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Supplement of

A long-running in situ experiment in clay: 12 years of the Bitumen–Nitrate–Clay interaction experiment at Mont Terri rock laboratory

Katrien Hendrix et al.

Correspondence to: Katrien Hendrix (katrien.hendrix@sckcen.be)

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for the Safety of
Nuclear Waste Management

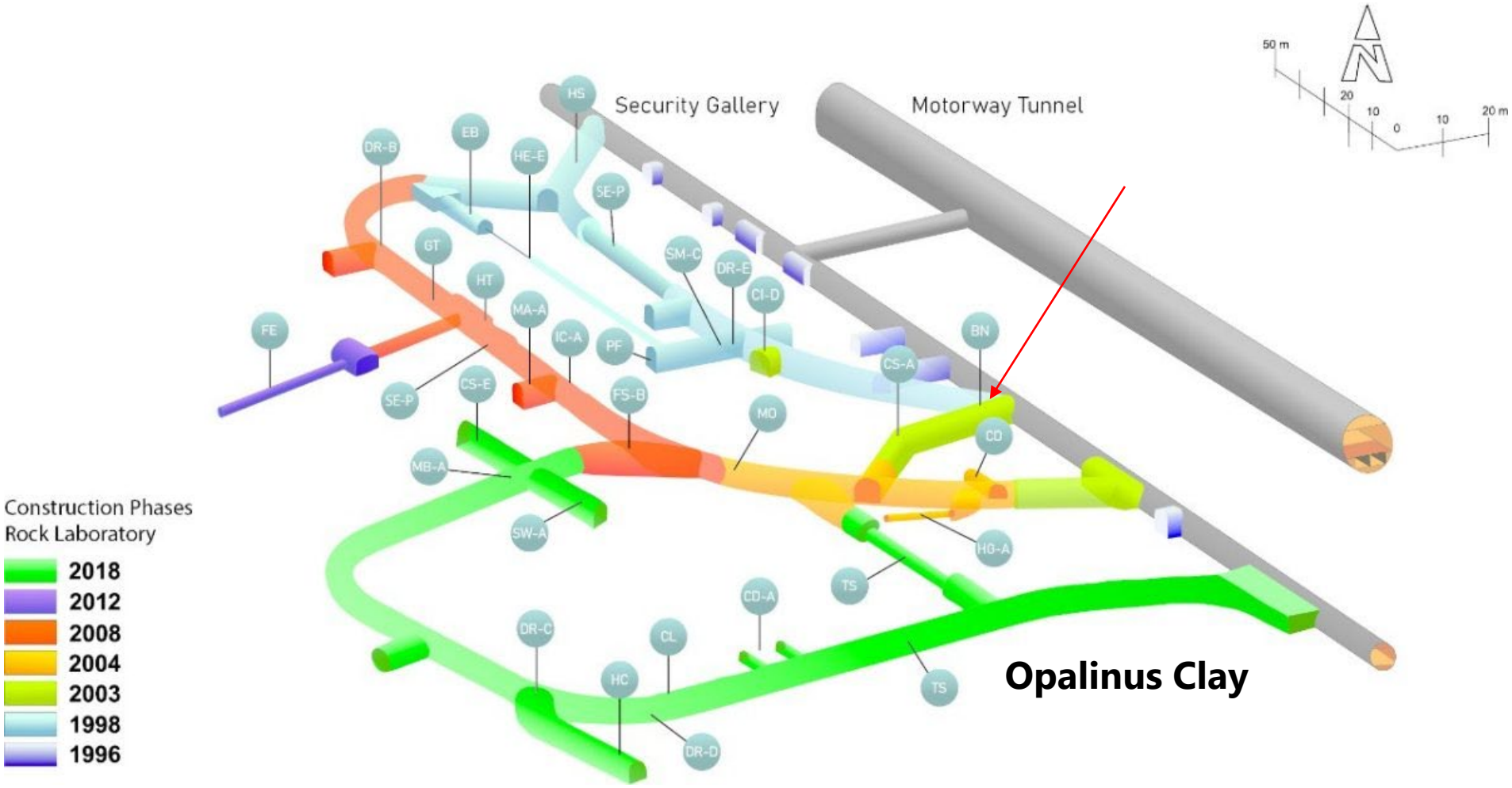
A long running in-situ experiment in clay: 12 years of the Bitumen-Nitrate-Clay interaction experiment at Mont Terri rock laboratory in Switzerland

Katrien Hendrix, Nele Bleyen, Kristel Mijnendonckx, Veerle Van Gompel, Achim Albrecht, Yannick Linard, Pierre De Cannière, Maryna Surkova, Charles Wittebroodt, Joe Small, Torben Weyand, Michael Jendras and Elie Valcke

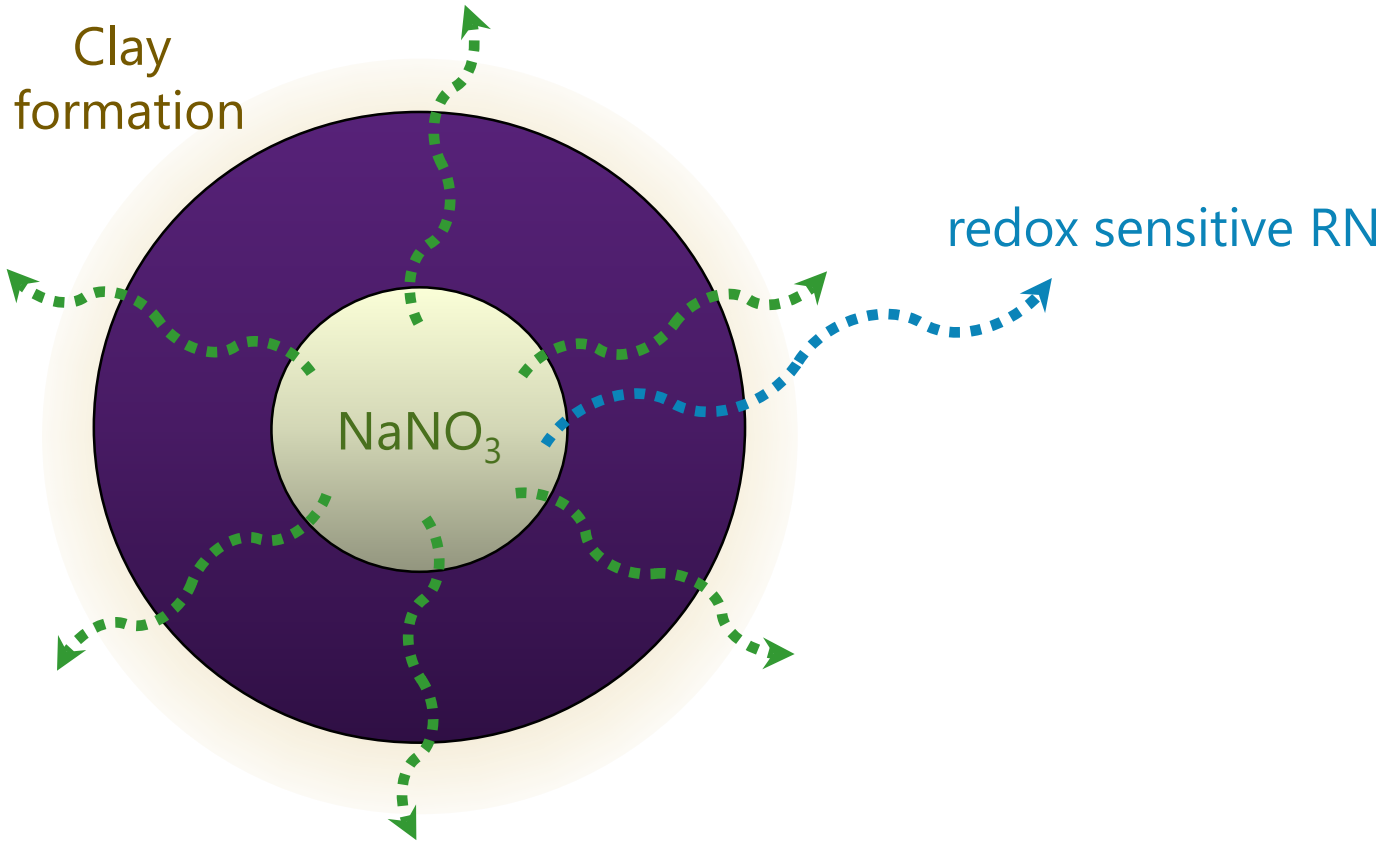
SafeND 2023

Berlin – 14/09/2023

BN: Bitumen-Nitrate-Clay interaction experiment one of the 28 most important and longest-running experiments at Mont Terri rock laboratory

