Using Inherent Fingerprints to Monitor CO_2 Storage

Stuart Gilfillan, Stephanie Flude, Sascha Serno, Gareth Johnson, Domokos Györe, Adrian Boyce, Fin Stuart, Stuart Haszeldine

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Using oxygen isotopes to measure residual CO_2 saturation at the Otway Stage 2B Extension Experiment

Sascha Serno, **Stuart Gilfillan,** Gareth Johnson, Stuart Haszeldine

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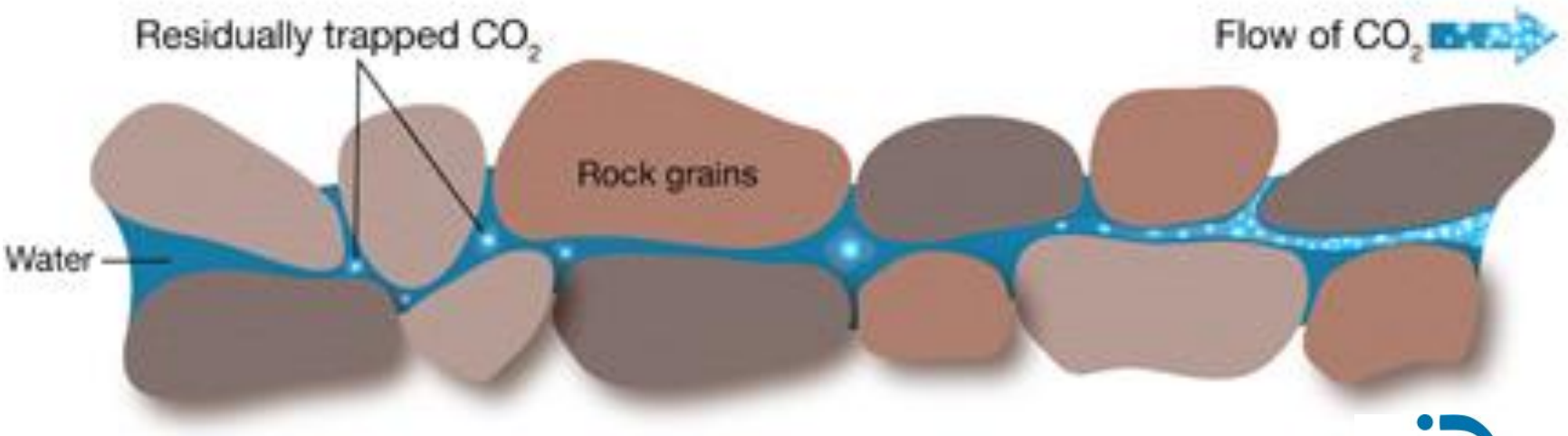
Why important?

- Residual trapping: Disconnected droplets of CO_2 in pore spaces which are immobile



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Why important?

- Residual trapping: Disconnected droplets of CO_2 in pore spaces which are immobile

- Assessment of CO_2 storage site capacity primarily based on predictive modelling of how the CO_2 will behave once injected
- Difficult to verify models when CO_2 is injected into the storage site

  - **Particularly difficult to assess degree of residual trapping**
  - **A monitoring technique to quantify residual trapping prior to or following commercial scale injection would be very useful**

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Why important?

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  - **Particularly difficult to assess degree of residual trapping**
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- Requirements for assessing if O isotopes are a useful monitoring tool:

  - **Do they provide reliable measurements over short timescales?**
  - **Are they comparable to other techniques?**

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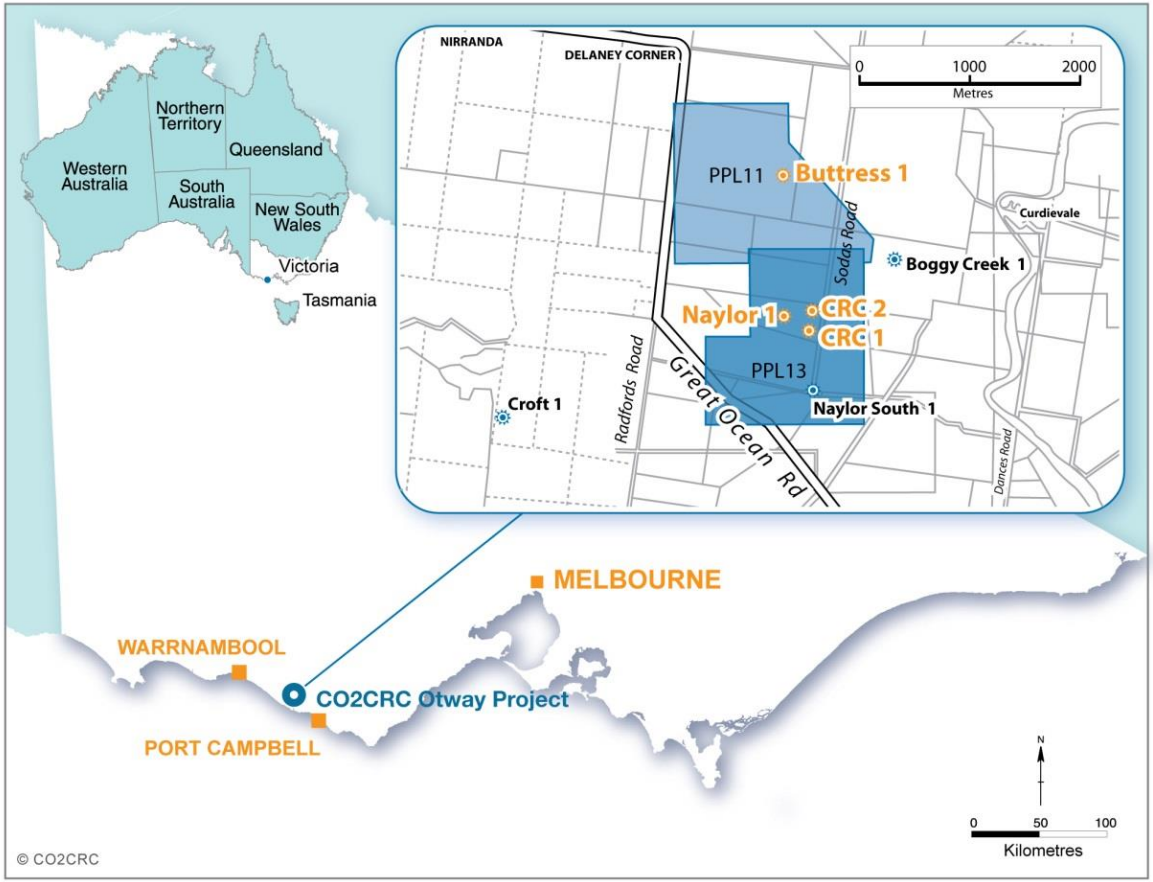
CO2CRC Otway site – Ideal for CO_2 injection tests



- Depleted gas field near Melbourne, Australia, run by CO2CRC
- Natural CO_2 production nearby at Buttress & Boggy Creek

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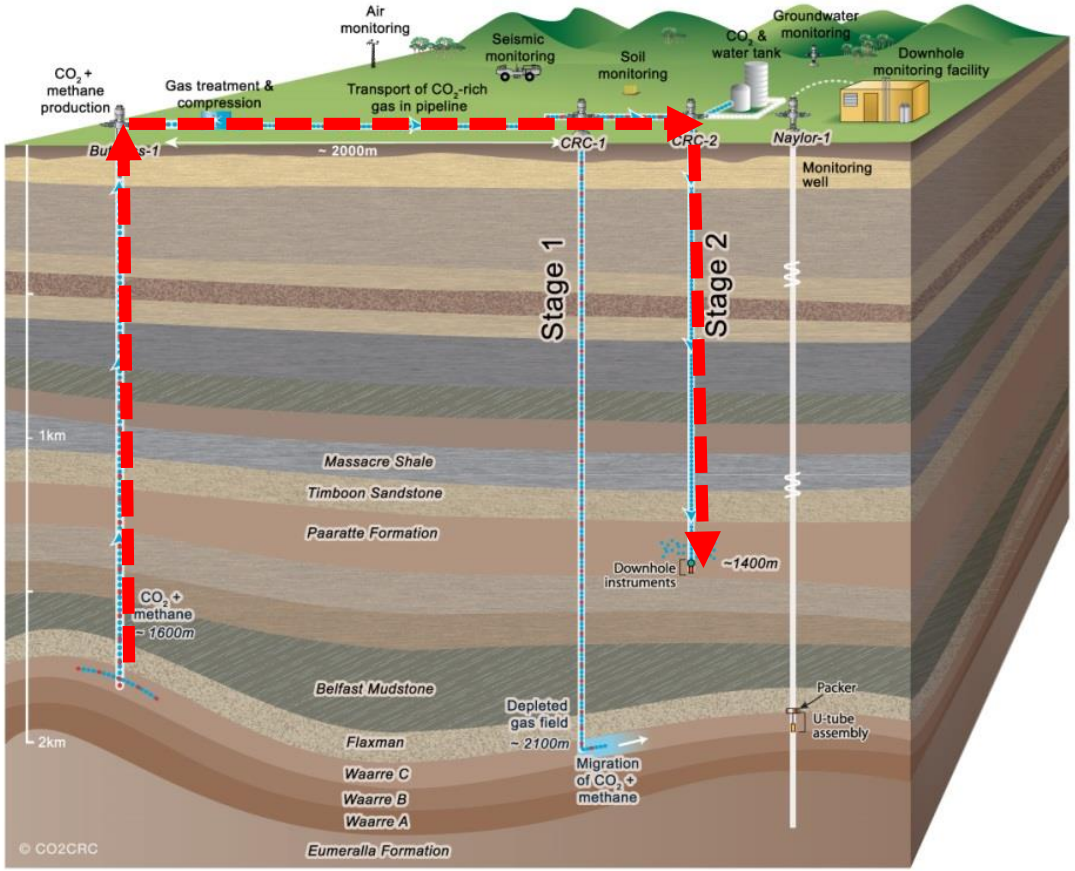
CO2CRC Otway Stage 2B & 2B Ext.



