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Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL

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# A natural analogue study of CO<sub>2</sub>-cement interaction: carbonation of calcium silicate hydrate-bearing rocks from Northern Ireland

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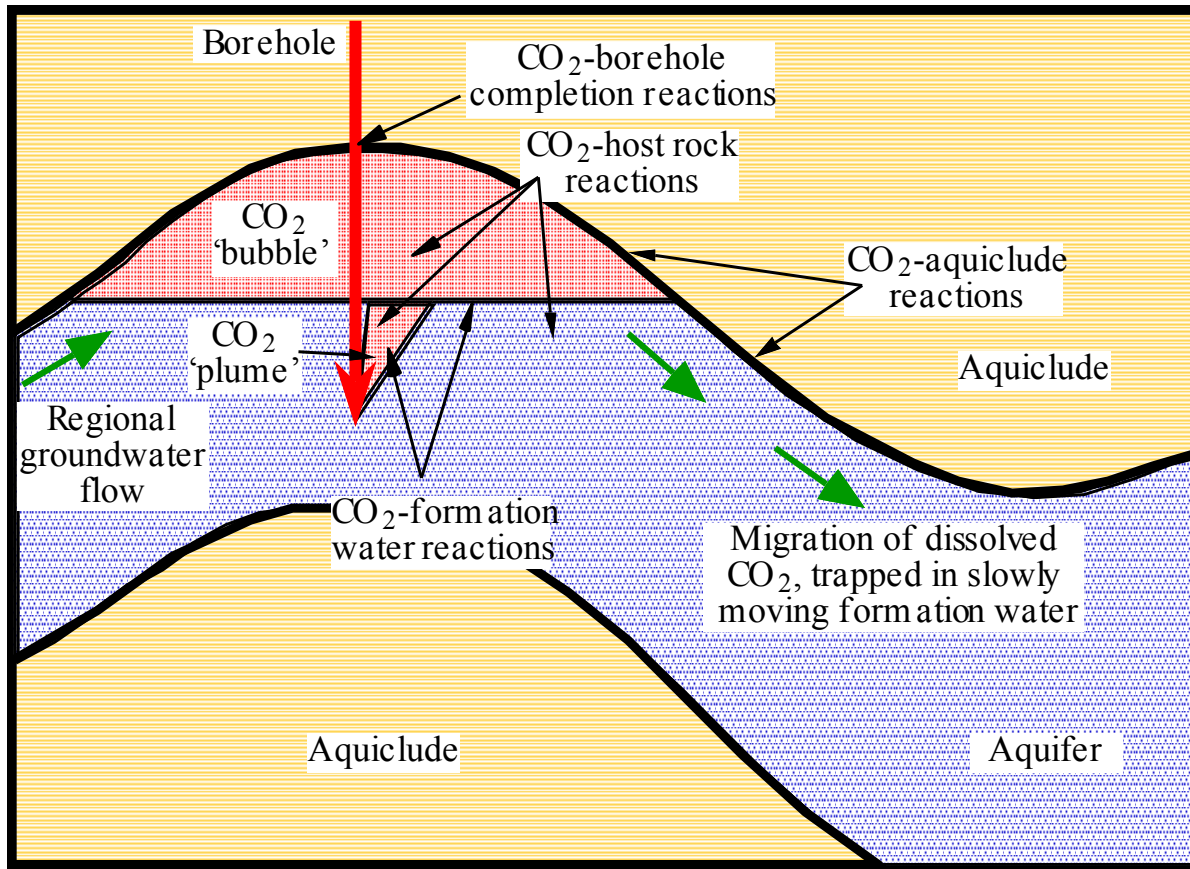
# Introduction - 1

- Storage of CO<sub>2</sub> as supercritical CO<sub>2</sub> in deep saline aquifers and depleted oil and gas reservoirs is being considered in Carbon Capture and Storage (CCS) solutions for controlling atmospheric CO<sub>2</sub> emissions
- Crucial aspect for underground CCS is that man-made seals must remain effective for thousands of years
- Oilfield cement technology will possibly be used for sealing injection wells
- Oilfield cements were used in old pre-existing hydrocarbon production and exploration wells completions