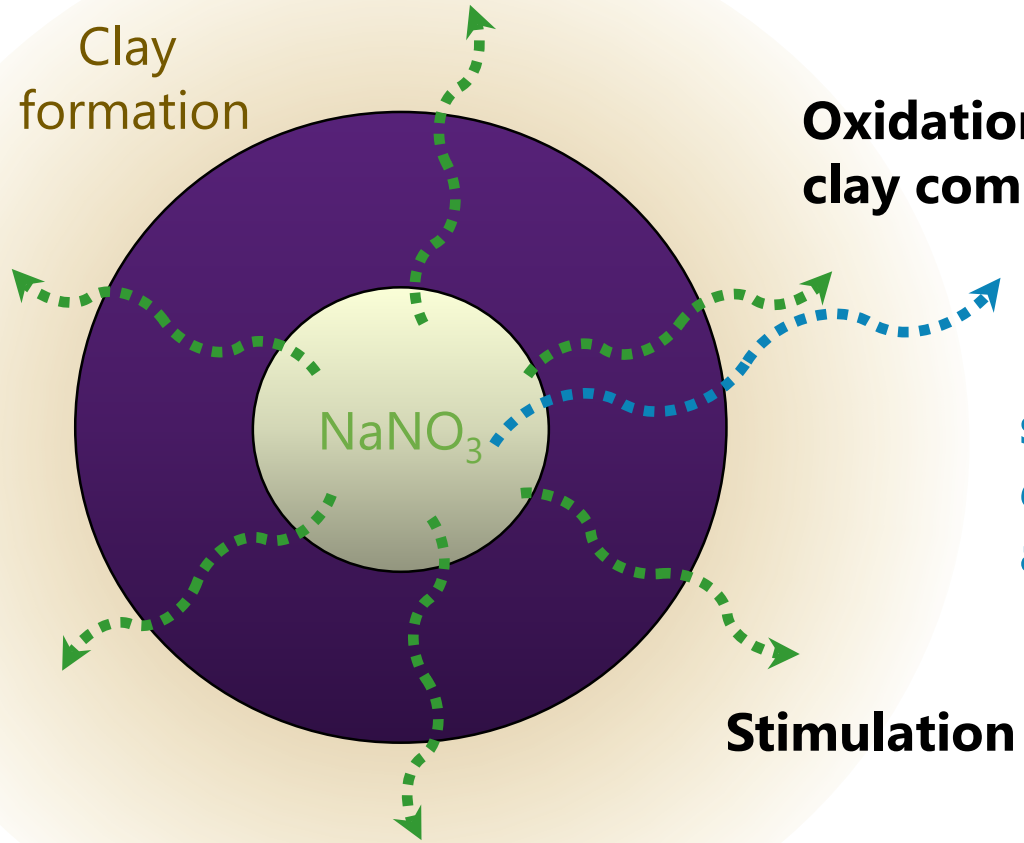


Nitrate plume from bituminized waste => possible perturbations in the near field



Nitrate perturbations studied in BN

Production of reduced N species



Oxidation of clay components

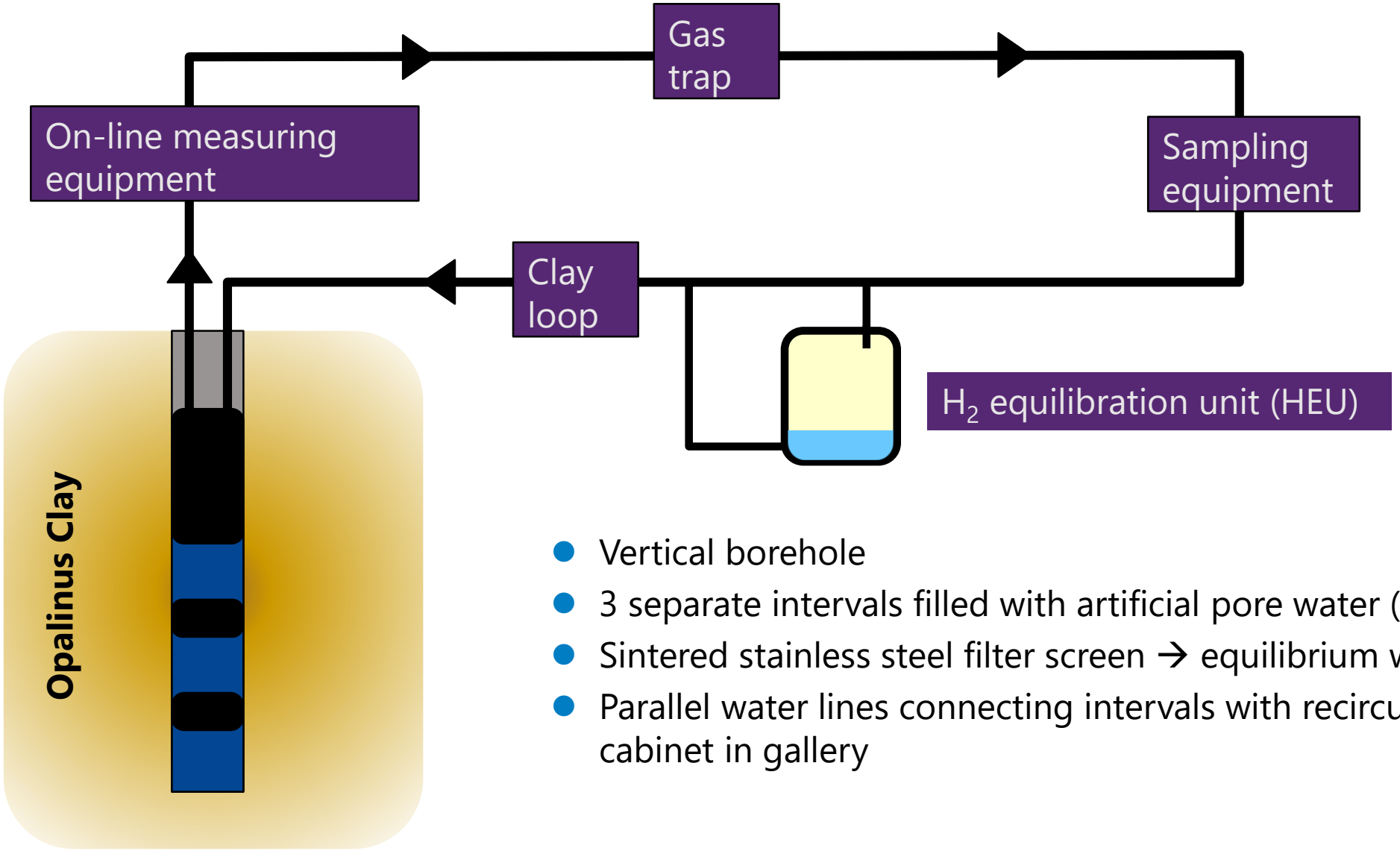
+ the effect of electron donors
- Acetate (bitumen degradation)
- H_2 (radiolysis, corrosion)

Redox sensitive RN
Effect of NO_3^- on speciation
***e.g.* ^{79}Se: in waste as SeO_4^{2+}**

Stimulation of microbial activity

Modelling of diffusion, (microbial) reactivity

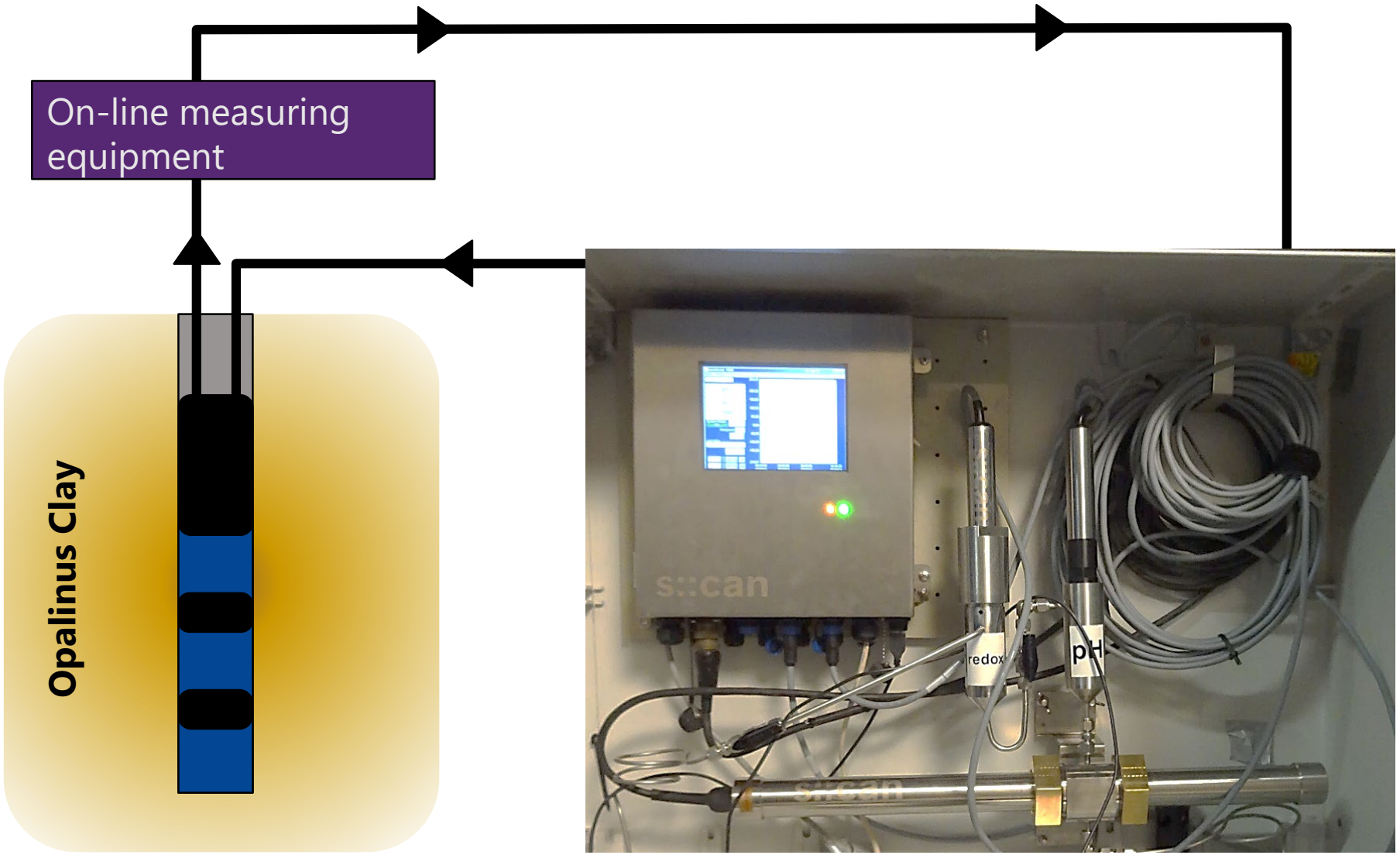
Experimental setup of BN experiment



- Vertical borehole
- 3 separate intervals filled with artificial pore water (APW)
- Sintered stainless steel filter screen → equilibrium with clay
- Parallel water lines connecting intervals with recirculation cabinet in gallery