Stage 2B: 2011, Injection of 150 tonnes of CO_2 into saline Paaratte Fm

Stage 2B Ext: 2014, Injection of 110 tonnes of CO_2 both via CRC-2 Well

Both **residual saturation tests** using a **push-pull single-well** technique

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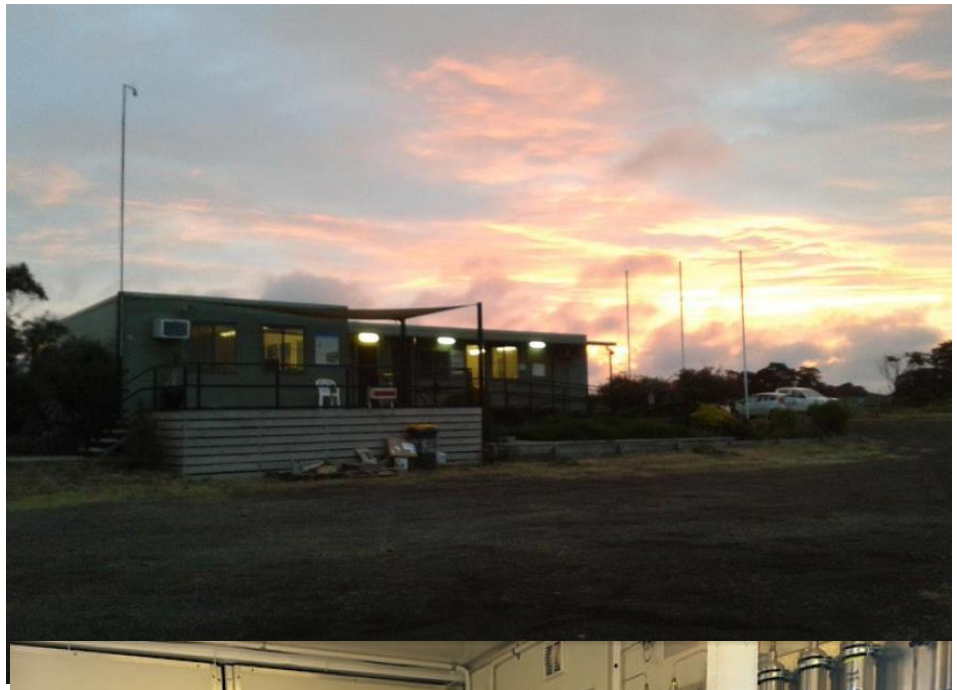
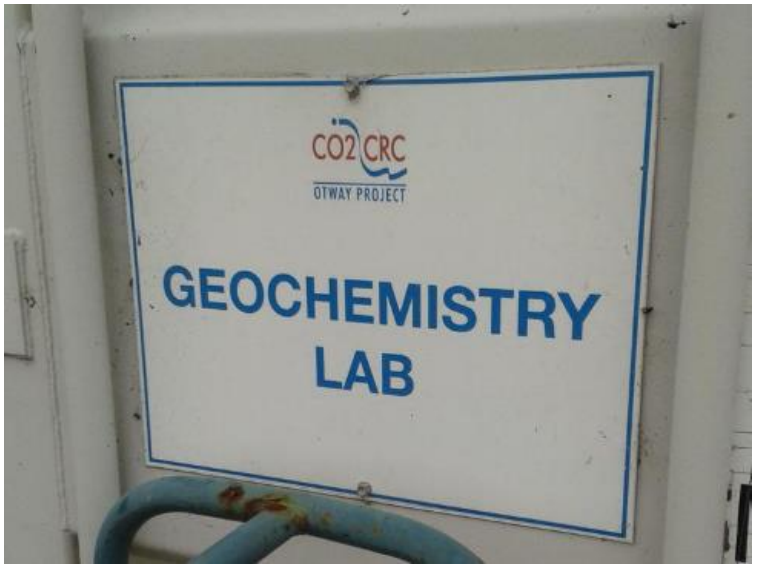
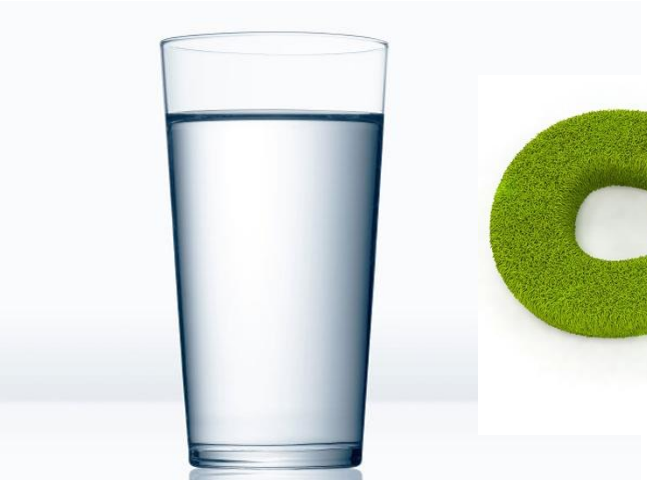
CO2CRC Otway Stage 2B Extension – Phase 2





Principle of using oxygen isotopes



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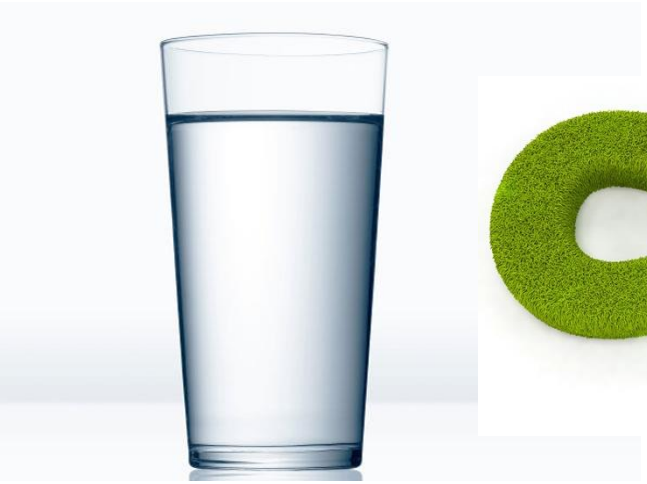

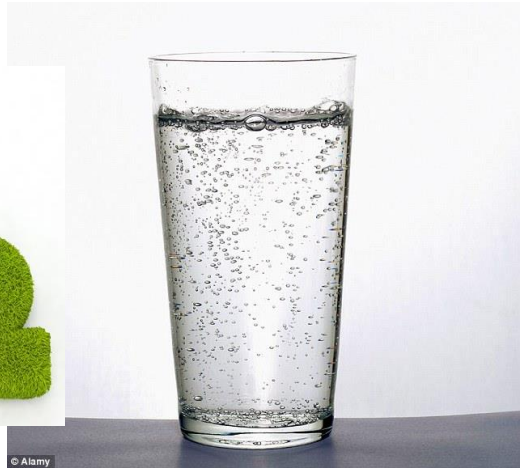

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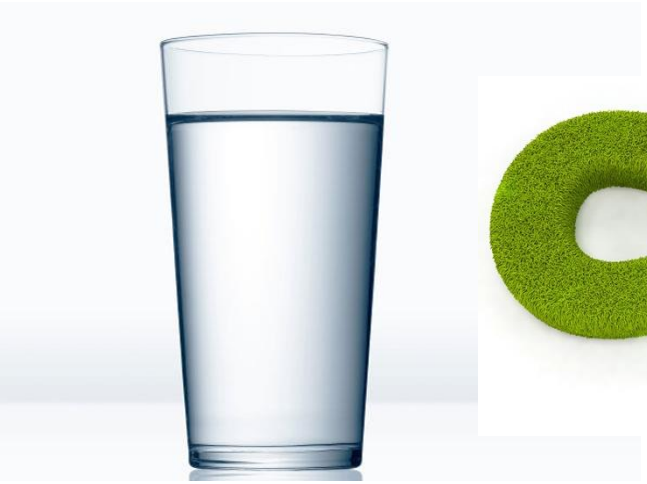

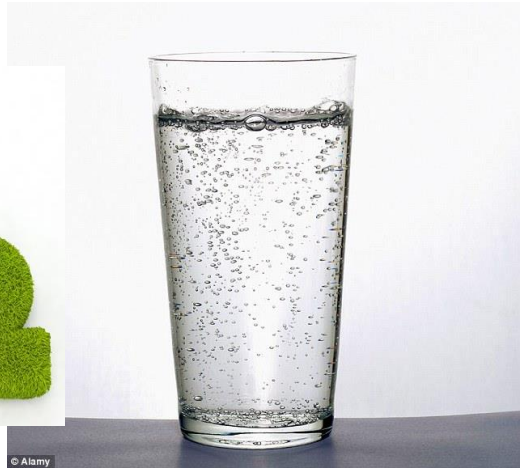

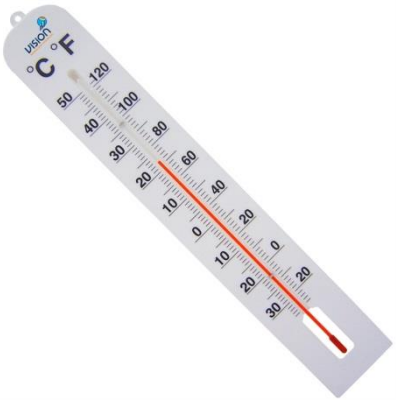

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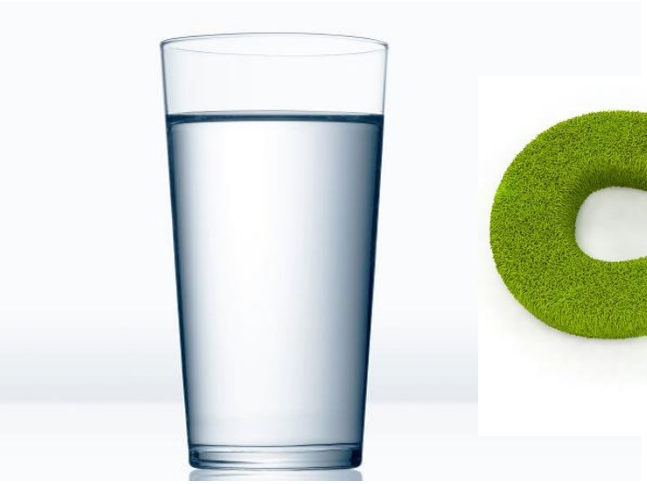

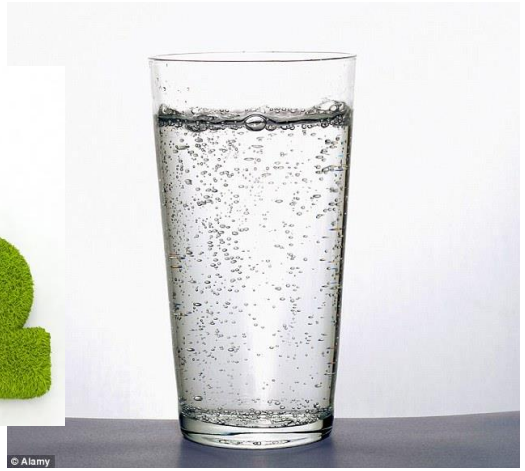

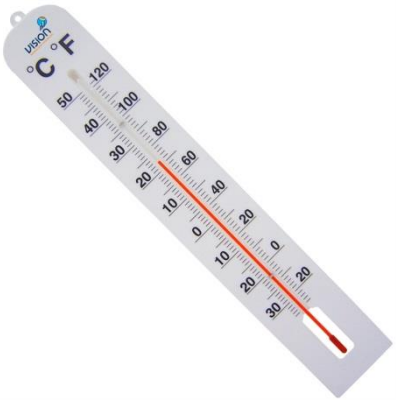

$$\delta^{18}O^{f}_{H_2O} = \left(\delta^{18}O^{i}_{H_2O} \bullet \left(1 - X^{O}_{CO2}\right)\right) + X^{O}_{CO2}\left(\delta^{18}O_{CO_2} - \varepsilon\right)$$

$$X^{O}_{CO_2} = \frac{AS_{CO_2} + BS_w}{AS_{CO_2} + BS_w + CS_w}$$

Johnson et al., 2011, *Chem. Geol*.