# Introduction - 2

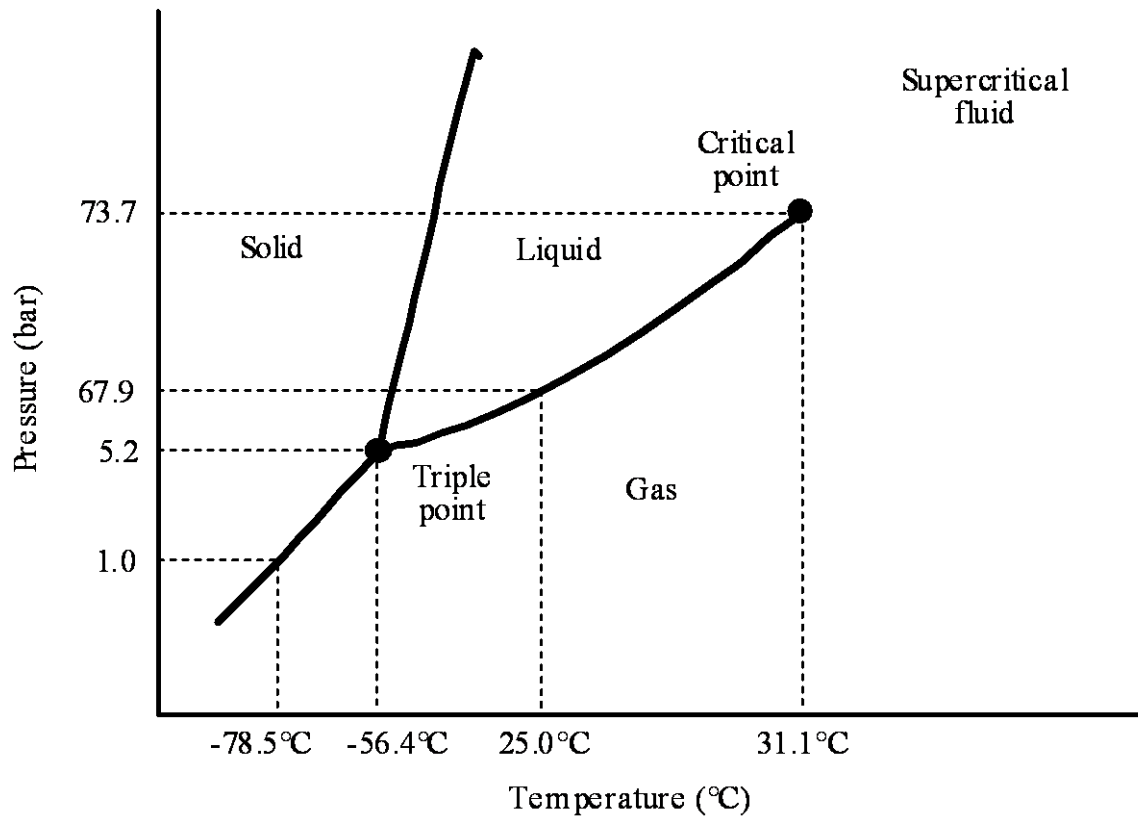
- Oilfield cements based on Ordinary Portland Cement (e.g. Type-G cement)
- Experimental data and observations for long-term behaviour of cement do not exist for such timescales
- Natural analogue systems may provide an insight into the long-term behaviour of cement used for well completion and sealing in CCS schemes

# Concept for CCS aquifer or reservoir storage



- Simple schematic diagram of different parts of the storage system
- Several CO<sub>2</sub> injection and interactions with formation water, interaction with host rock
- Interaction with caprock
- Interaction with borehole completions

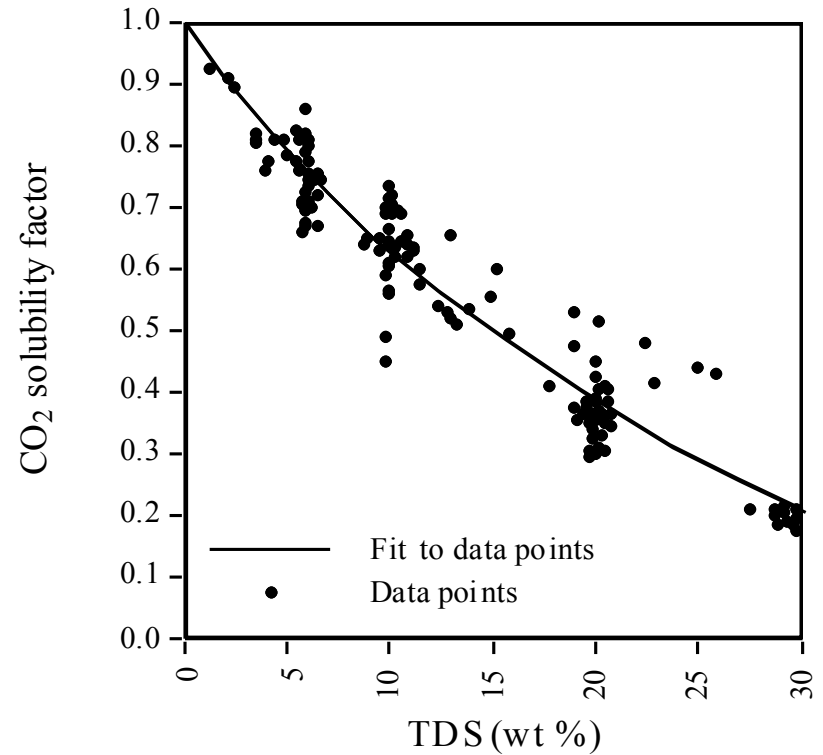
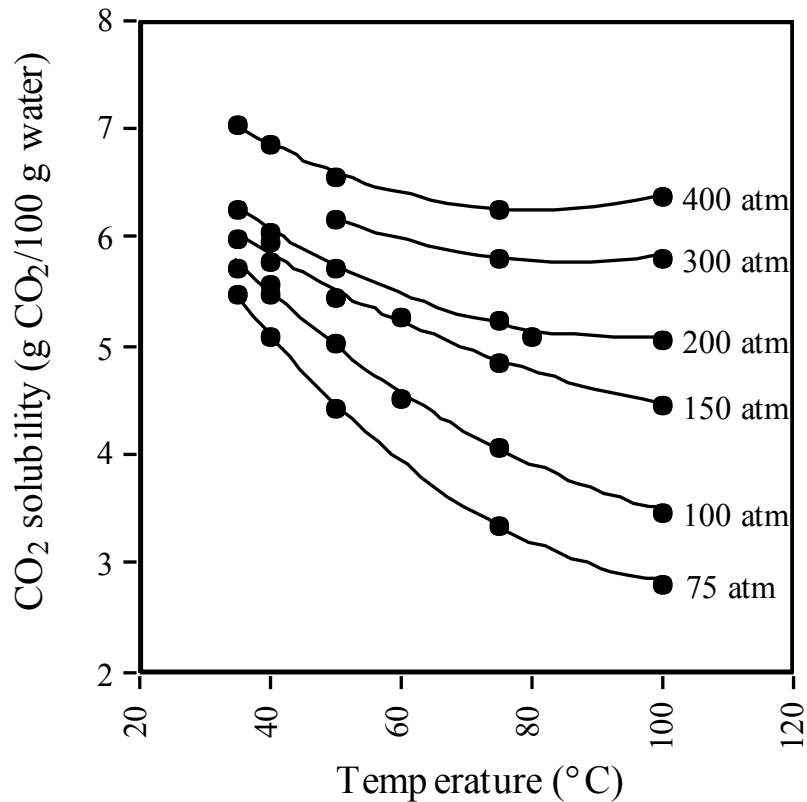
# Efficient CCS requires storage as supercritical CO<sub>2</sub>