Bleyen *et al.* (2017)

Experimental setup of BN experiment



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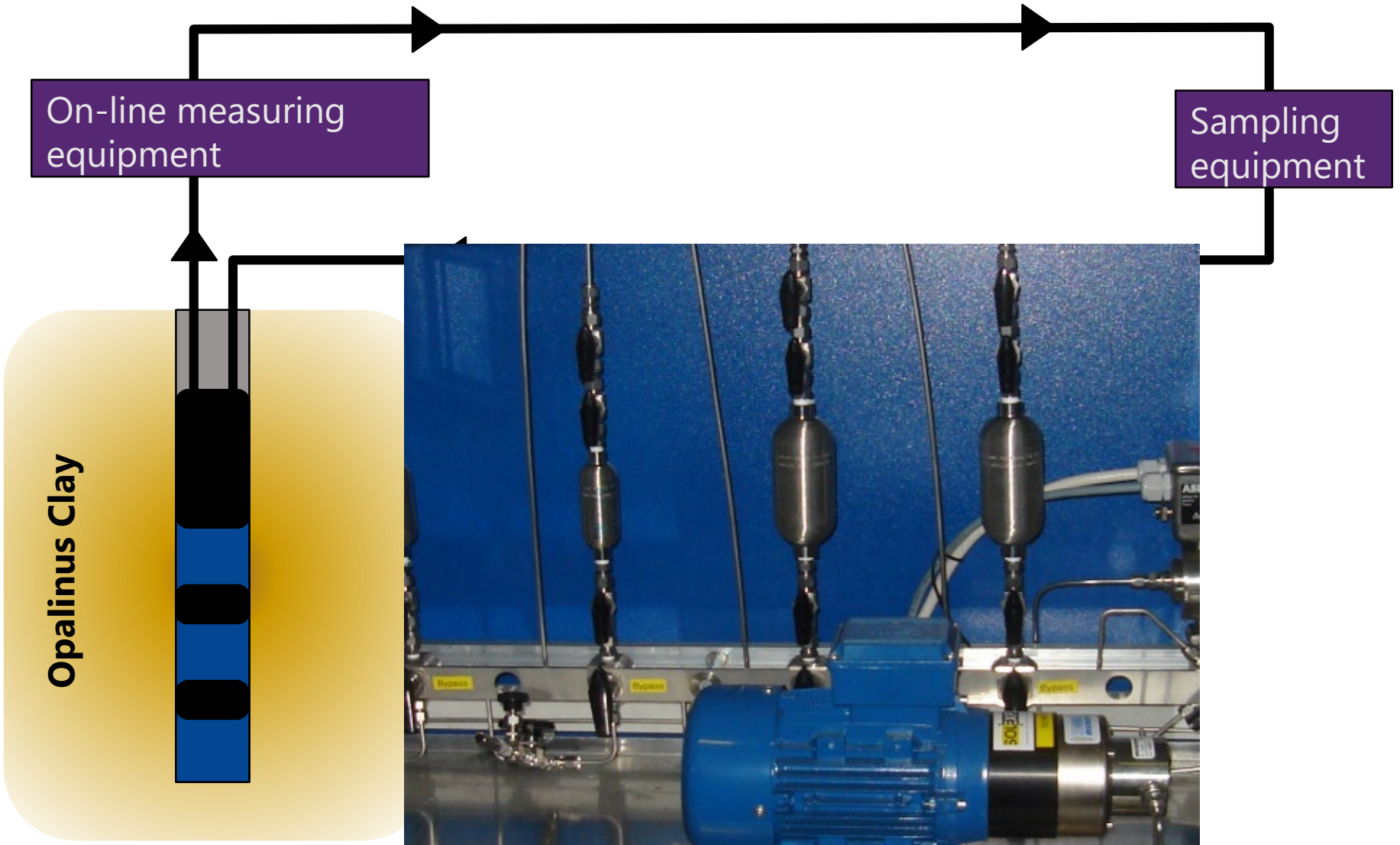
Experimental setup of BN experiment



Bleyen *et al.* (2017)

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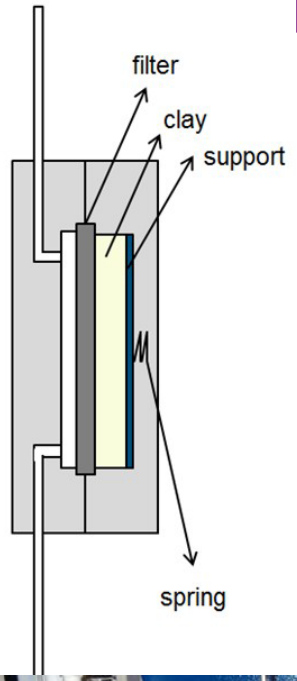
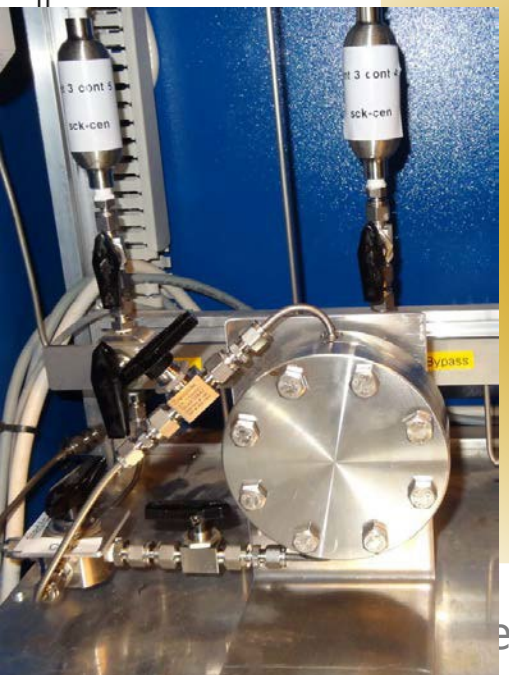
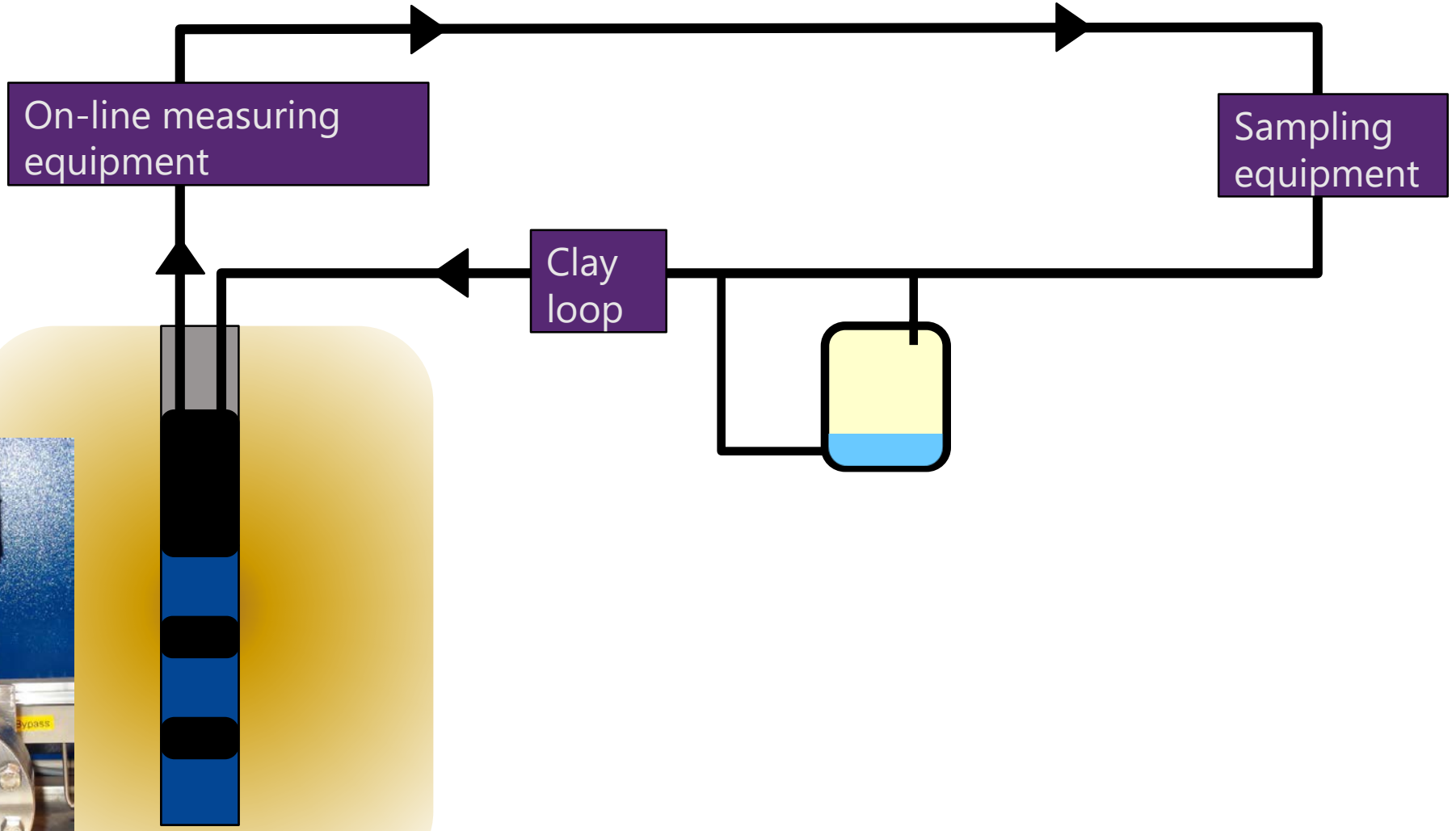
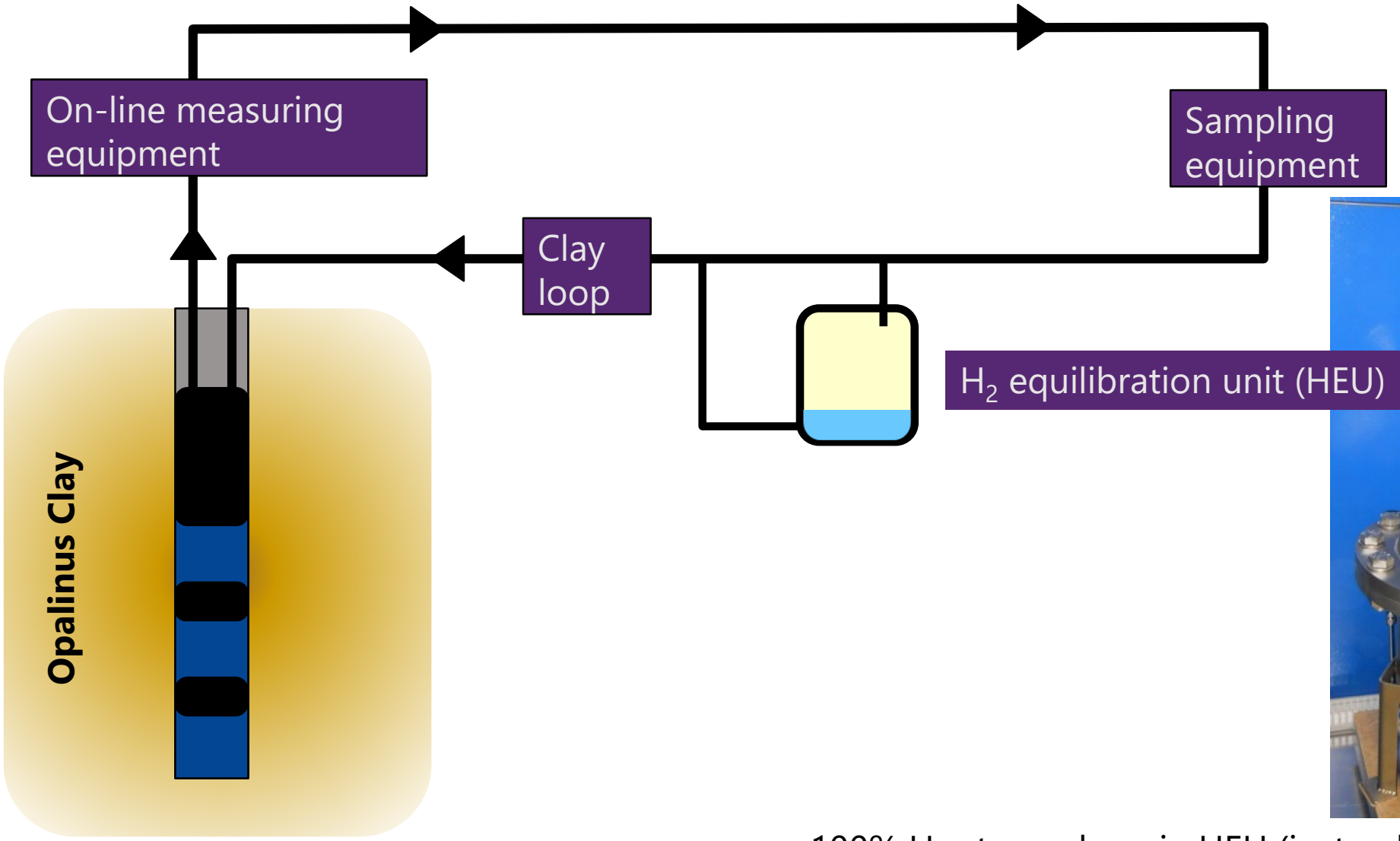