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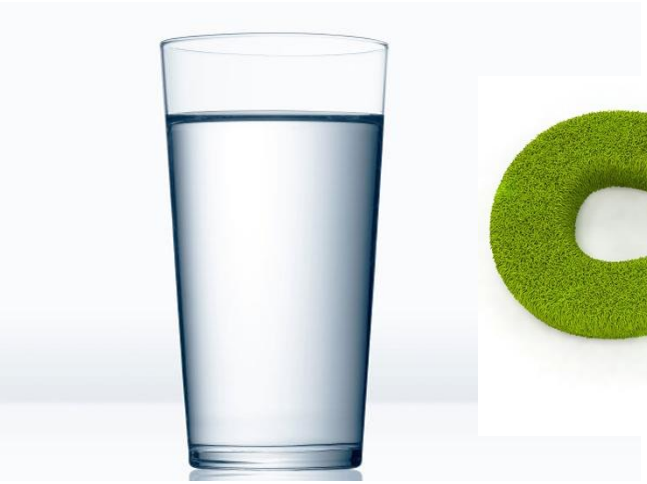
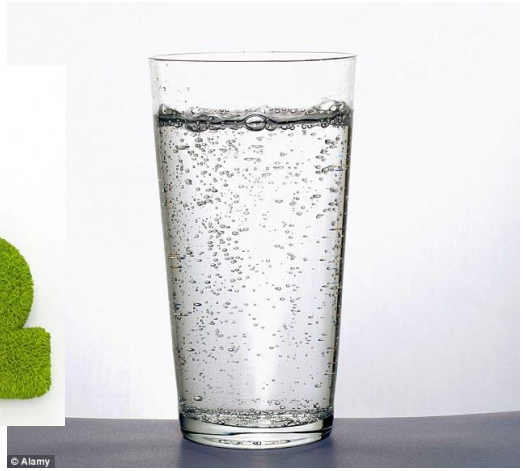
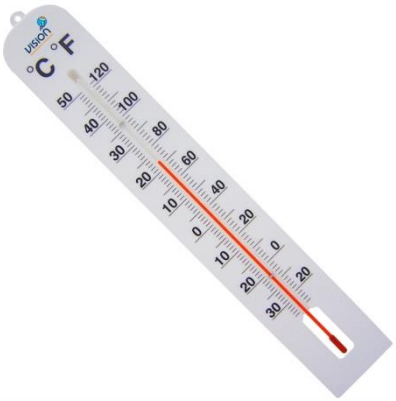
Principle of using oxygen isotopes







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Fraction of oxygen sourced from CO_2

$$X^{O}_{CO_2} = \frac{AS_{CO_2} + BS_w}{AS_{CO_2} + BS_w + CS_w}$$

Residual CO_2 saturation

Johnson et al., 2011, *Chem. Geol.*

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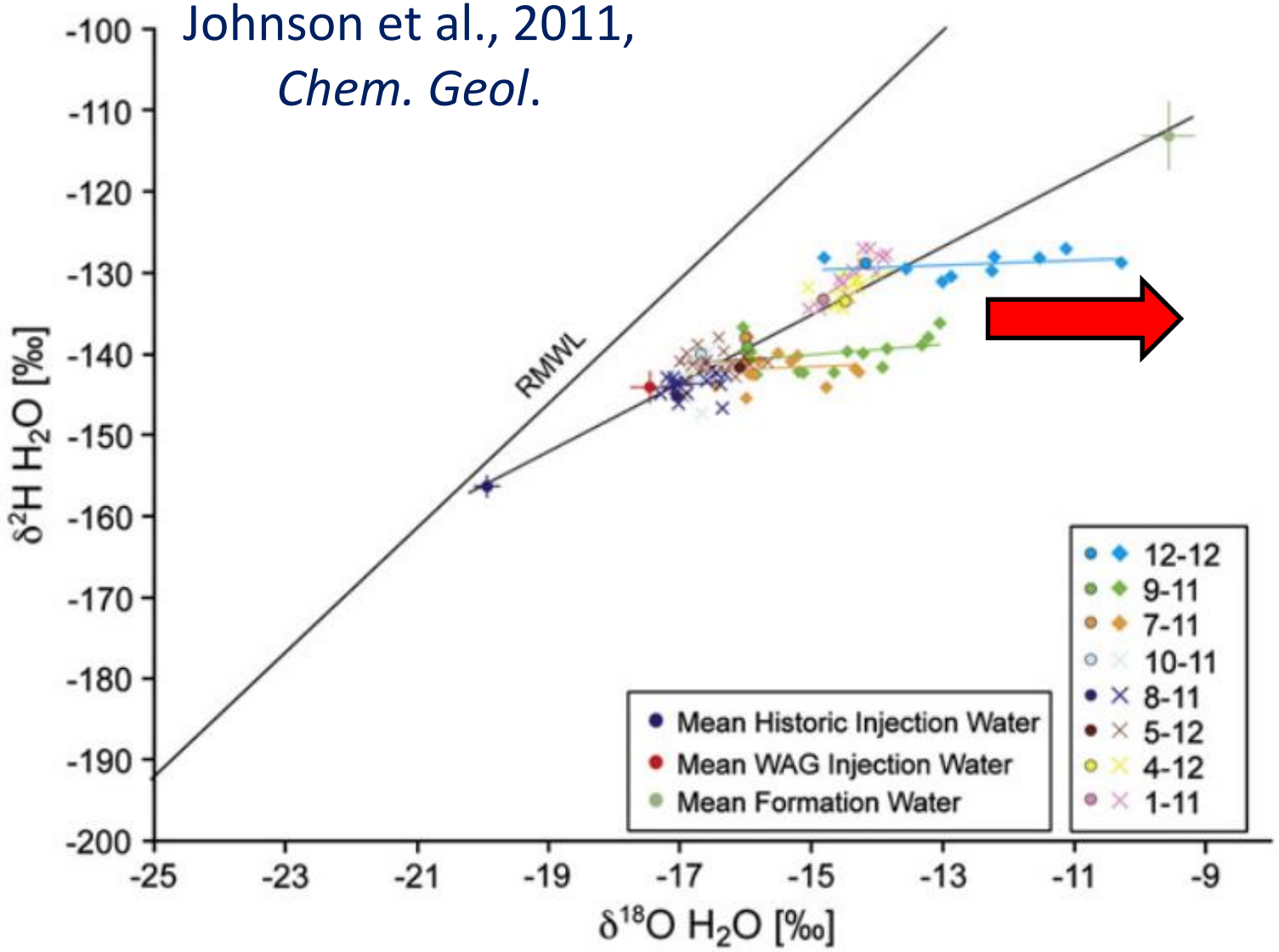
O isotope shift in Pembina CO_2-EOR field

Johnson et al., 2011,
Chem. Geol.



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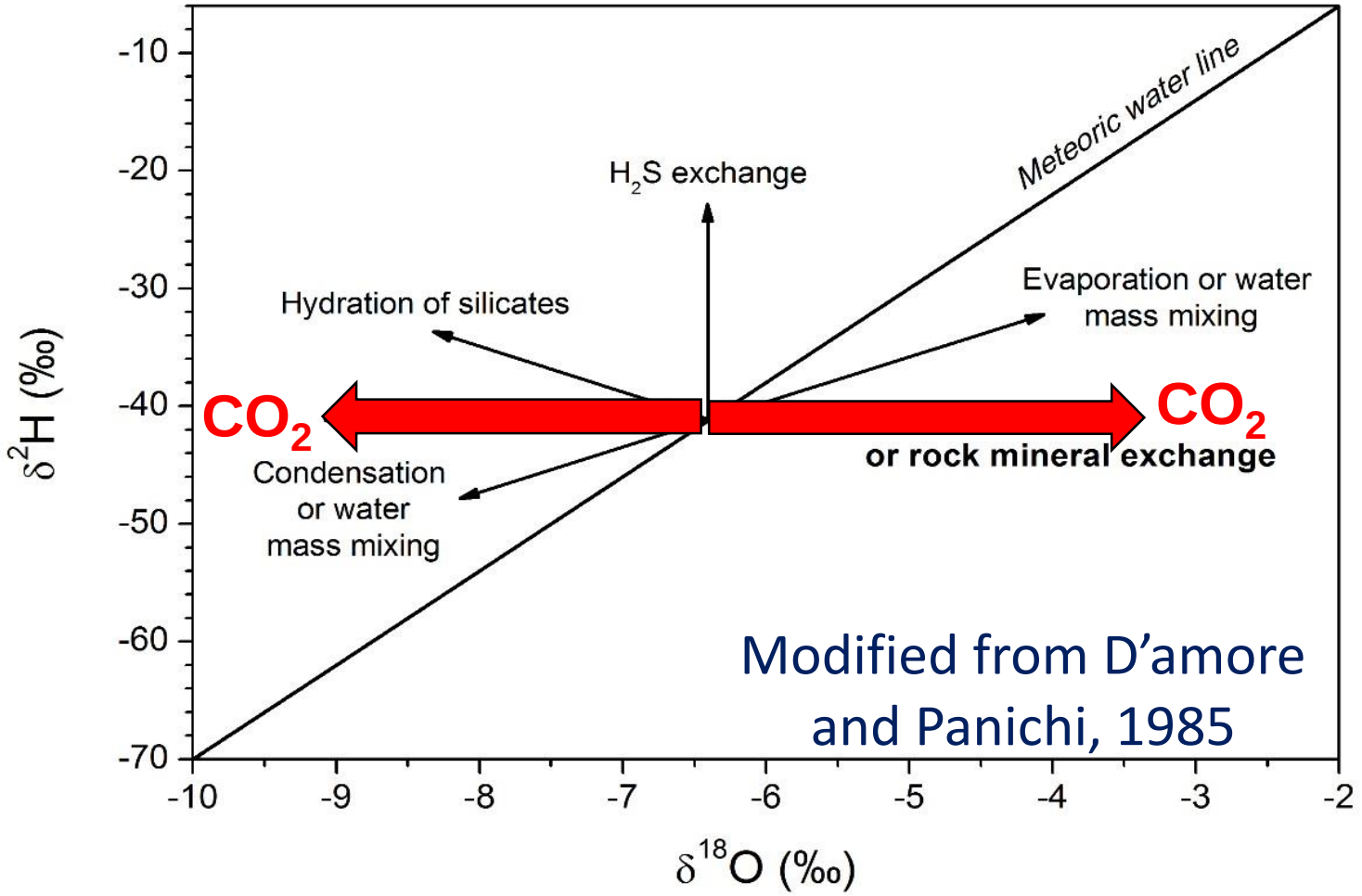
Oxygen isotopes – Principle