➤ Storage as supercritical CO<sub>2</sub> reduces volume requirement

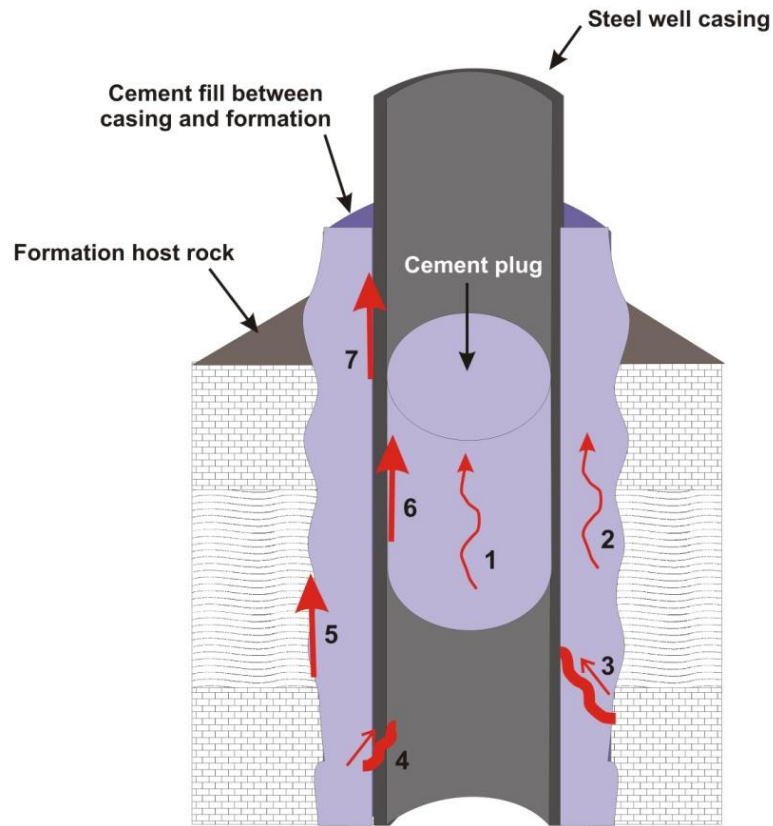
➤ Requires depth >800 m in most reservoirs or aquifers under normal geothermal gradient (UK, western Europe)

# Solubility of CO<sub>2</sub> in water



- Solubility increases with pressure
- Solubility decreases with temperature
- Solubility decreases with salinity

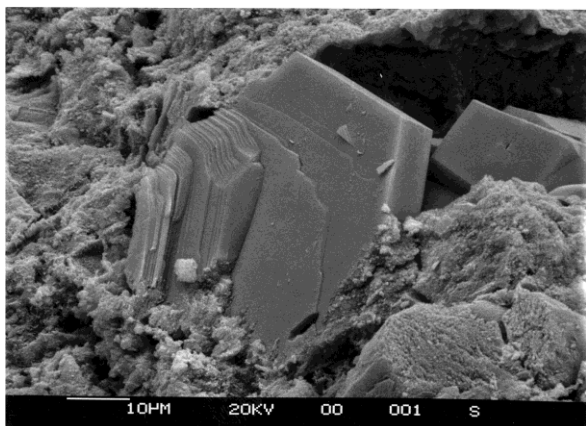
# Issues 1 – CO<sub>2</sub> leakage pathways



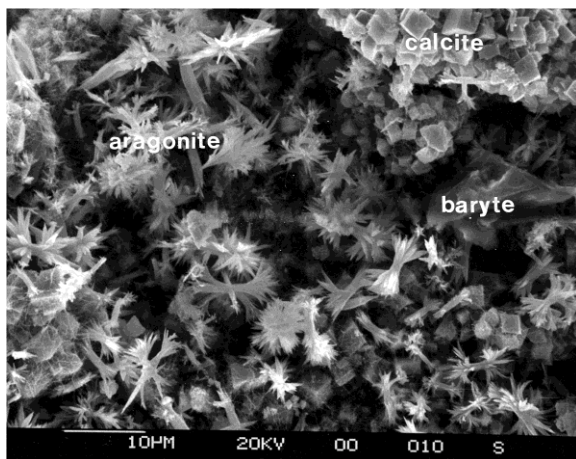
Schematic diagram illustrating CO<sub>2</sub> leakage at interfaces in a well completion (Milodowski et al., based on Gasda et al., 2004)

1. Leakage through cement plug matrix within the well casing
2. Leakage through cement matrix fill between the well casing and the host formation
3. Leakage from the formation into the well through fractures in the casing-formation cement fill
4. Leakage from the formation into the completed well through corrosion failure of the steel casing
5. Leakage along an external annulus developed between the formation and the cement fill
6. Leakage along an annulus developed between the cement plug and the internal casing wall
7. Leakage along an annulus developed between the cement fill and the external casing wall.