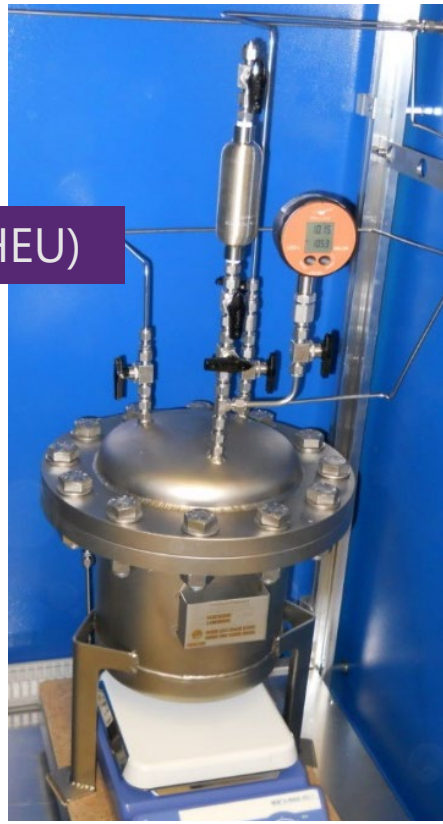




en *et al.* (2017)

Experimental setup of BN experiment

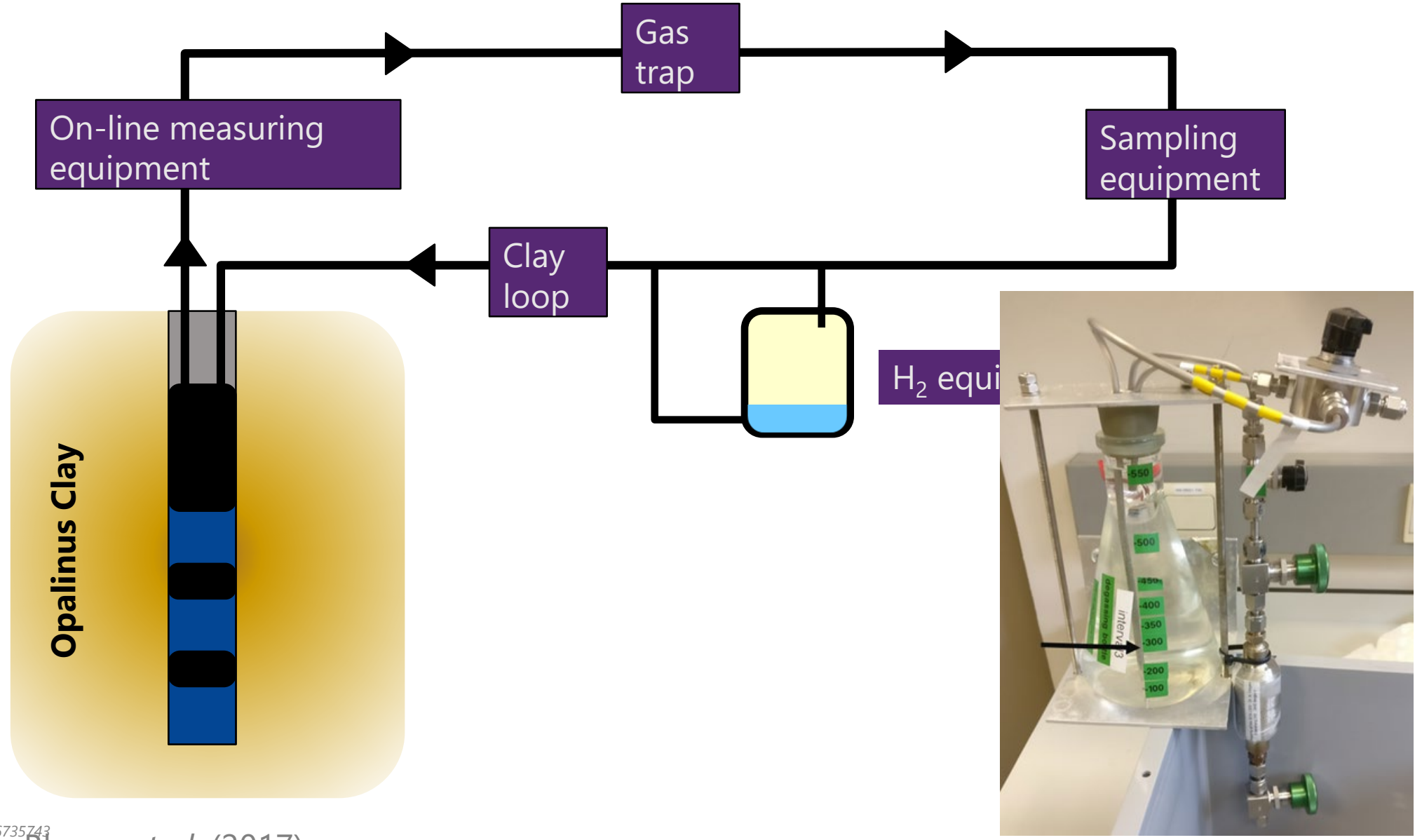




- 100% H_2 atmosphere in HEU (instead of Ar)
- max 1.6 to 2.3 mM dissolved H_2 in the solution

