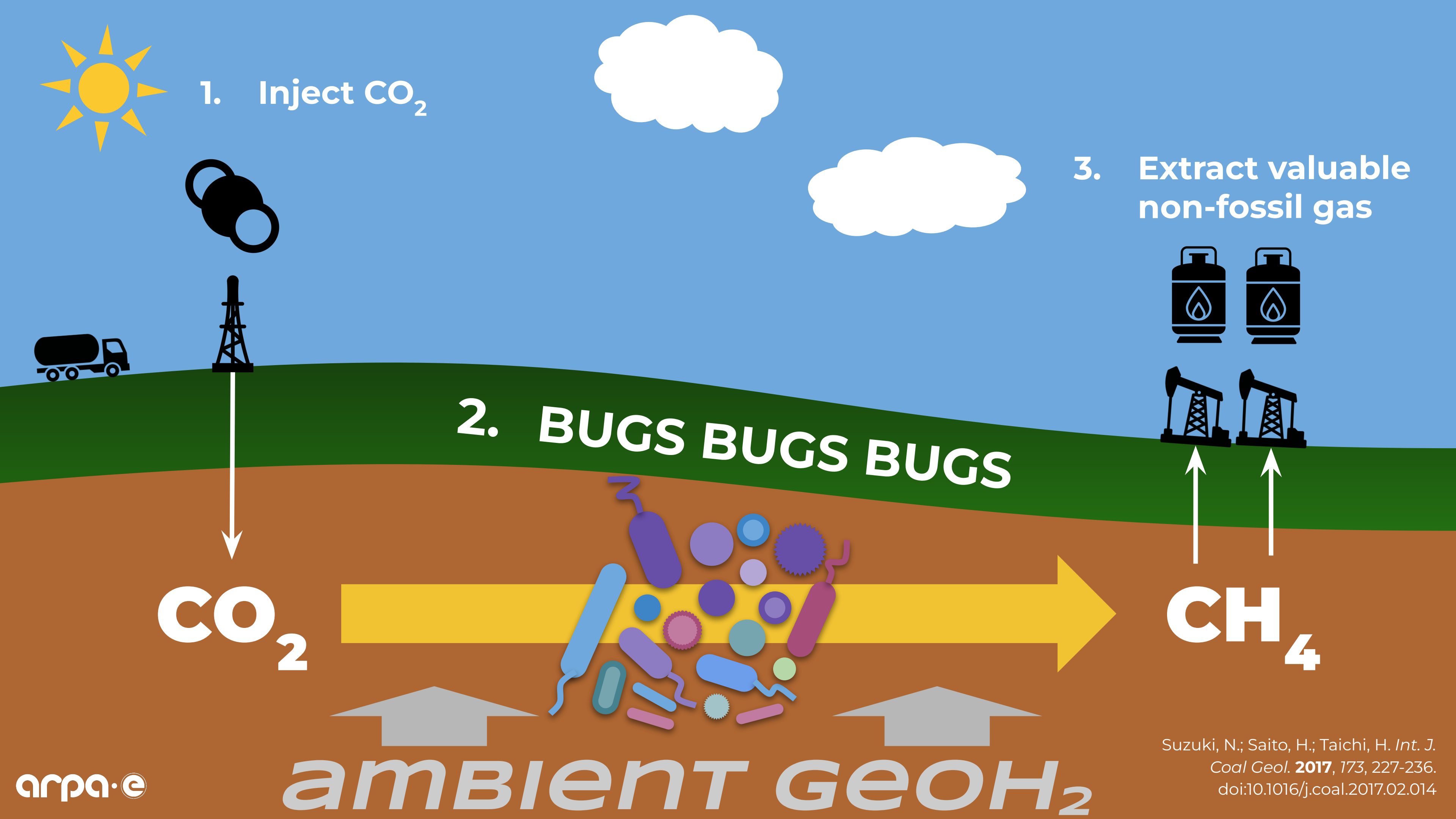

1. Inject $CO_2$
$CO_2$
arpa·e



1. Inject $CO_2$
2. BUGS BUGS BUGS
$CO_2$
arpa·e



1. Inject $CO_2$
2. BUGS BUGS BUGS
$CO_2$
$CH_4$
ambient GeoH2
arpa·e
Suzuki, N.; Saito, H.; Taichi, H. *Int. J. Coal Geol.* **2017**, *173*, 227-236. doi:10.1016/j.coal.2017.02.014