# Issues 2 – behaviour of cement with CO<sub>2</sub>



Hydrated Type-G oilfield cement fabric (Robins & Milodowski, 1982)



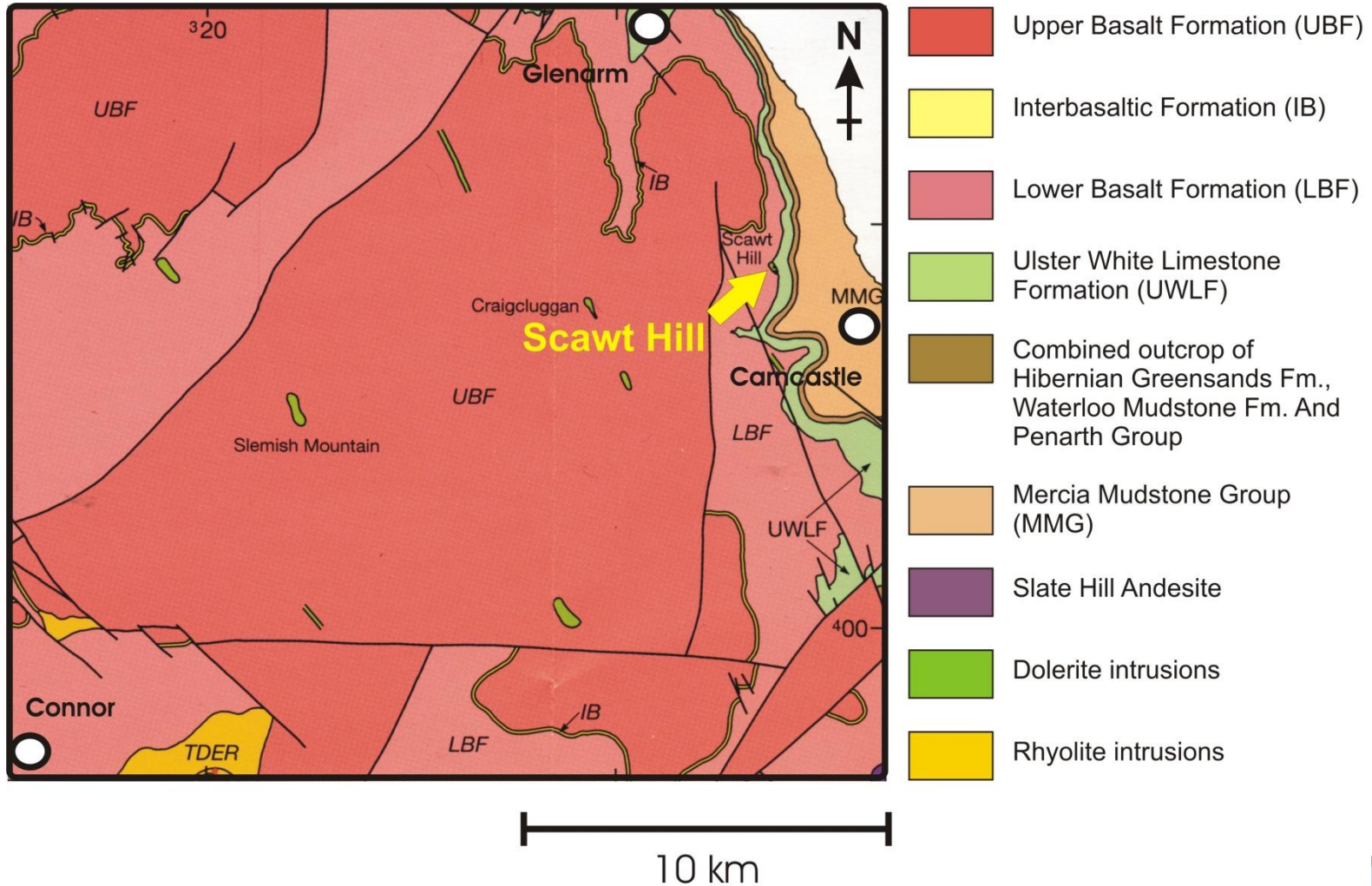
Hydrated Type-G reacted with supercritical CO<sub>2</sub> (Robins & Milodowski, 1982)

- Stability and integrity of cement seal is important to prevent CO<sub>2</sub> leakage and corrosion of steel liners
- The formation of carbonate occurs either by:
  1. Reaction of HCO<sub>3</sub> – CO<sub>2</sub> dissolved in groundwater
  2. Direct reaction with supercritical CO<sub>2</sub>
  3. Reaction with gaseous CO<sub>2</sub>
- Major change in molar volume between cement phases and carbonate alteration products but dependant on quality of molar volume data available (Rochelle et al., 2004)
  - Carbonation of tobermorite [CSH(I)] +17% to -33% predicted depending on molar volume database used
- Disagreement in literature on the impact of CO<sub>2</sub> with cement
  - Some experimental studies suggest sealing of cement porosity
  - Some experimental studies suggest increased porosity and loss of strength and structure