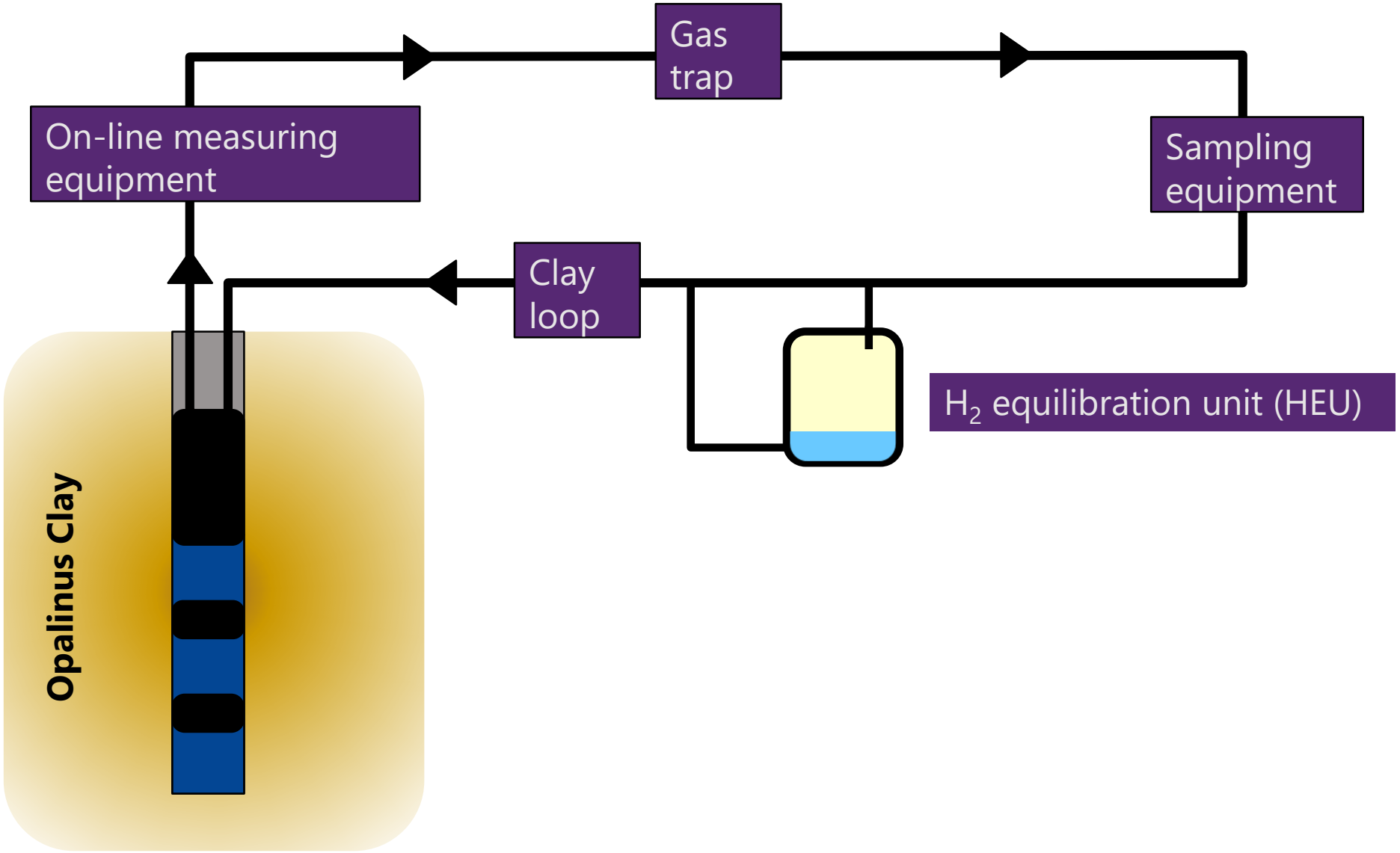
Bleyen *et al.* (2017)

Experimental setup of BN experiment



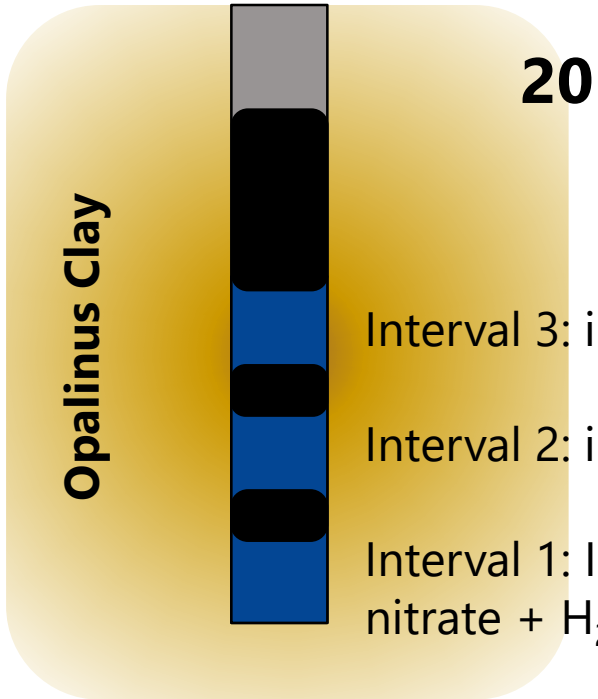
Bleyen *et al.* (2017)

Experimental setup of BN experiment



Bleyen *et al.* (2017)

Timeline of injections



2011 - 2019:

Interval 3: injection of nitrate

Interval 2: injection of nitrate + acetate

Interval 1: Injection of nitrate, nitrate + H_2

2019 – 2023:

Interval 3: selenate, selenate + nitrate

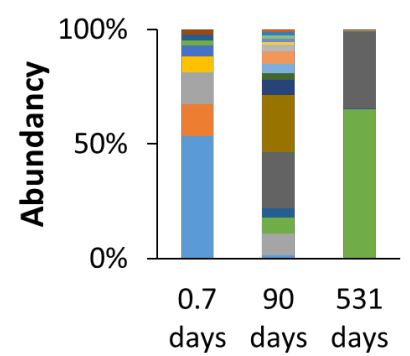
Interval 2: selenate (ongoing)

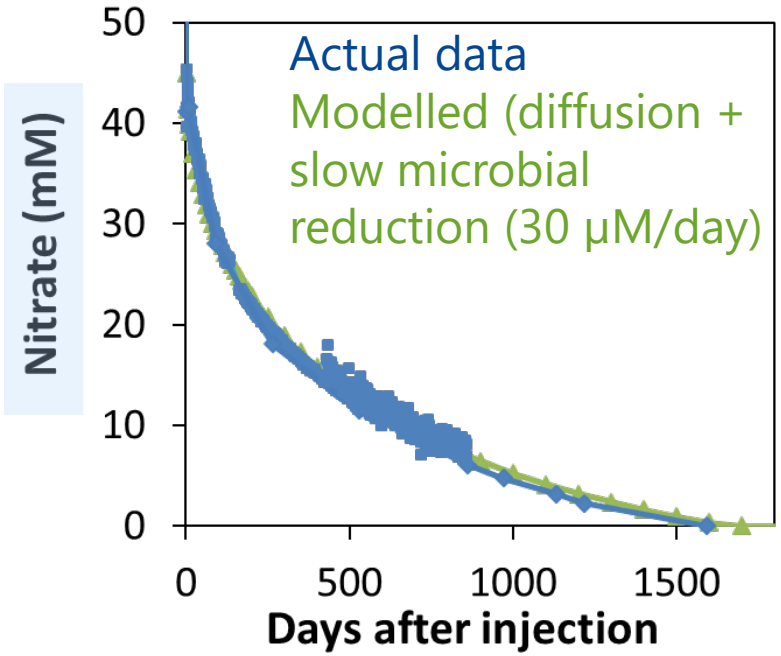
Interval 1: selenate (ongoing)