1. Inject $CO_2$
2. BUGS BUGS BUGS
3. Extract valuable non-fossil gas
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ambient GeoH2
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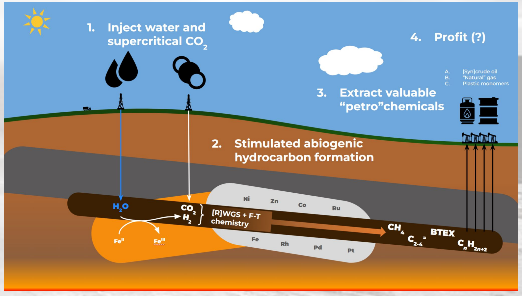
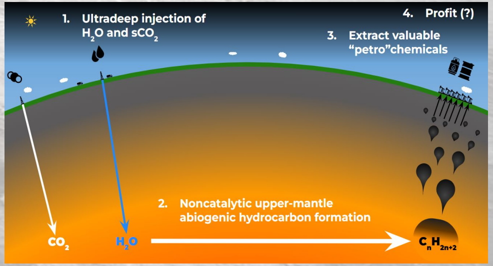
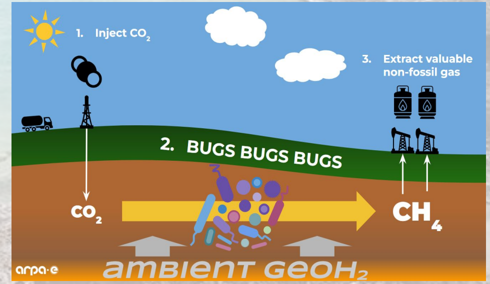
2. Upper-mantle non-catalytic
   a. extreme T+P, extreme depth
   b. massive potential
3. Biologically mediated
   a. low T+P, shallow depth
   b. rate limitation



# non-fossil ~~abiogenic~~ hydrocarbons, three ways

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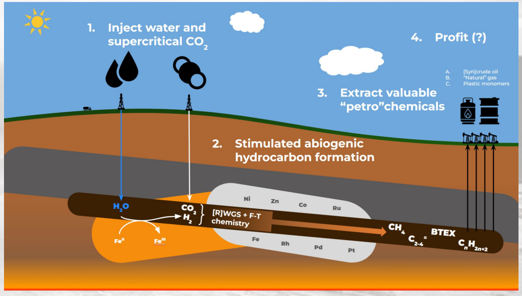
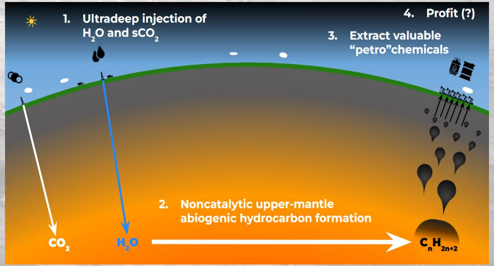
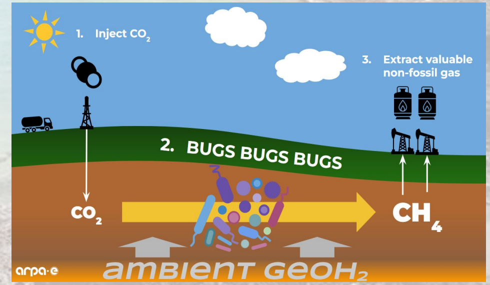