CO_2 mixing or mineral exchange can shift O isotopes with no ^2H shift
Shift can be either side of MWL, controlled by Ɛ & injected CO_2 isotopes

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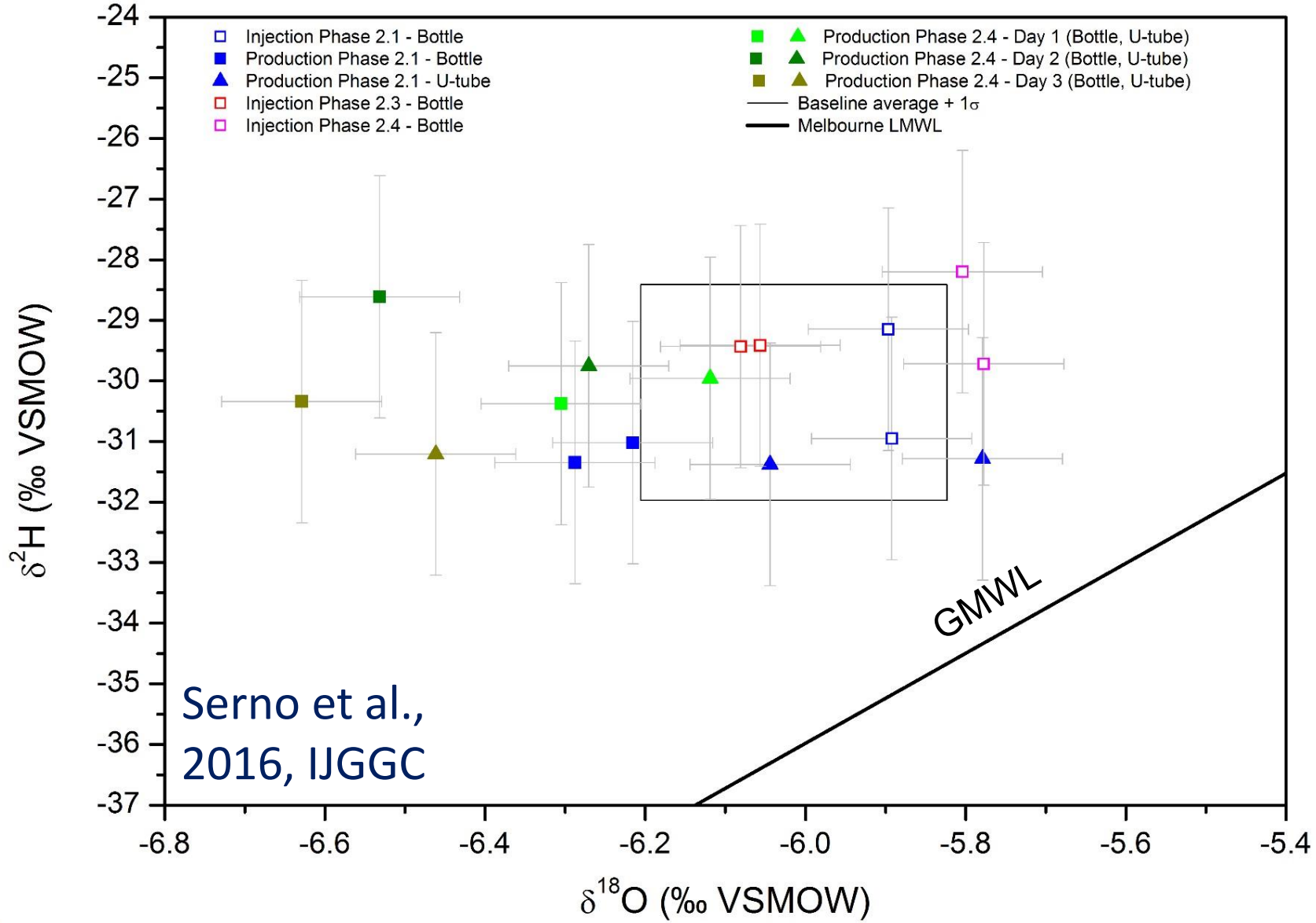
Otway - oxygen isotope results



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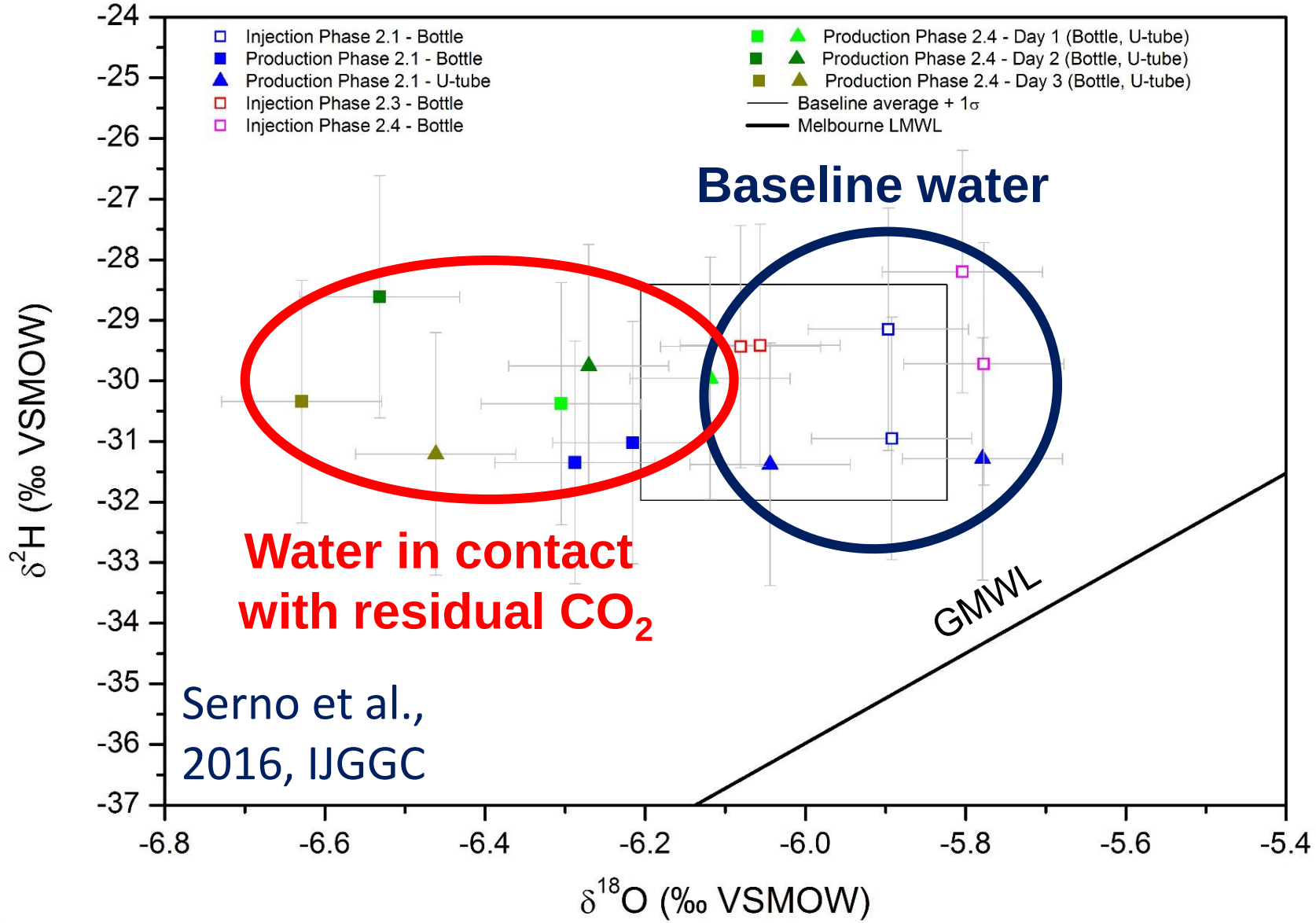

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Otway - oxygen isotope results

- **Change in oxygen isotope signature of reservoir water within a day due to residual CO_2-water interaction**
- Change in $\delta^{18}O$ of reservoir water after 1-2 days provides an estimate of **14 ± 9 %** for **residual CO_2 saturation**

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- **Comparison with other methods used in 2011 test:**

Pulsed neutron logging: **7-32 %, Av. 20 %** (Dance & Paterson, 2016)

Noble gas tracer test: range of **13 – 18 %** (LaForce et al., 2014)

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Noble gas tracer test: range of **13 – 18 %** (LaForce et al., 2014)

- **Comparison with other methods used in 2014 test:**

Neutron logging: **~5 - 10 %** across the formation (Ennis-King, 2016)

Noble gas: **7 - 8 %** using 2011 partition coefficents (Ennis-King, 2016)

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Otway - oxygen isotopes - Summary

- Oxygen isotopes can quantifying residual CO_2 saturation in a single-well field experiment
- High uncertainty due to small isotopic distinction between two CO_2 (oxygen) sources used during Otway 2B Extension

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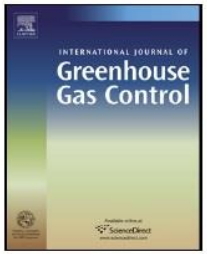

https://doi.org/10.1016/j.ijggc.2016.06.019

Using oxygen isotopes to quantitatively assess residual CO_2 saturation during the CO2CRC Otway Stage 2B Extension residual saturation test

Sascha Serno[a,*], Gareth Johnson[a], Tara C. LaForce[b,c], Jonathan Ennis-King[b,c], Ralf R. Haese[b,d], Christopher J. Boreham[b,e], Lincoln Paterson[b,c], Barry M. Freifeld[f], Paul J. Cook[f], Dirk Kirste[b,g], R. Stuart Haszeldine[a], Stuart M.V. Gilfillan[a]

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Otway - oxygen isotopes - Outlook

- With careful planning, oxygen isotopes are a powerful inherent tracer to monitor CO_2 pore-space saturation
- Potential to combine O isotopes with evolving seismic techniques to quantify amount of CO_2 residually trapped

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Oxygen isotopes as a tool to quantify reservoir-scale CO_2 pore-space saturation

Sascha Serno [a, 1], Stephanie Flude [a, b], Gareth Johnson [a], Bernhard Mayer [c], Rūta Karolytė [a], R. Stuart Haszeldine [a], Stuart M.V. Gilfillan [a]

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Water sampling technique paves way for safe storage of CO2