# Northern Ireland Natural Analogues - Location



# Scawt Hill - Geology

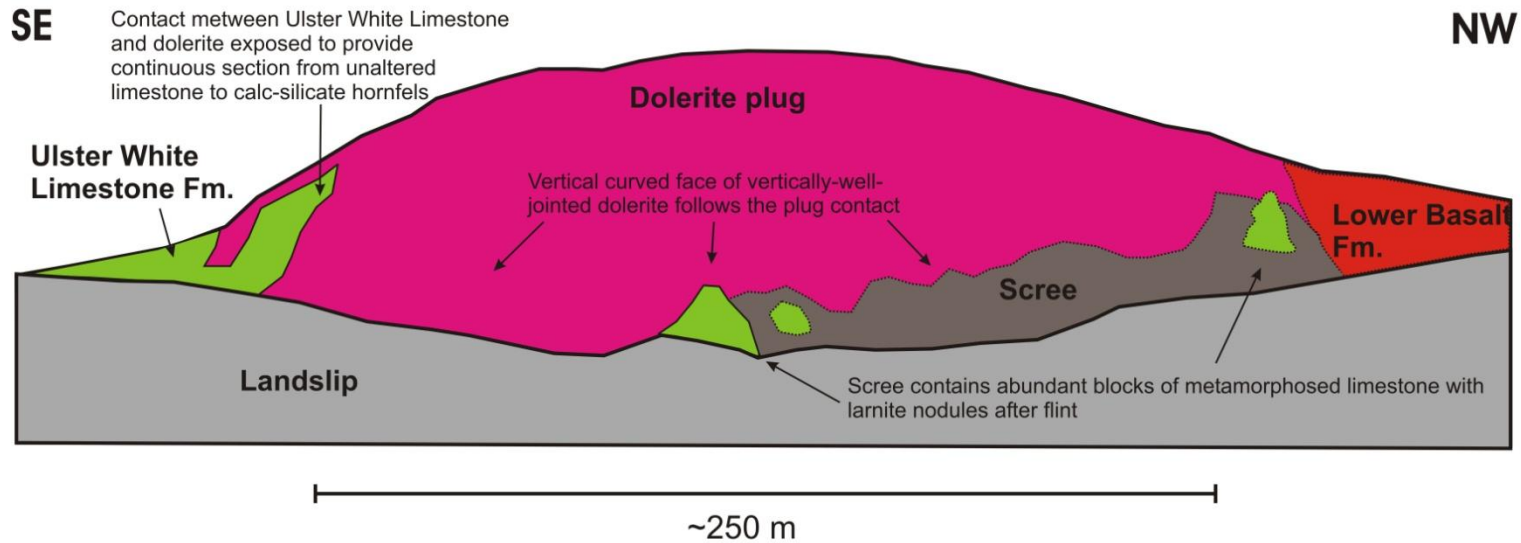


# Scawt Hill, Co. Antrim



The hill rises as a prominent knoll above the flat Antrim Plateau Escarpment (Tertiary Lower Basalt Formation)

# Scawt Hill – Schematic geology



# Scawt Hill – Metamorphic contact zone



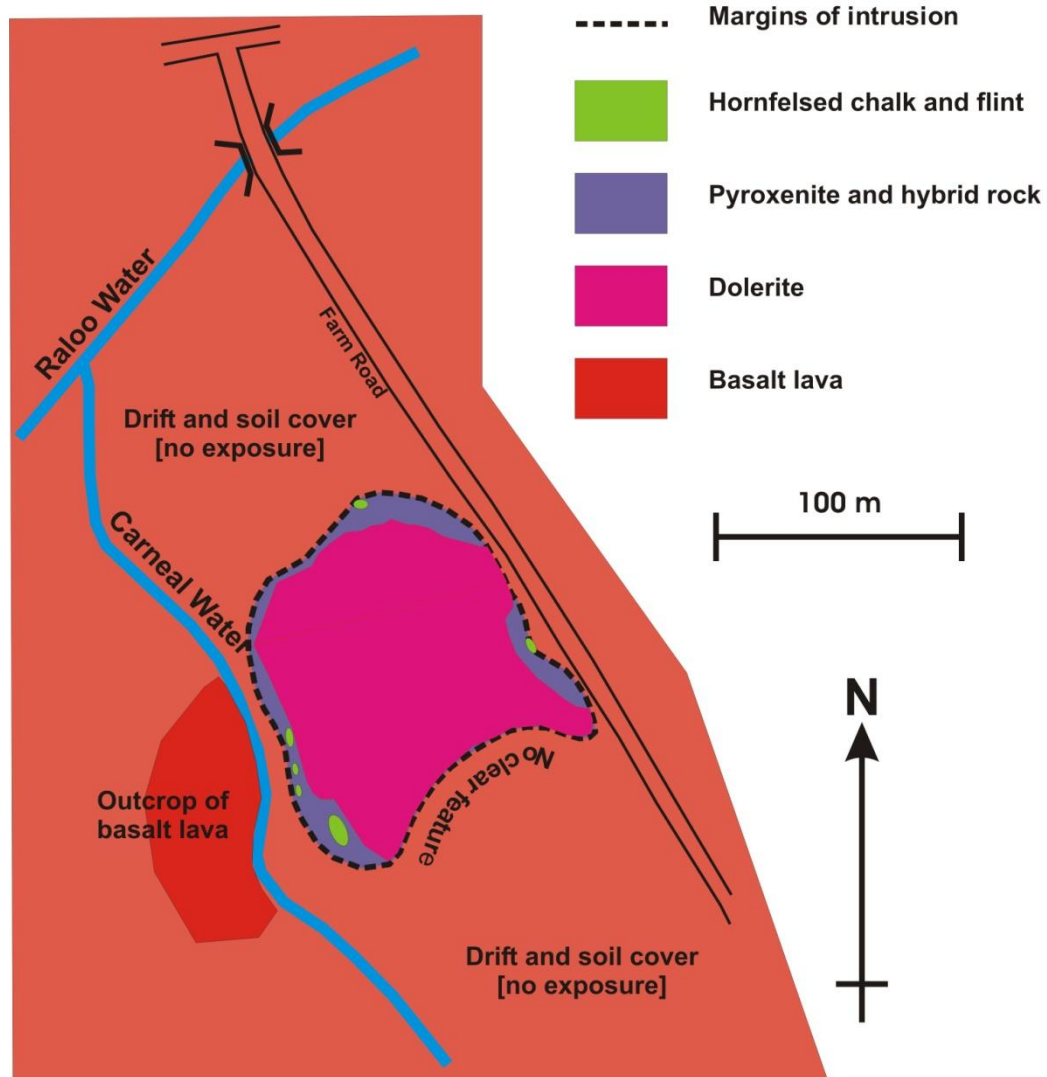
# Scawt Hill – Metamorphosed chert (flint)