# Microbial methanogenesis at Olla

***Slide by Dr. Rebecca Tyne (WHOI)***

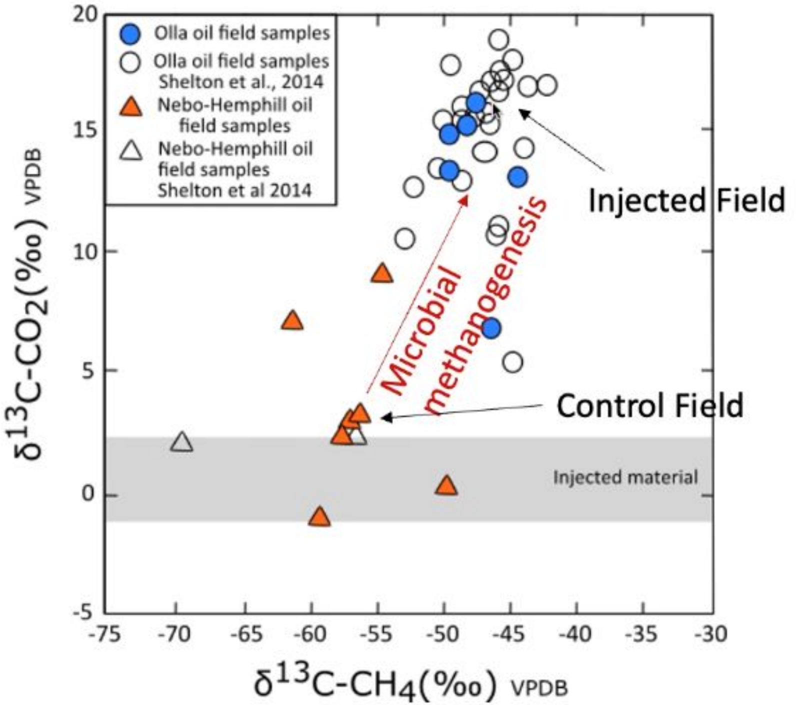
Microbial Methanogenesis is the biological consumption of $CO_2$ and conversion to $CH_4$.

Results in a progressive increase in $\delta^{13}C$ of both $CO_2$ and $CH_4$.

Microbial methanogenesis →

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

← Anaerobic oxidation of methane (AOM)




*Tyne et al., 2021, Nature*

# Effect of $CO_2$ injection phase

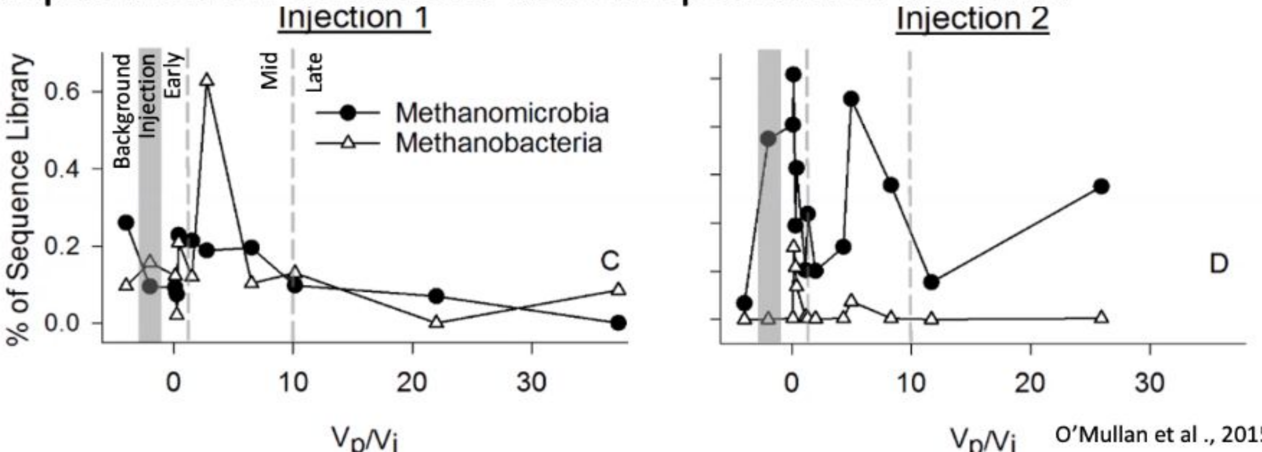
*Slide by Dr. Rebecca Tyne (WHOI)*

$CO_2$ injection will most likely be in the supercritical phase

Originally thought supercritical $CO_2$ would sterilize the environment

More recent experiments and pilot injection projects show increase in microbial community numbers after injection then either a return to background or sustained larger community