12 Jul 2016
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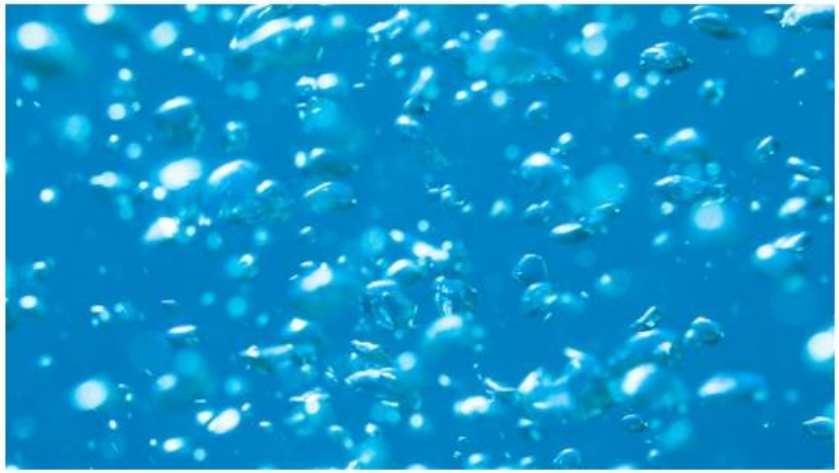

Trials of the method will help the development of Carbon Captur and Storage (CCS) technology

Inherent Tracer Fingerprints in Captured CO_2

Stephanie Flude, Domokos Györe, Fin Stuart, Adrian Boyce, Stuart Haszeldine, & **Stuart Gilfillan**

EPSRC funded: £295,222

EP/K036033/1

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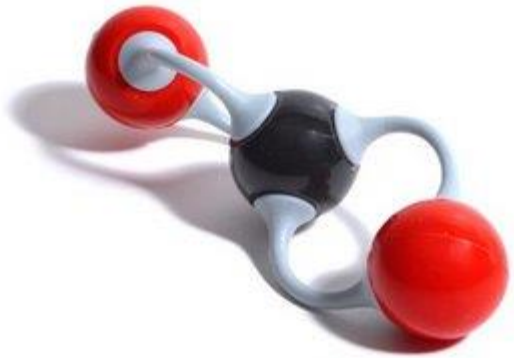
Fingerprinting CO_2?

Anthropogenic CO_2 molecule

Natural CO_2 molecule



www.phenomenica.com

^{12}C	^{13}C	^{14}C
12.00000 98.89%	13.00335 1.11%	14.0 $t_{1/2}$ = 5715yrs
Stable	Stable	Radioactive Cosmogenic/ anthropogenic

^{16}O	^{17}O	^{18}O
15.9949 99.76%	16.9991 0.04%	17.9991 0.20%
Stable	Stable	Stable

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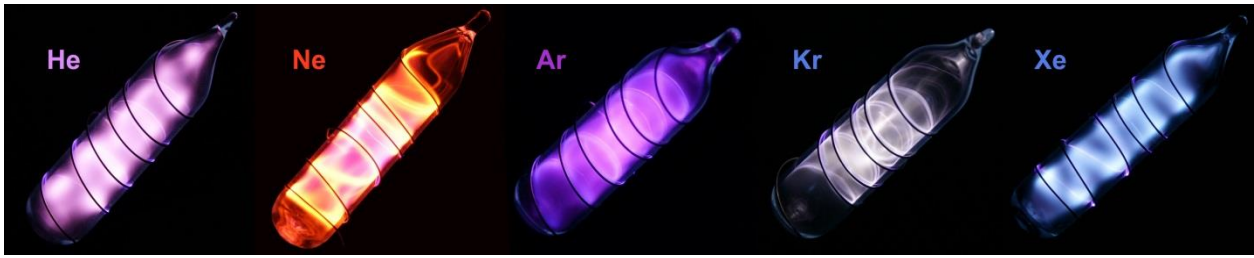

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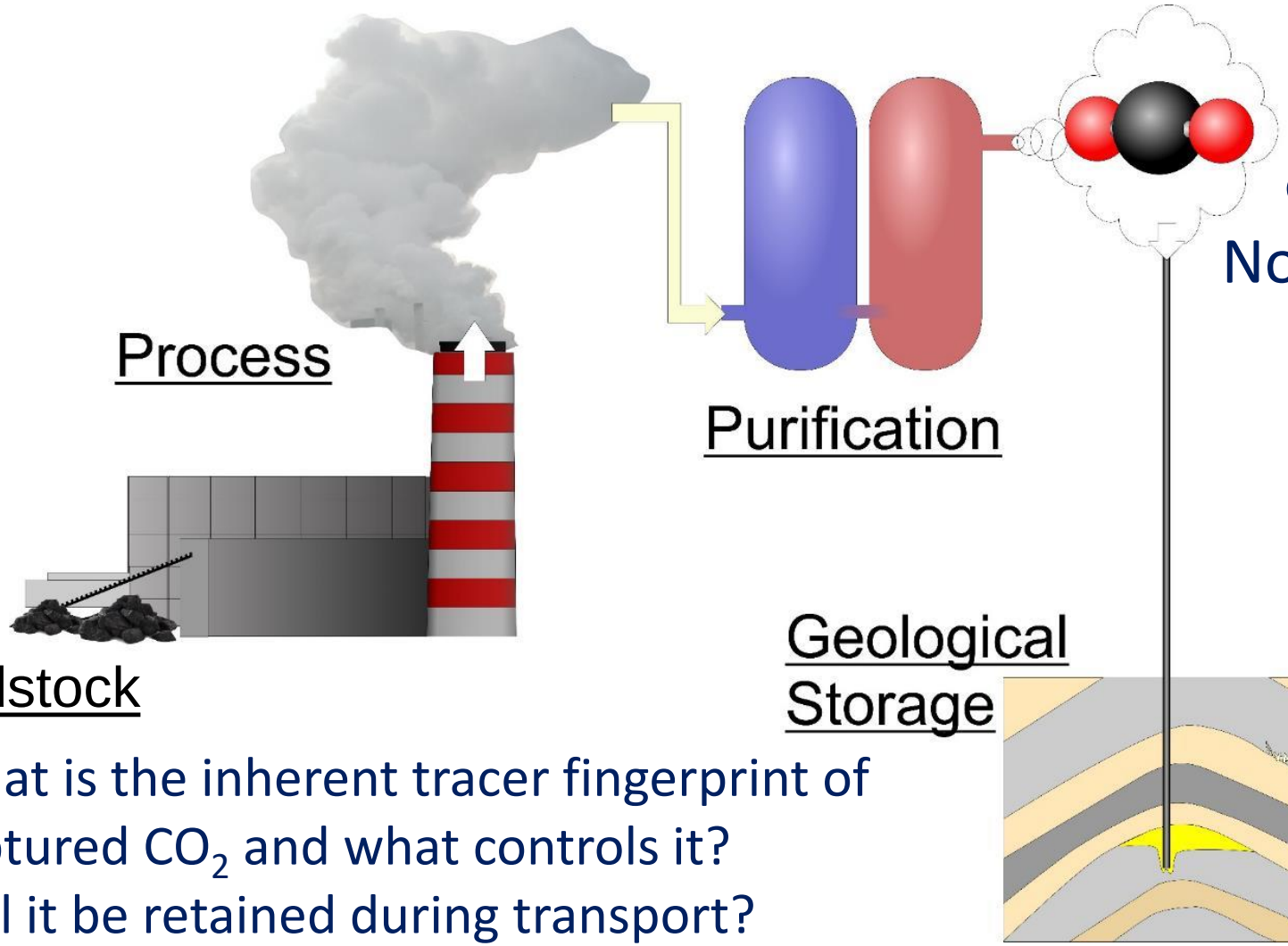
What is the fingerprint of captured CO_2?



- What is the inherent tracer fingerprint of captured CO_2 and what controls it?
- Will it be retained during transport?
- Will it be a useful subsurface tracer?

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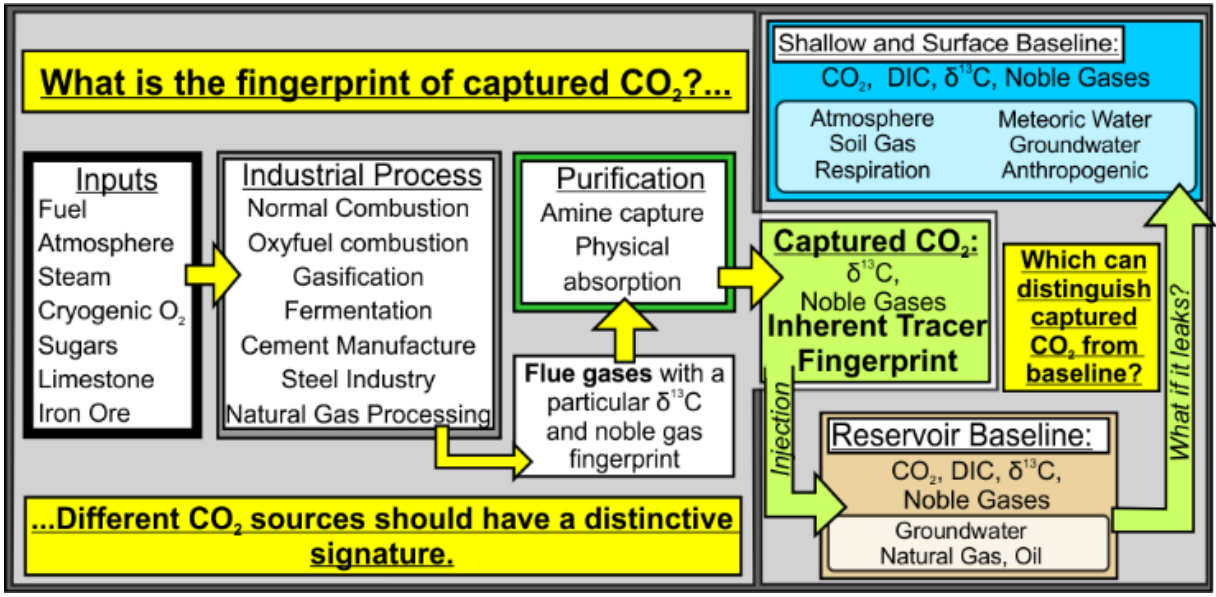
Predicting fingerprints of captured CO_2

- $\delta^{13}C$ controlled by feedstock
- $\delta^{18}O$ controlled by water involved at any stage & ε (temperature)
- Noble gas concentrations controlled by capture process
- Noble gas ratios controlled by feedstock



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Environ. Sci. Technol. 2016, 50, 7939−7955

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Inherent Tracers for Carbon Capture and Storage in Sedimentary Formations: Composition and Applications

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[‡]Isotope Geosciences Unit, Scottish Universities Environmental Research Centre, Rankine Avenue, East Kilbride G75 0QF, U.K.