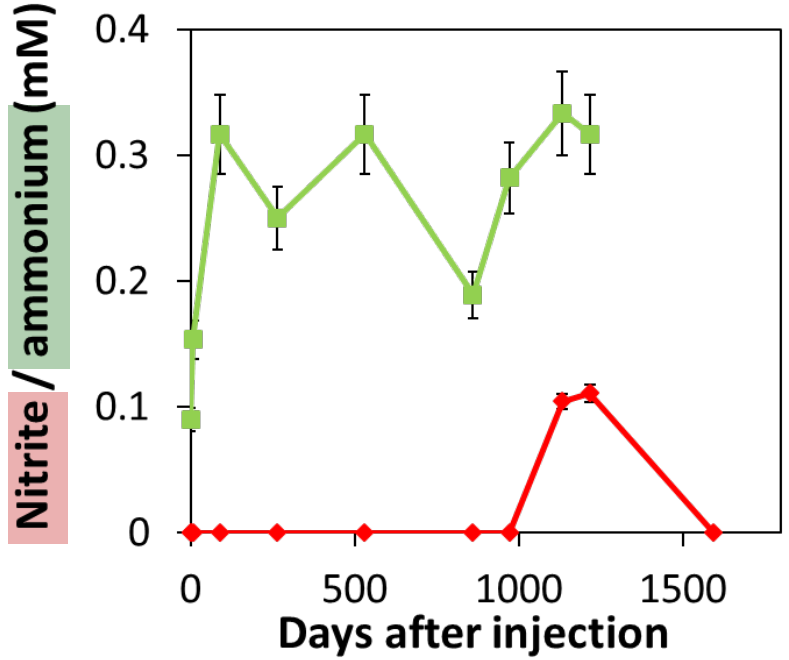
Nitrate injection tests

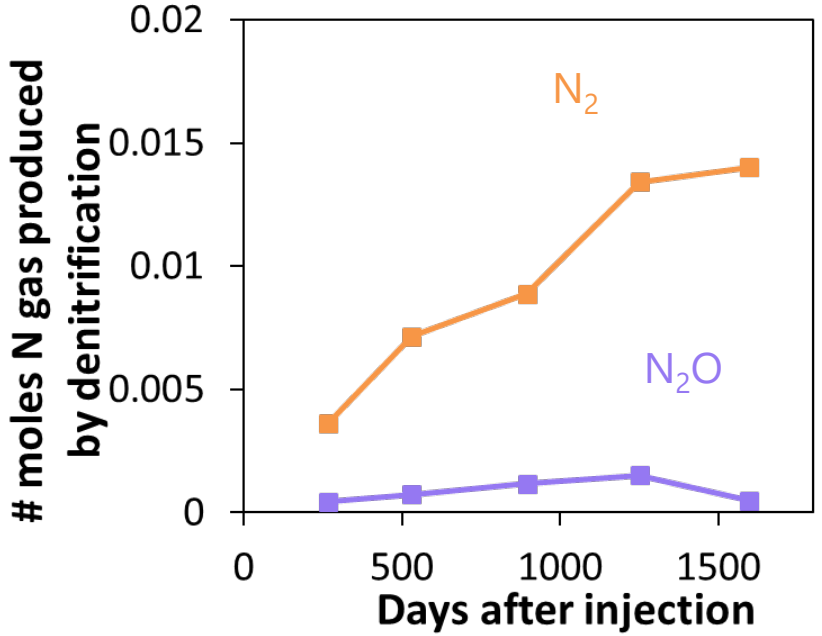
Nitrate reduction

- Slow nitrate decrease: mainly diffusion
- Very slow microbial nitrate reduction by clay electron donors: denitrification
- Shift in population towards denitrifiers that are organotrophs





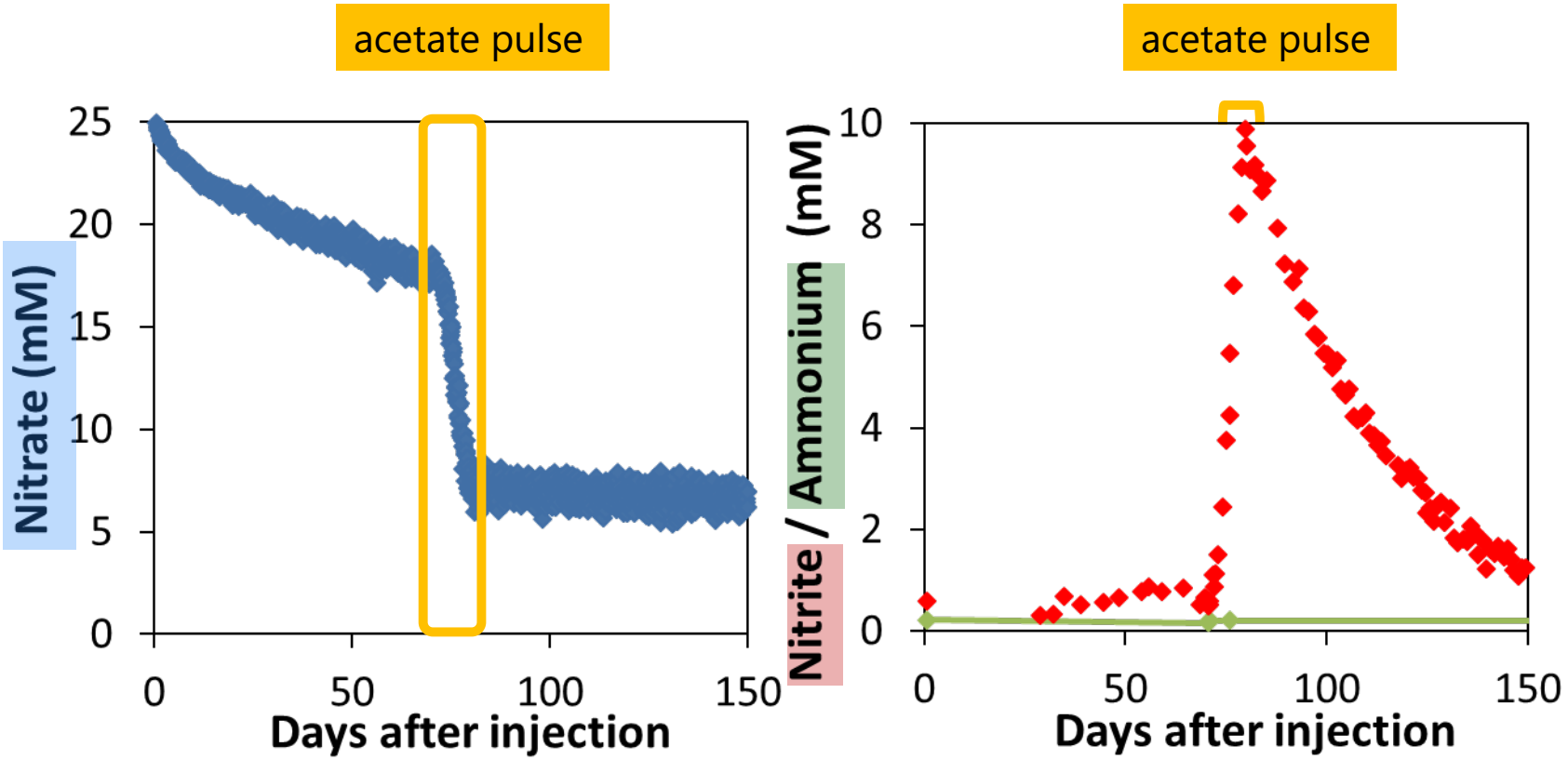


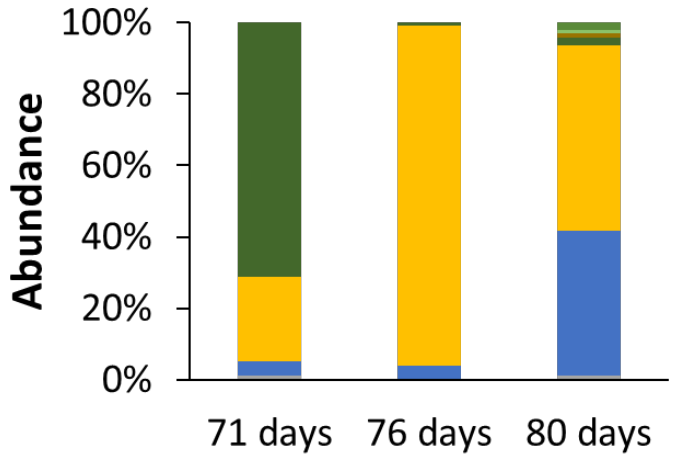


Possible e^- donors:

- Most likely: dissolved organic matter (DOM)
- Pyrite FeS_2
- Fe^{2+} containing minerals