- Original chert (flint) nodules metamorphosed to calcium silicates (e.g. Larnite)
- Very hydrous CSH gel-like phases formed by hydration and alteration of a calcium silicate (larnite) nodule, which was revealed in a freshly broken open block of marble from Scawt Hill.
- CSH gels freshly exposed are very moist and gel-like

**PLEASE NOTE: FLINTS CAN BE VERY SHARP!!!!!!**  
**When not altered!**

# Carneal Plug – Geology



# Carneal Plug – Metamorphosed chert (flint)



➤ Metasomatised and partially assimilated xenolith of Ulster White Limestone Formation exposed in old quarry

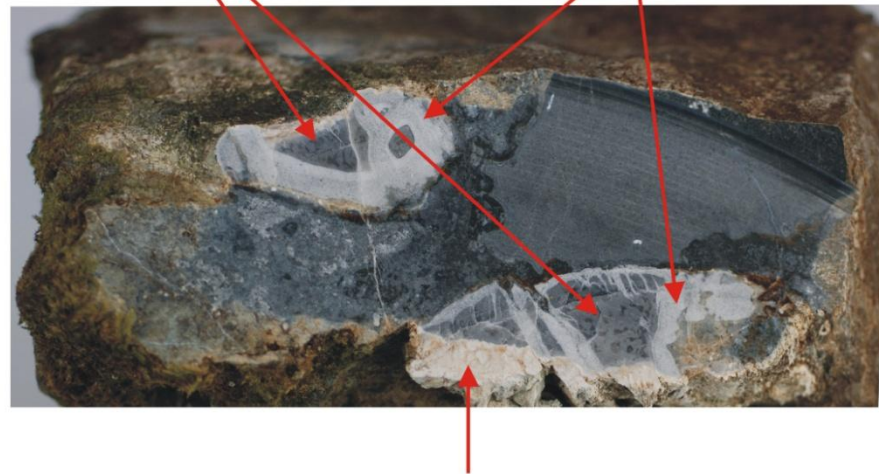


➤ Highly metasomatised and partially assimilated hornfelsed xenolith of Ulster White Limestone Formation rock, containing metamorphosed chert concretions. The rock is irregularly veined by dark hybrid pyroxenite.

# Calcium silicate nodule alteration – Carneal Plug 1

Core of metamorphosed chert nodule, composed mainly of quartz and calcite

Rim of metamorphosed chert nodule, composed mainly of quartz and wollastonite, with minor xonotlite