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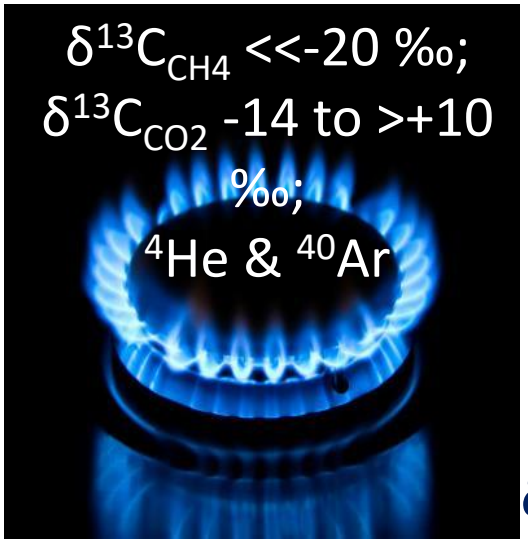
Expected fingerprints from different feedstocks

$\delta^{13}C$ -25 to -20 ‰; ^{4}He & ^{40}Ar



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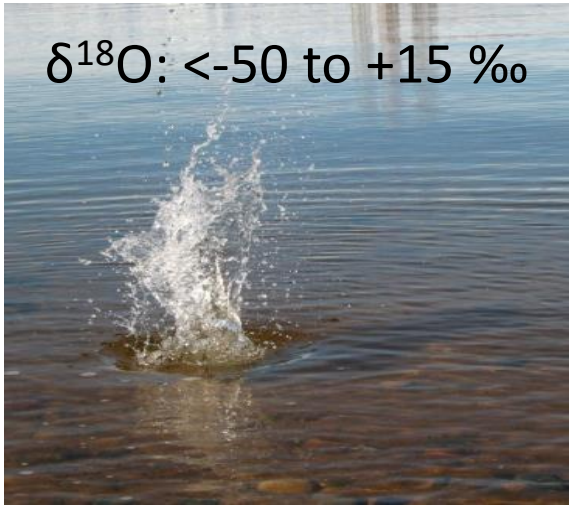

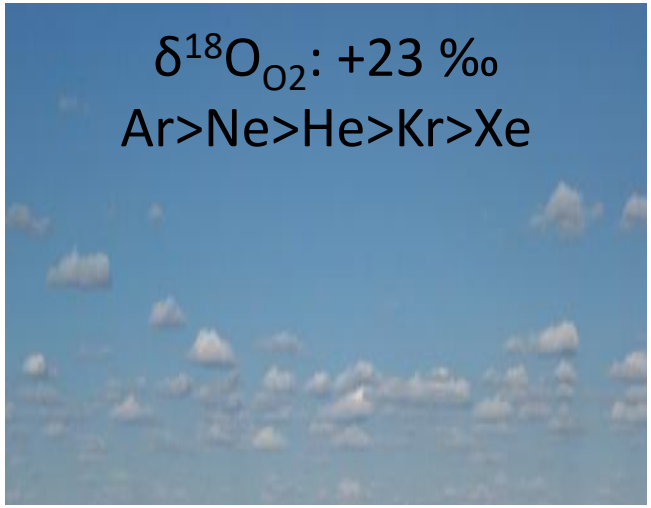

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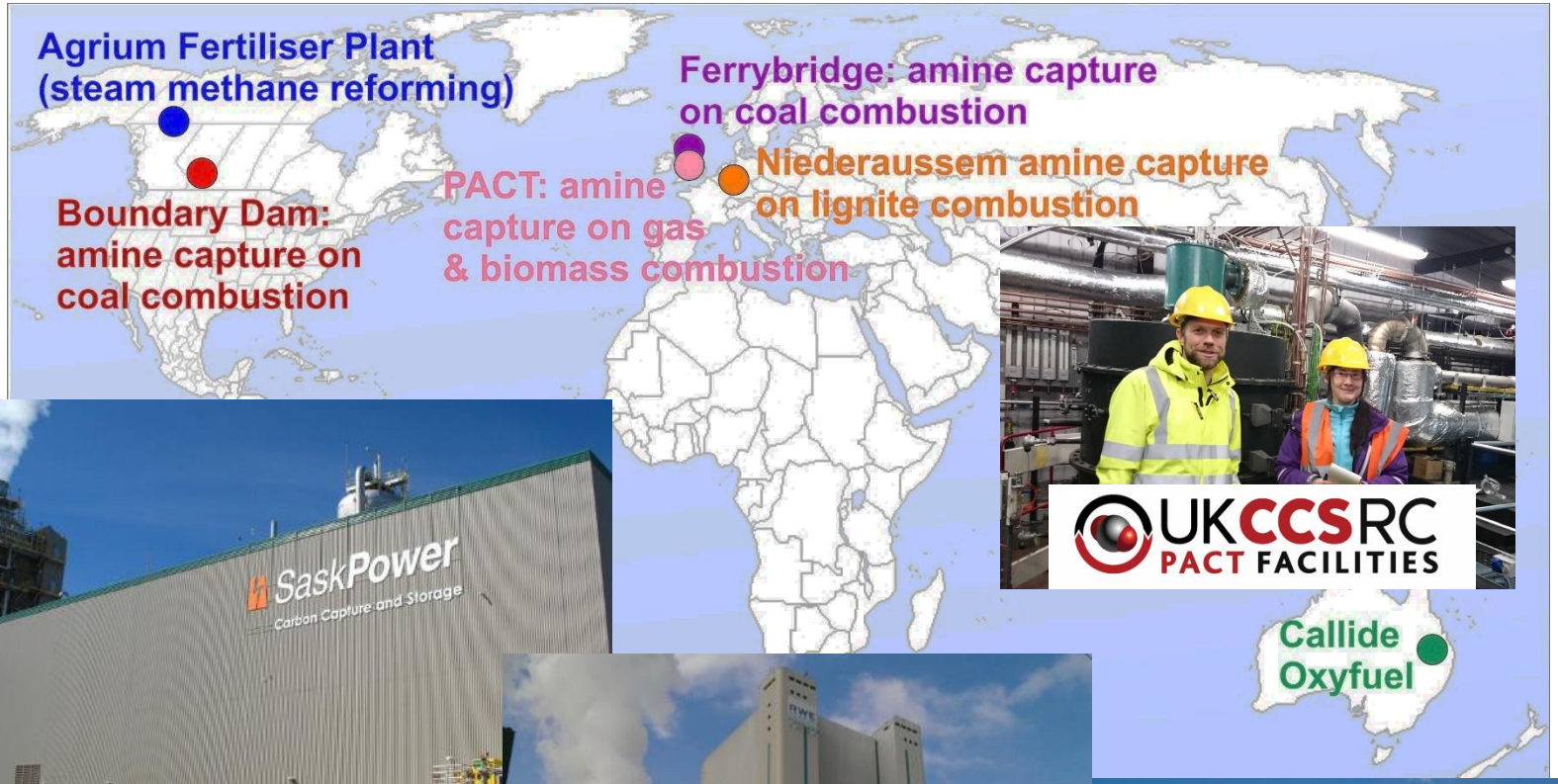
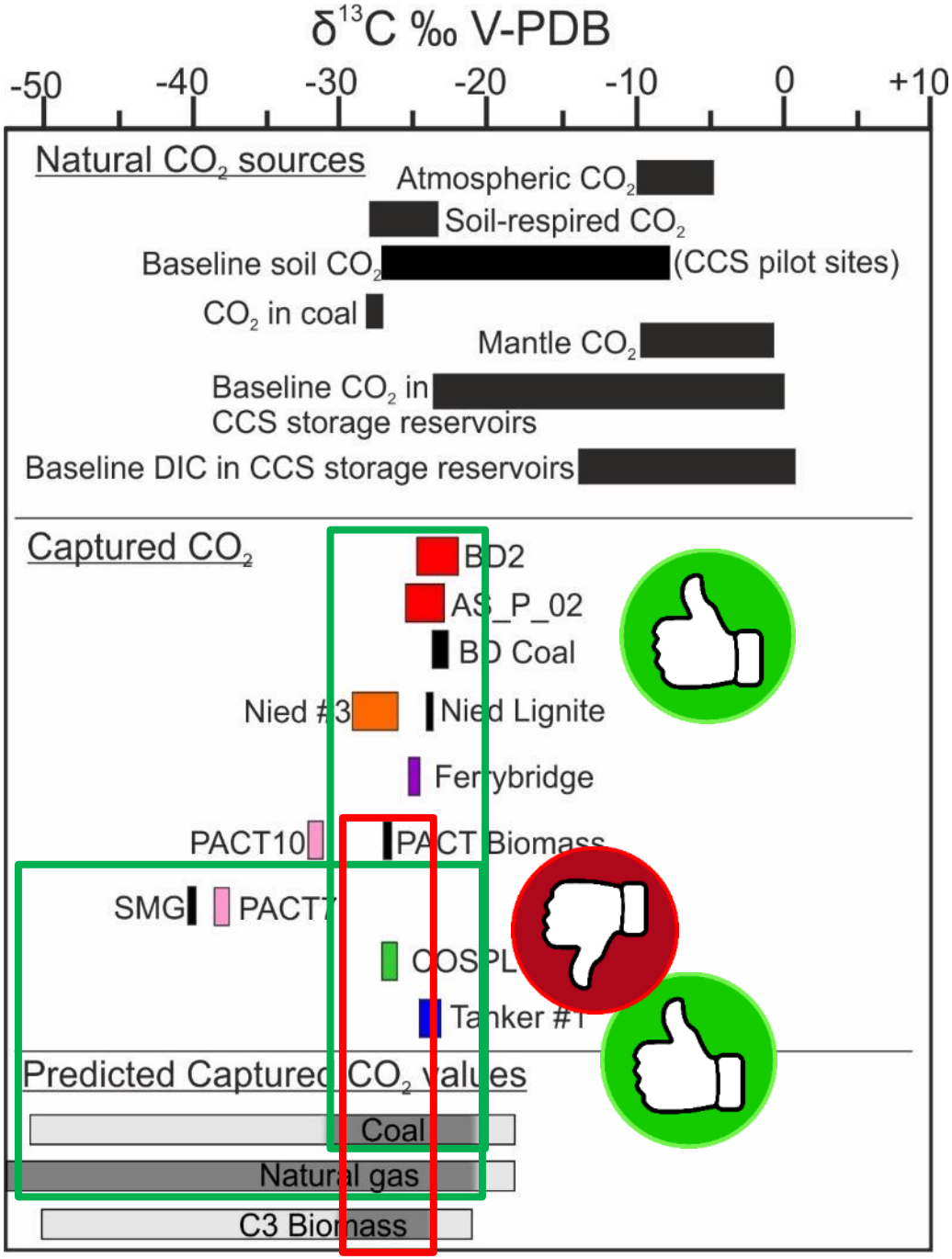
Captured CO_2 samples collected from:



sse

Results - $\delta^{13}C$

- Majority of coal and gas samples agree with expected fingerprints
- Biomass + amine capture samples show larger fractionation than expected
- Inherent $\delta^{13}C$ will be a useful tracer in many cases e.g. Shell QUEST Project