Nitrate reduction with acetate as external electron donor

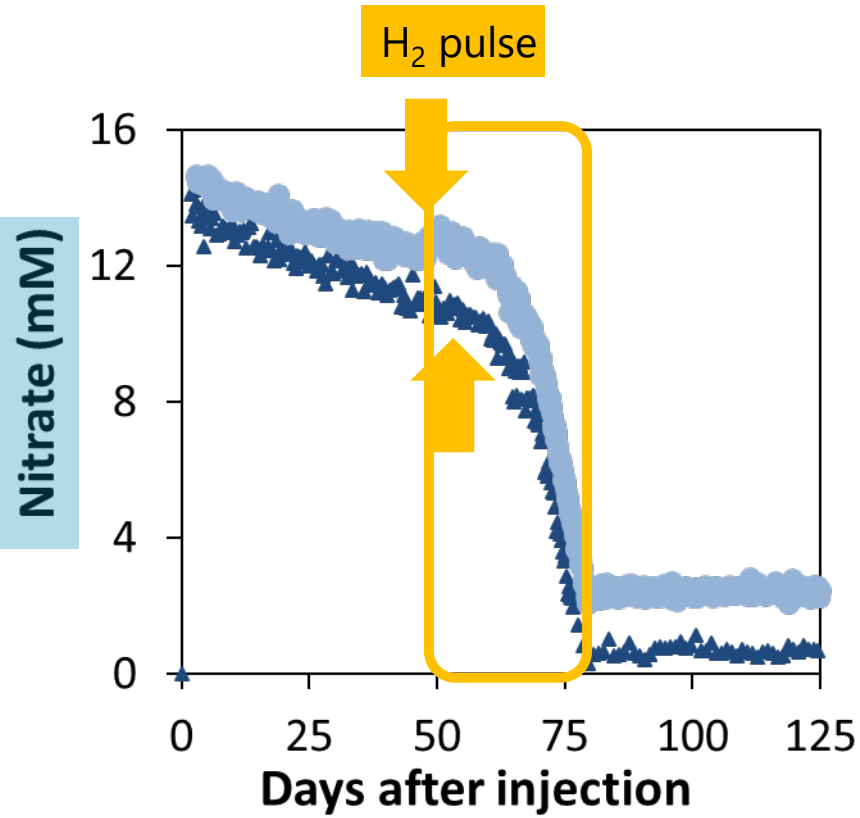


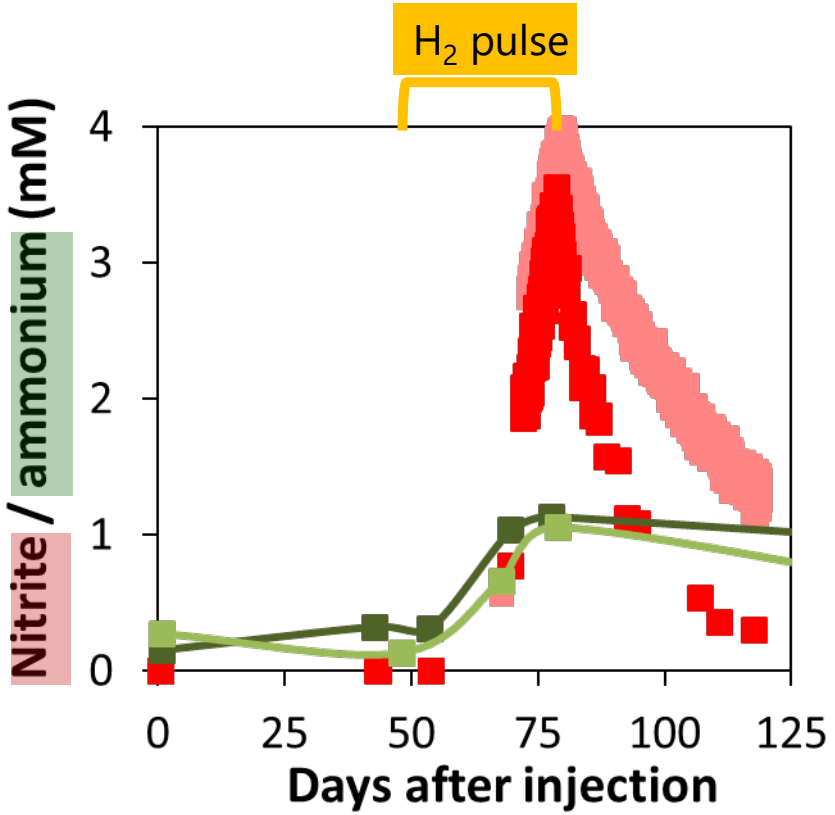


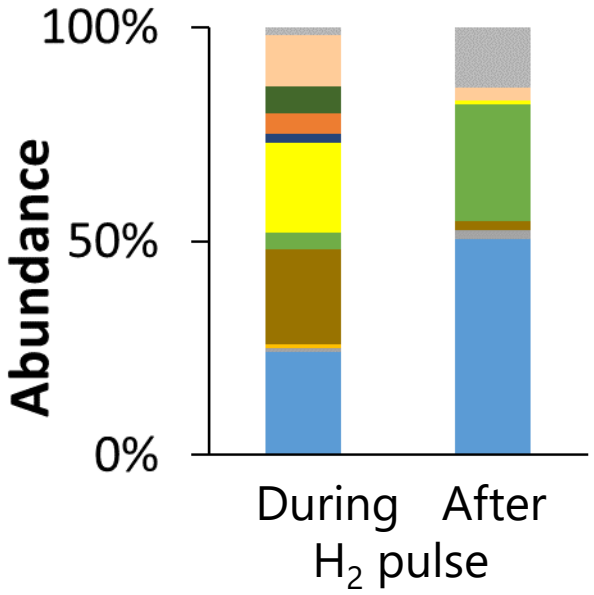
- 1-2 days lag phase
- Fast microbial nitrate reduction → mainly NO_2^- production with ~10% denitrification to N_2

Shift towards 3 main genera
Phenylobacterium: organotrophy
Pseudomonas: organotrophic nitrate reducers
Acidovorax: can use Fe(II), but also acetate as electron donor

Nitrate reduction with H_2 as external electron donor







- 7-10 days lag phase
- Fast nitrate and pH_2 ↓ due to reduction of NO_3^- by H_2 → NO_2^-, NH_4^+, N_2
- Production of ammonium can be biotic or abiotic (Fe surface-catalyzed)

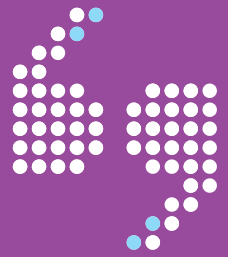
Hydrogenotrophs:

Rhodocyclaceae

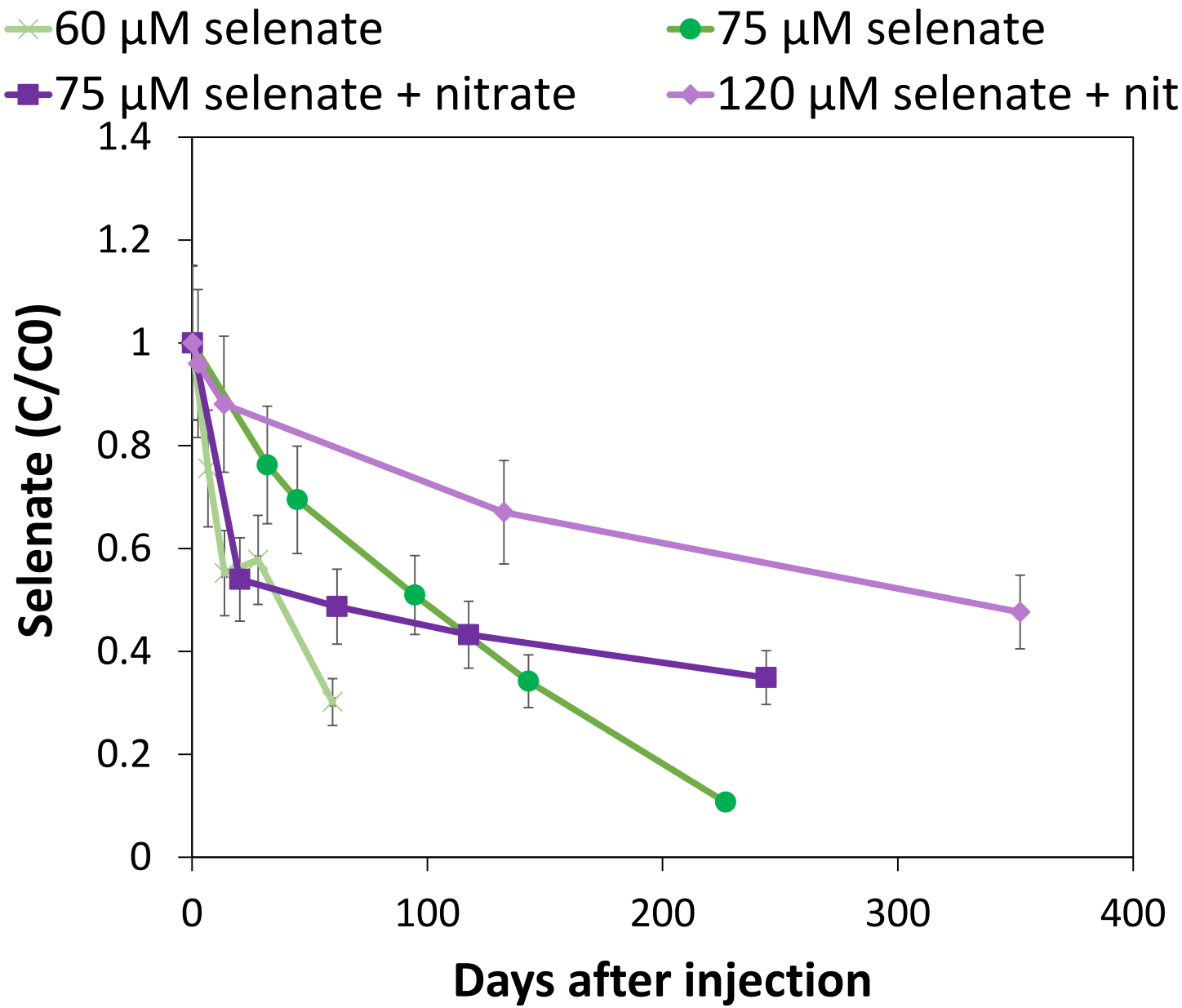
Actinomycetales

Clostridium

Acidovorax



Selenate (+ nitrate) injection tests

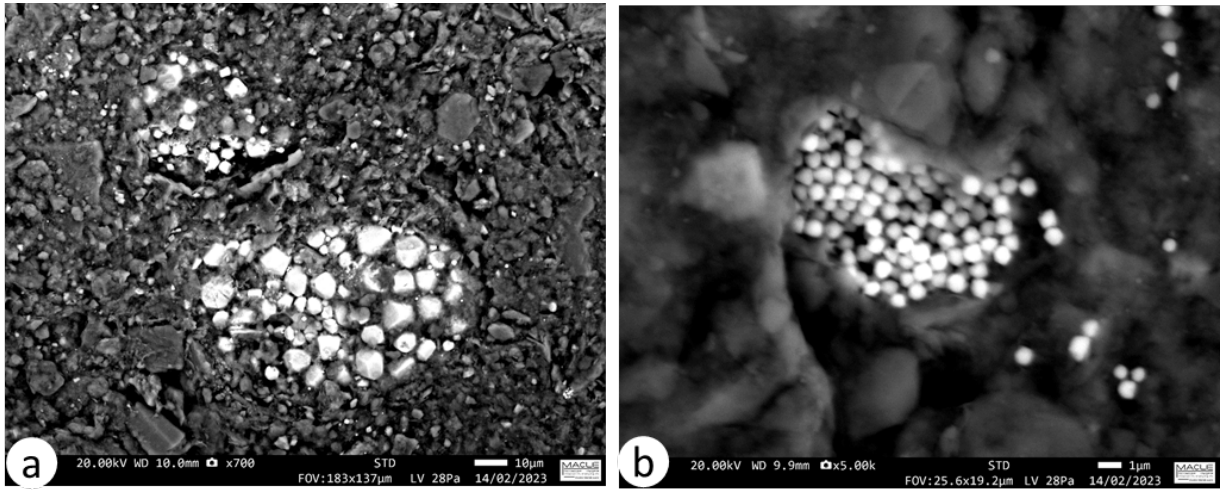


- Long-term: slower selenate removal rate in **presence** of nitrate, faster in **absence** of nitrate
- Nitrate suppressed the microbial reduction of selenate