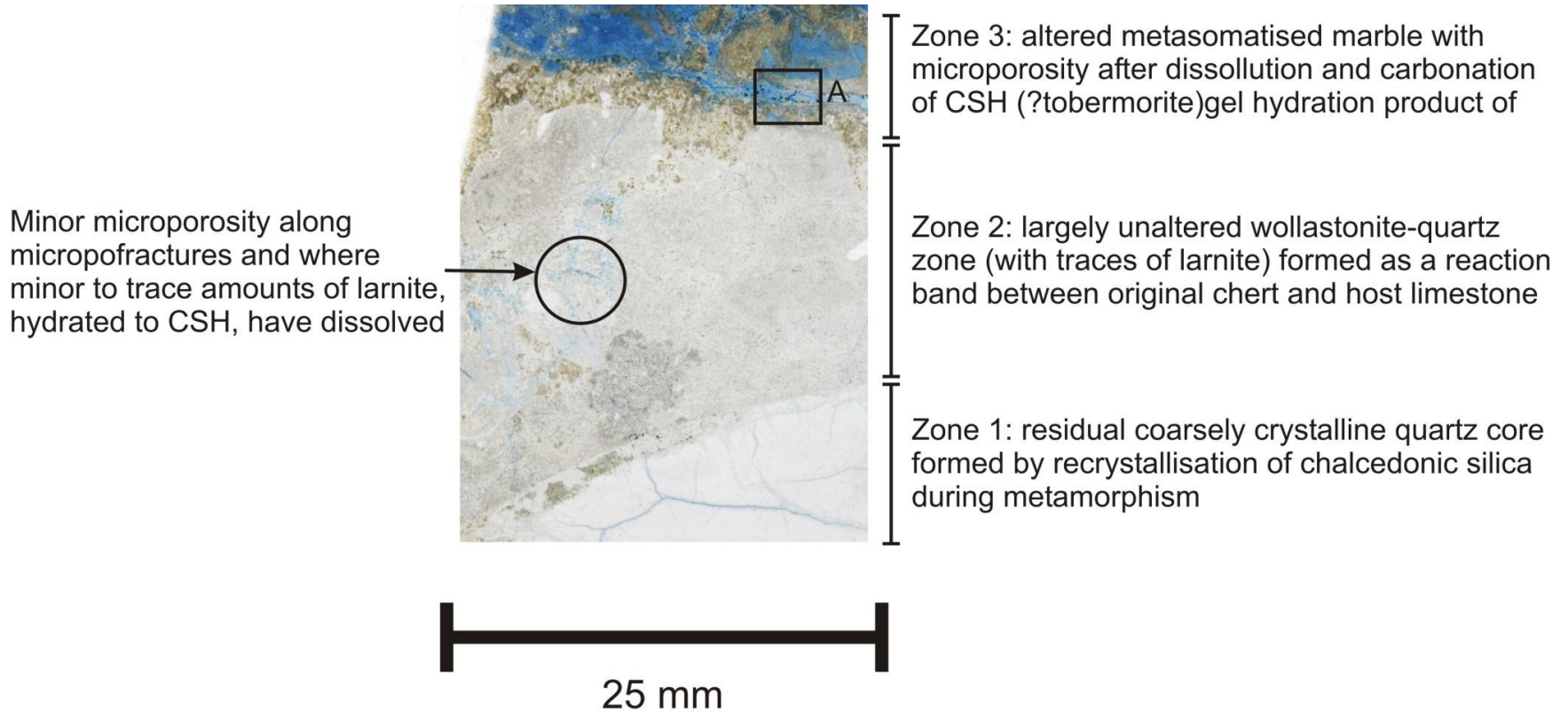


Carbonate and silica-rich weathering alteration on exposed surface of block



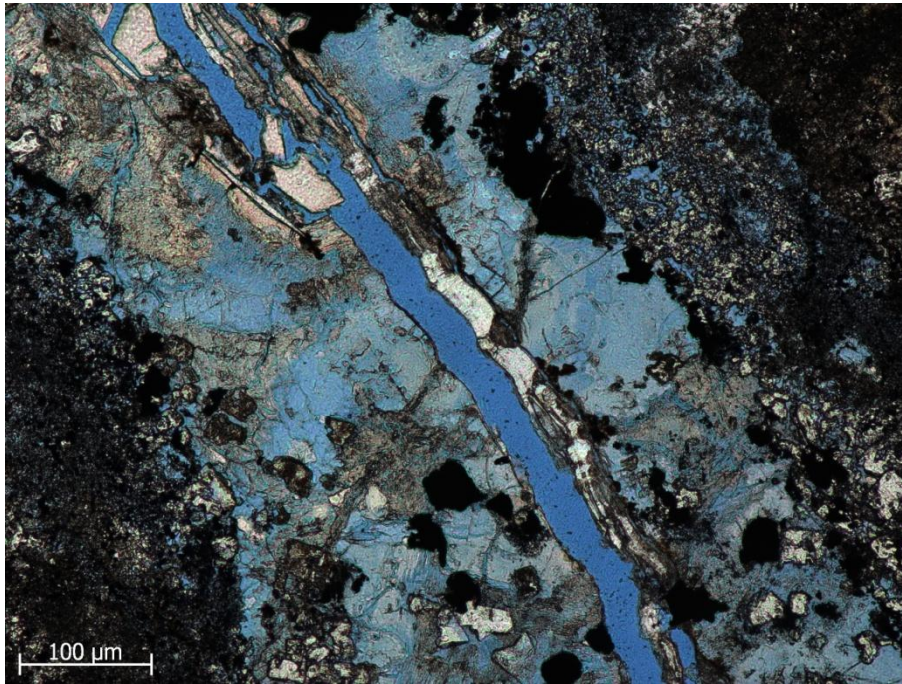
Section through an altered calcsilicate nodule from Carneal Plug

# Calcium silicate nodule alteration - Carneal Plug 2



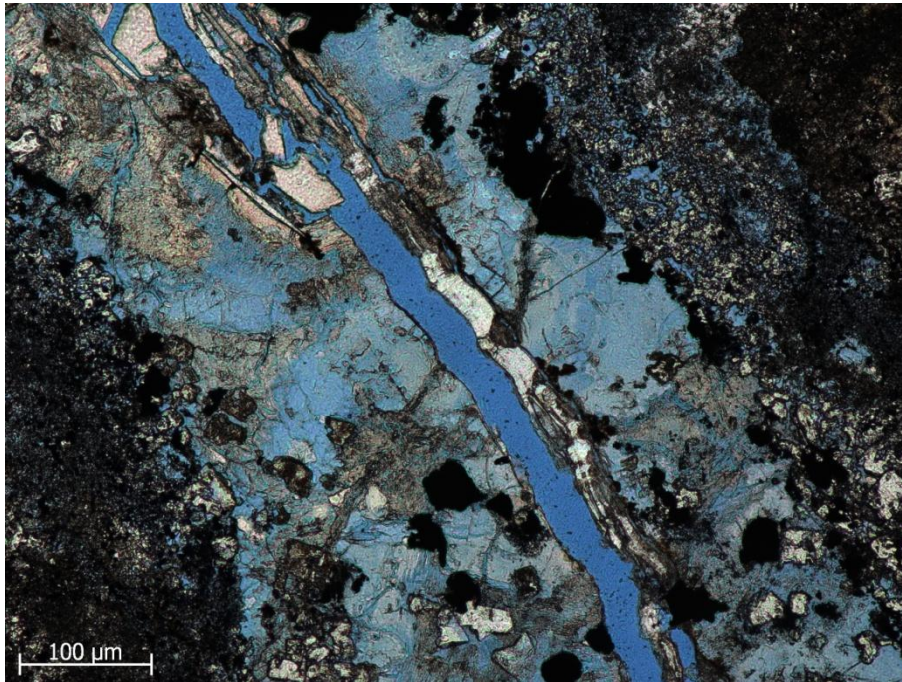
Optical petrography of an altered calcsilicate nodule from Carneal Plug.