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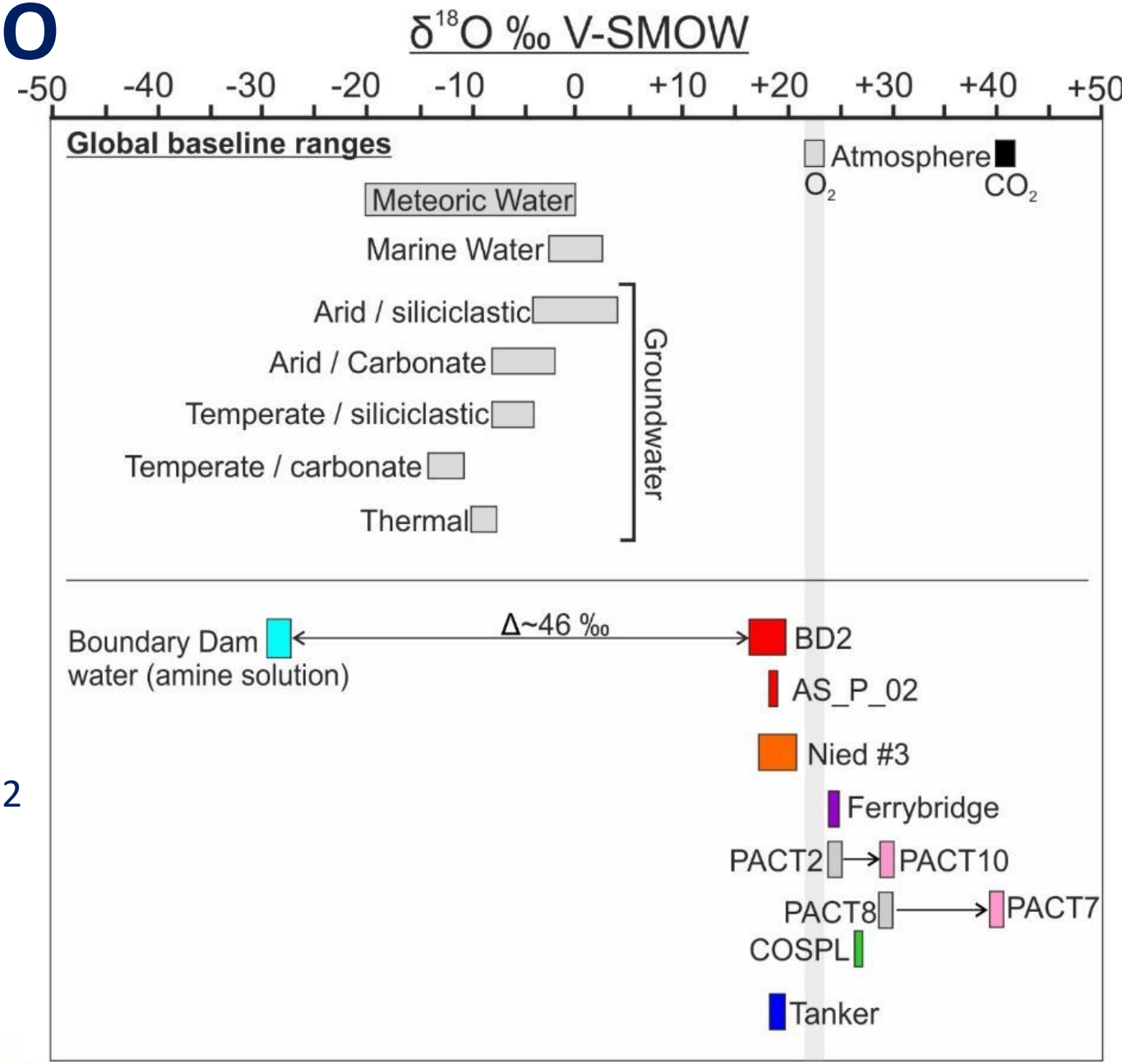
Results - $\delta^{18}O$

- Majority within 5‰ of atmosphere
- Influence of $\delta^{18}O_{H2O}$ is small
- Inherent $\delta^{18}O$ fingerprints will be useful for determining CO_2 pore space saturation in many cases



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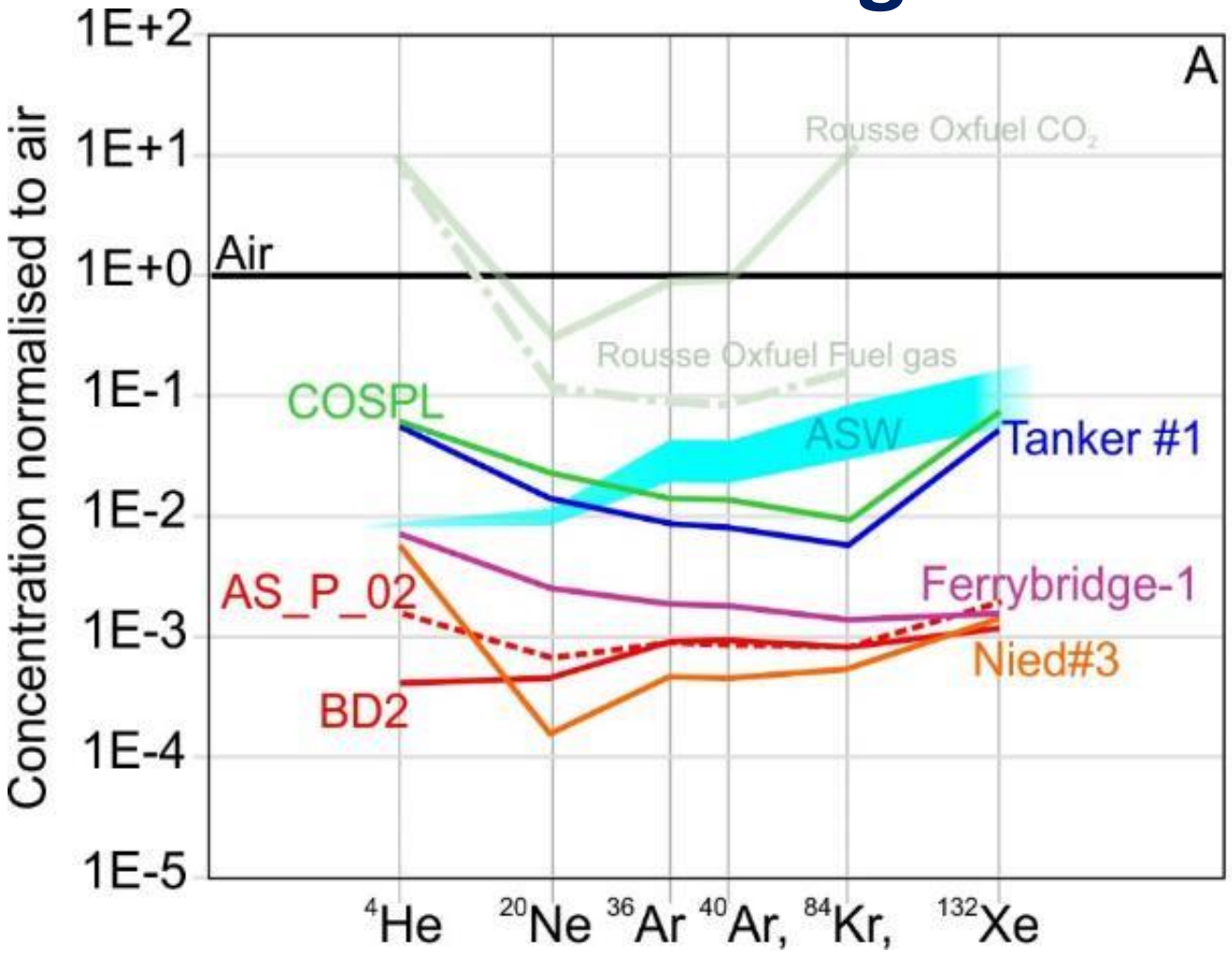
Results – Noble gases



- All exhibit low concentrations, with small radiogenic He component
- Significantly lower than air, and different to air-saturated water (ASW)

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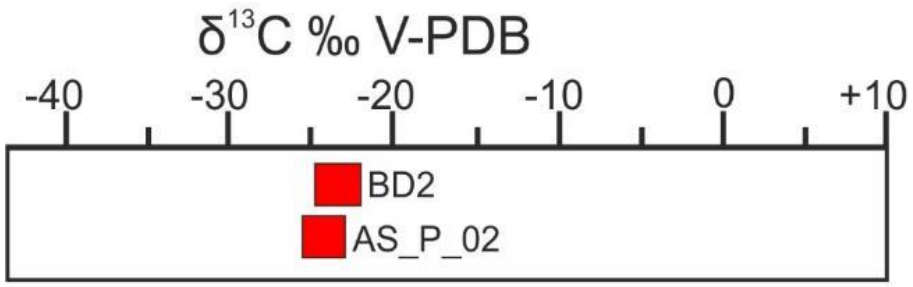
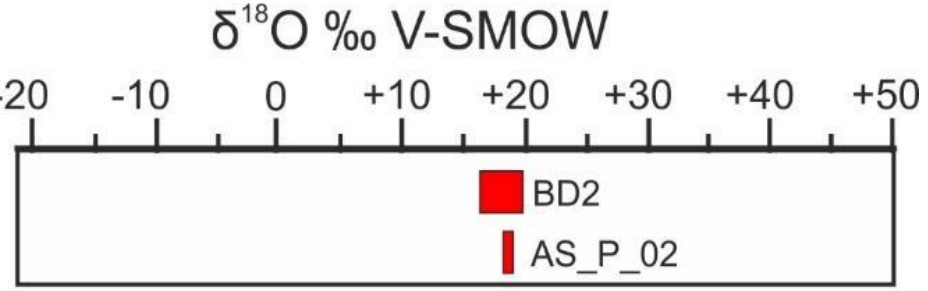
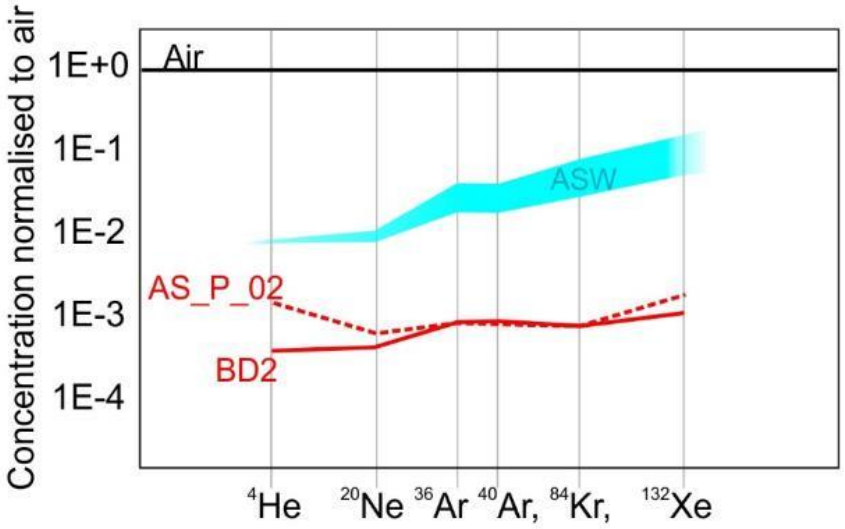
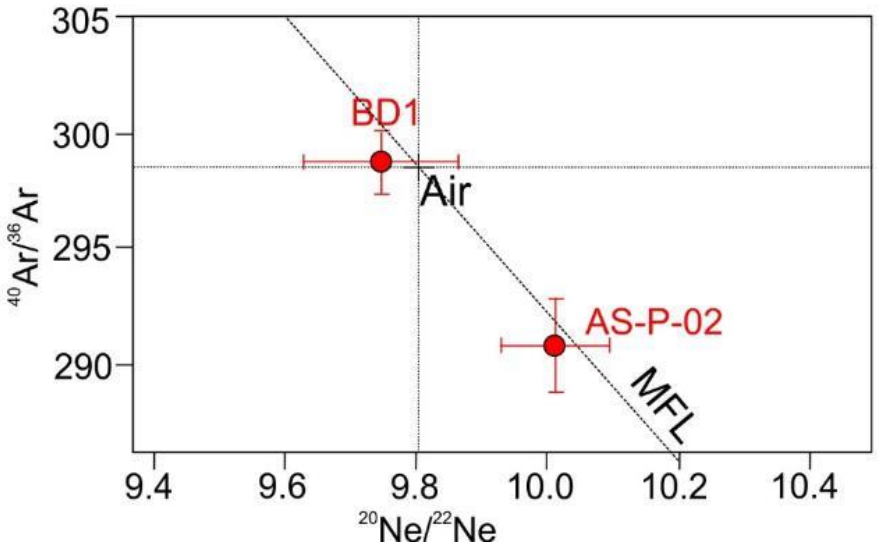
Are fingerprints retained after transport?