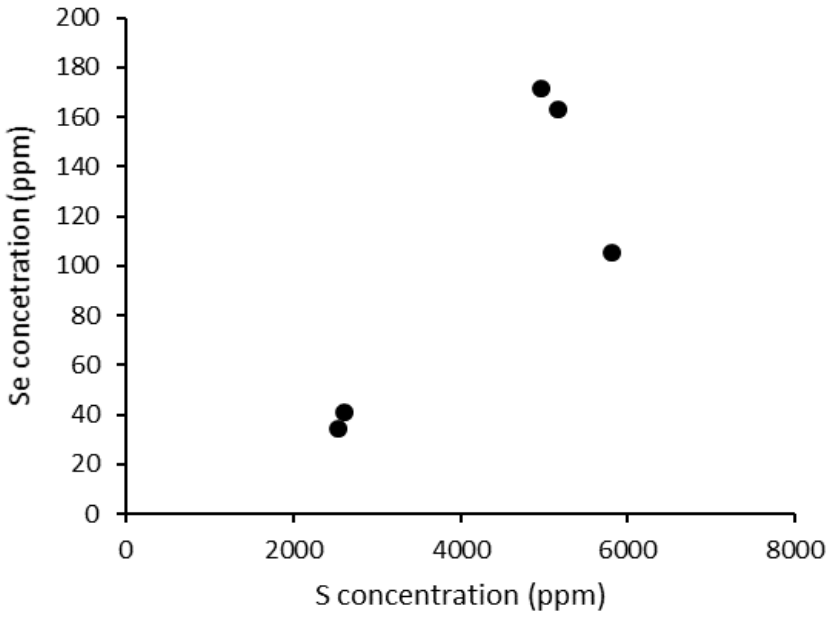
Measurements performed at BRGM by Catherine Lerouge

Fate of selenate in the BN borehole

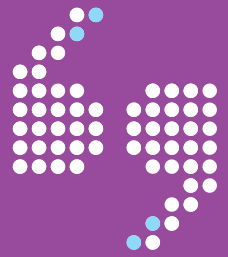
Solid phase characterized by SEM-EDX and laser ablation coupled with QQQ-ICP-MS



depth in clay (µm)	10	20	30	40	50	60	70	80	90	100
average Se (ppm)	257	114	89	75	68	67	73	72	77	78
stddev	149	57	40	24	25	19	34	25	32	29



- Selenium was mostly found in pyrite and correlated with sulfur in the sample
- Likely reduced Se species on the solid phase

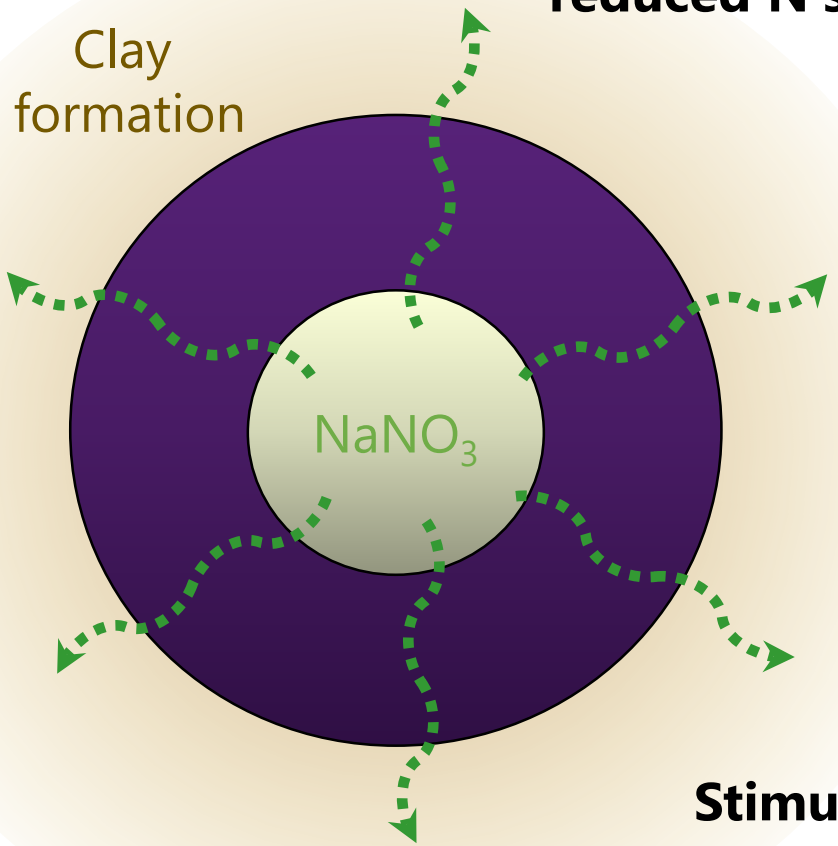


BN experiment – what have we learned

Conclusions: fate of nitrate

Production of reduced N species

- Gaseous species N_2 and N_2O observed
- With acetate / H_2: fast reaction to nitrite
- Nitrite is (microbially and abiotic) reduced, faster reduction than nitrate



Oxidation of clay components

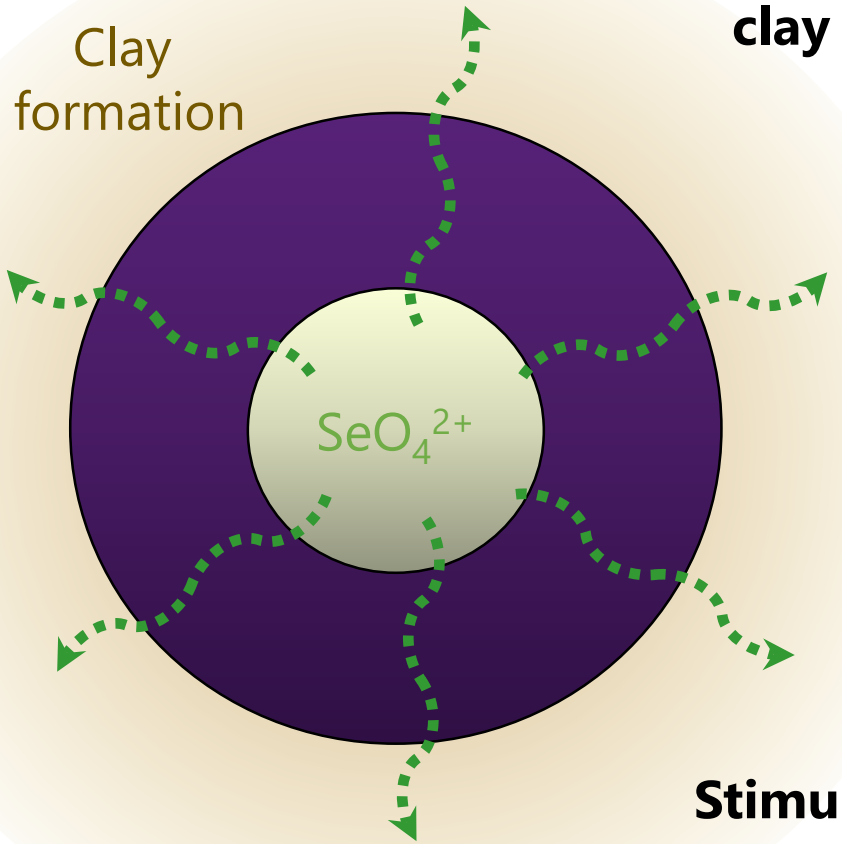
- Dissolved organic matter in clay seems important e^- donor based on microbiology
- Without external electron donors: slow denitrification reaction, nitrate removal mainly by diffusion
- Limited oxidation of clay minerals

Stimulation of microbial activity

- Shift towards nitrate reducing microbes

Modelling in PhreeqC gives good fit

Conclusions: fate of selenate



Oxidation of clay components

- Slow microbial reaction
- Limited oxidation of clay components expected

Production of reduced Se species

- Selenite is formed to some extend
- Selenium species are found on the solid phase, associated with pyrite

Stimulation of microbial activity

- With selenate: sulfate reducing microbes can also reduce selenate, however slowly
- Once nitrate is introduced: shift back to denitrifiers

Modelling in PhreeqC gives good fit

Further reading

- Bleyen, N., Smets, S., Small, J. *et al.* (2017) Impact of the electron donor on in situ microbial nitrate reduction in Opalinus Clay: results from the Mont Terri rock laboratory (Switzerland). *Swiss Journal of Geosciences*
- Nussbaum, C., Bernier, F., Bleyen, N., *et al.* (2023). 25 years of cross-fertilization between HADES and Mont Terri rock laboratory. *Geological Society, London, Special Publications*
- Bleyen, N., Smets, S., Small, J., *et al.* (2018). Impact of the electron donor on in situ microbial nitrate reduction in Opalinus Clay: results from the Mont Terri rock laboratory (Switzerland). *Mont Terri Rock Laboratory, 20 Years: Two Decades of Research and Experimentation on Claystones for Geological Disposal of Radioactive Waste*
- Bleyen, N., Small, J. S., Mijnendonckx, K., *et. al.* (2021). Ex and in situ reactivity and sorption of selenium in Opalinus clay in the presence of a selenium reducing microbial community. *Minerals*
- Bleyen N., Albrecht A., De Cannière P., *et.al.* (2019). Non-destructive on-line and long-term monitoring of in situ nitrate and nitrite reactivity in a clay environment at increasing turbidity. *Applied Geochemistry*

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