Microbial communities vary dependent on conditions and competition at the time

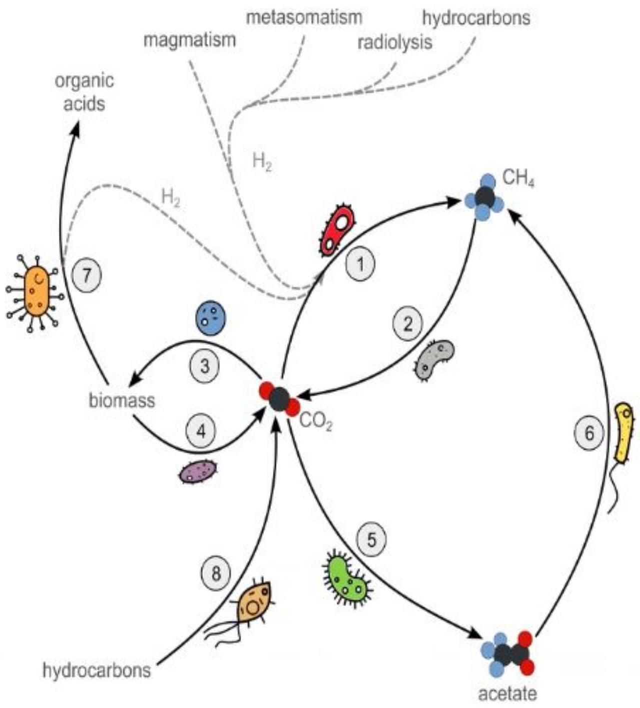



O'Mullan et al ., 2015

# Methanogenesis potential in CCS environments

***Slide by Dr. Rebecca Tyne (WHOI)***

| | Saline aquifers | Depleted hydrocarbon fields | Basalts | Coal beds |
|---|---|---|---|---|
| pH | ✓ | ✓ | ✓ | ✓ |
| Temperature | ✓ | ✓ | ✓ | ✓ |
| Nutrient availability | ✓ | ✓ | ✓ | ✓ |
| Methanogens detected? | ✓ | ✓ | ✓ | ✓ |
| $H_2$ present?* | low | high | mid | high |




* Relative amounts compared to other storage settings

Note: ✓ means could have the right conditions rather than always does!

Tyne et al., in review ES&T

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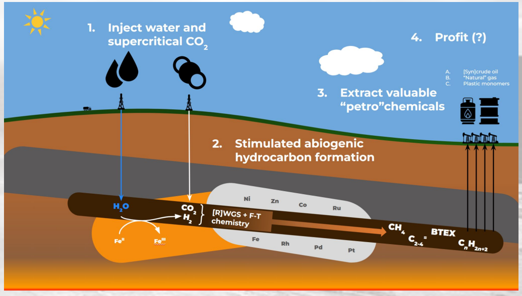
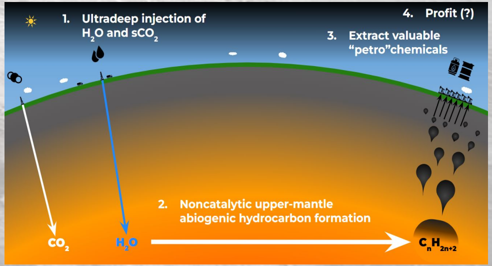
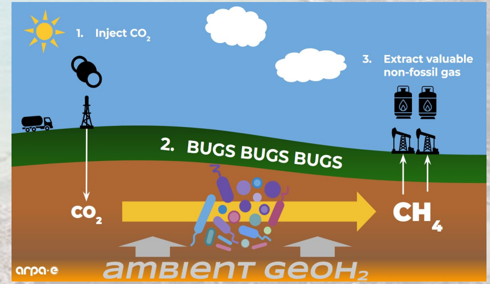
   a. low T+P, shallow depth
   b. rate limitation



# Technical Whitespaces

| whitespace | Natural F-T Georeactors | Upper Mantle Non-Catalytic | Microbial Biogeochemistry |
|---|---|---|---|
| detection & sensing | ✗ | ✗ | ✗ |
| product recovery | ✗ | ✗ | ✗ |
| product selectivity | ✗ | ✗ | |
| georeactor prospecting | ✗ | | ✗ |
| increasing reaction rate | ✗ | | ✗ |
| catalyst coinjection | ✗ | | |
| drilling deeper | | ✗ | |
| artificial biogeoreactors | | | ✗ |
| microbe gene editing | | | ✗ |

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