- Stable Isotopes of $\delta^{13}C$ and $\delta^{18}O$ are not significantly altered
- Noble gases appear fractionated by mass – could be due to sampling?

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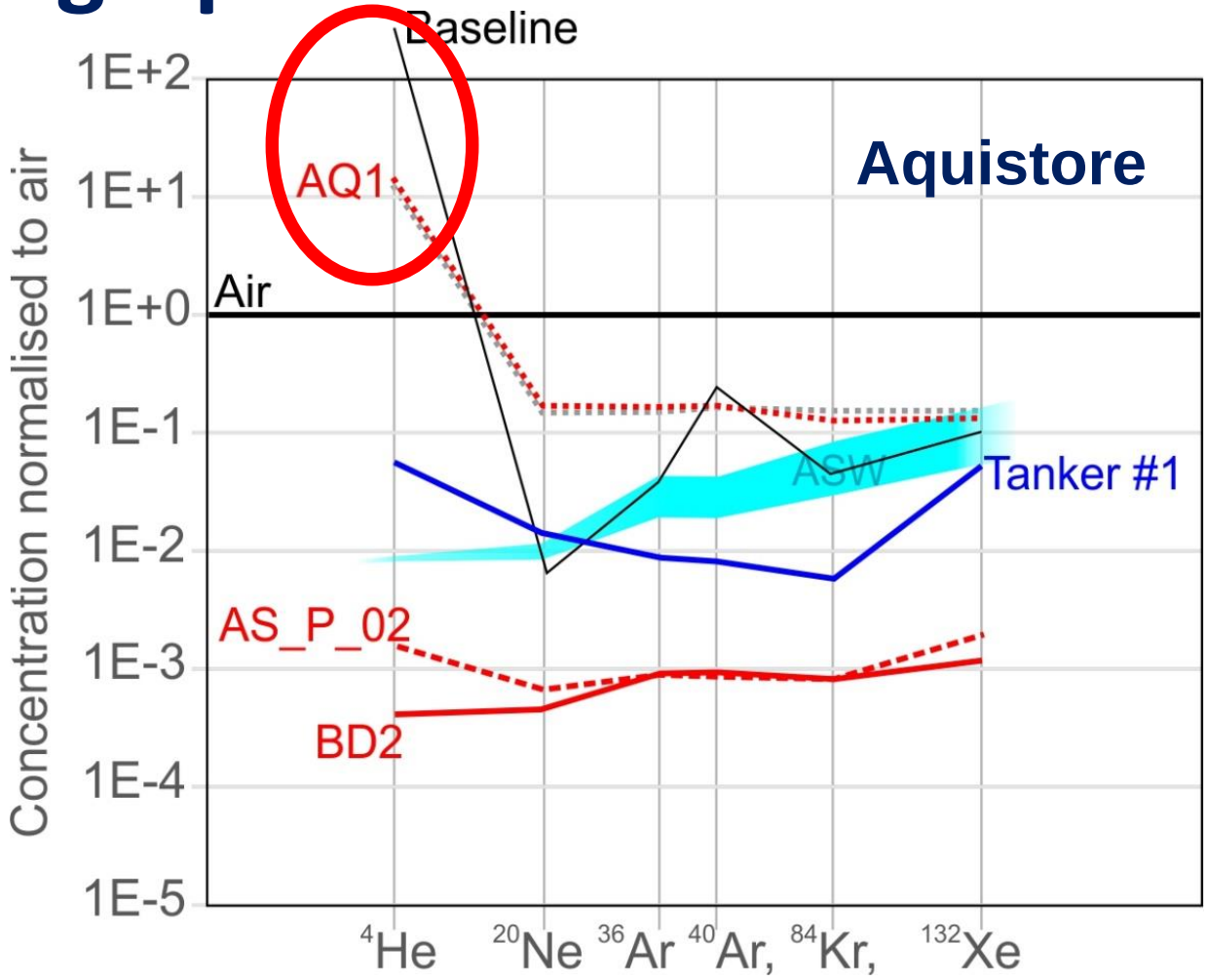
Are fingerprints retained after storage?



- AQ1 – produced CO_2 fingerprint complicated by air contamination
- Sample has inherited the high ^4He signature from the reservoir

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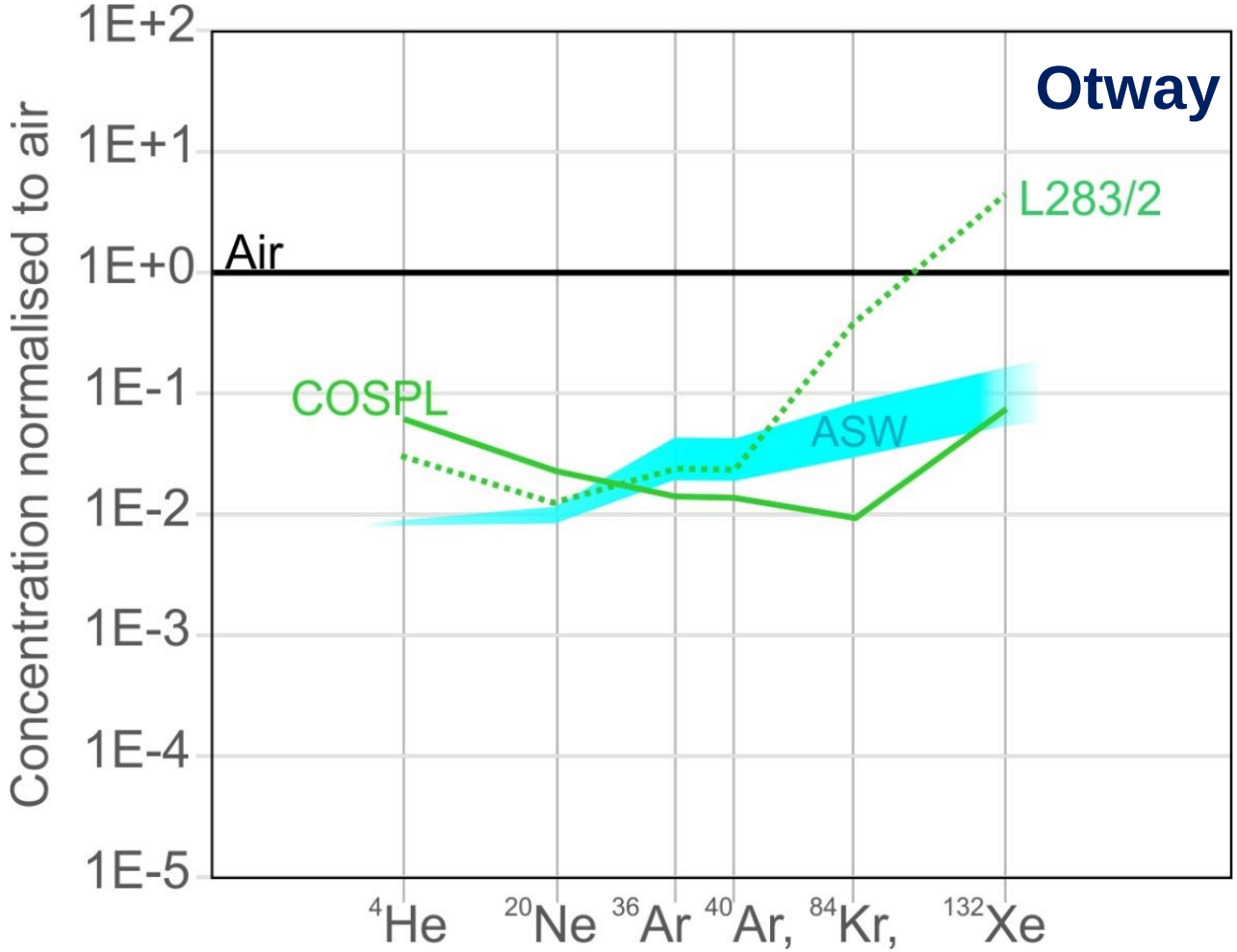
Are fingerprints retained after storage?



- L283/2 produced CO_2 shows mix of injected COSPL CO_2 with ASW
- Enrichment in Kr & Xe is due to artificial tracers added for Otway test

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The inherent tracer fingerprint of captured CO_2

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Scientists apply fingerprint test for CO2 storage

June 23, 2017

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A test developed by University scientists to check for leaks from carbon capture and storage (CCS) sites has been used for the first time.

Researchers made use of their pioneering test for CCS – in which man-made carbon dioxide emissions are stored deep underground – at a storage site in Canada.

Researchers from Scottish Carbon Capture & Storage (SCCS) have developed a way to measure tiny traces of inactive natural gases, known as noble gases, found in CO2.

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Summary

What is the inherent fingerprint of captured CO_2 & what controls it?

- $\delta^{13}C$ will be within 5 ‰ of the feedstock
- $\delta^{18}O$ will be similar to atmospheric O_2 for combustion derived CO_2 but influenced by combustion and capture efficiency
- Noble gas concentrations are low with relative element abundances and isotope ratios distinct from those in subsurface

Will it be retained during transport? **- Yes**

- Stable isotope fingerprint is preserved, noble gases may fractionate

Will it be a useful subsurface tracer? **- Yes**, but with caveats

- Stable isotopes can fractionate & be overprinted by natural CO_2
- Radiogenic noble gas fingerprint from reservoir will be inherited by injected CO_2 and serve as a distinctive tracer for CO_2 migration

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