# Calcium silicate nodule alteration - Carneal Plug 3



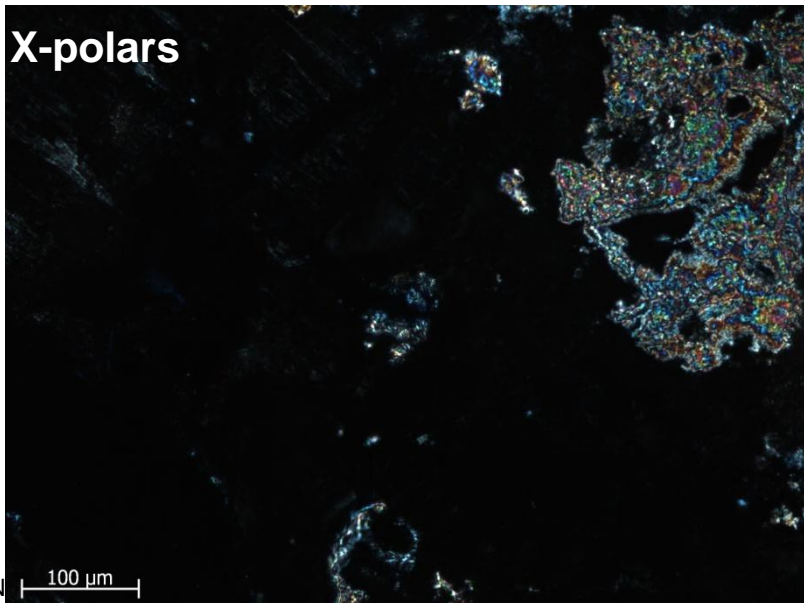
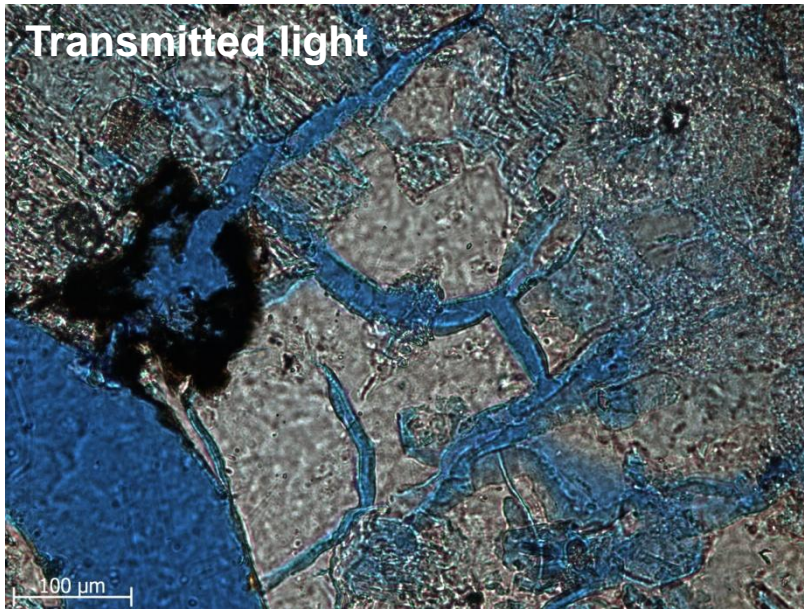
- Interface between granular wollastonite-quartz zone (bottom left) and larnite-bearing skarn host rock containing abundant opaque magnetite (top right).
- Microporous CSH gel (shown by blue epoxy-resin impregnation) is largely altered to Si-rich gel
- Diffuse relicts of gel-like CSH with a higher Ca:Si ratio (seen as areas that are less intensely coloured by the blue epoxy-resin).
- The CSH alteration preserves the original grain outlines of the primary larnite.
- Microgranular calcium carbonate (uncoloured) nucleated within the altered CSH gel and coarse calcite lines a microfracture created by shrinkage of the altered CSH gel.

# Calcium silicate nodule alteration - Carneal Plug 4



- Interface between granular wollastonite-quartz zone (bottom left) and larnite-bearing skarn host rock containing abundant opaque magnetite (top right).
- Microporous CSH gel (shown by blue epoxy-resin impregnation) is largely altered to Si-rich gel
- Diffuse relicts of gel-like CSH with a higher Ca:Si ratio (seen as areas that are less intensely coloured by the blue epoxy-resin).
- The CSH alteration preserves the original grain outlines of the primary larnite.
- Microgranular calcium carbonate (uncoloured) nucleated within the altered CSH gel and coarse calcite lines a microfracture created by shrinkage of the altered CSH gel.

# Calcium silicate nodule alteration - Carneal Plug 5



➤ Shrinkage of CSH gel (CSH (I)/tobermorite

➤ Replacement of CSH by micogranular calcite

# Calcium silicate nodule alteration – Scawt Hill



Zone 3: porous, leached, weathered outer layer (Zone III) composed of major calcite, with minor to trace quartz, silica, residual CSH, scawtite

Zone 2: tight, finely crystalline intergrowth of calcite with minor to trace gypsum, quartz and scawtite

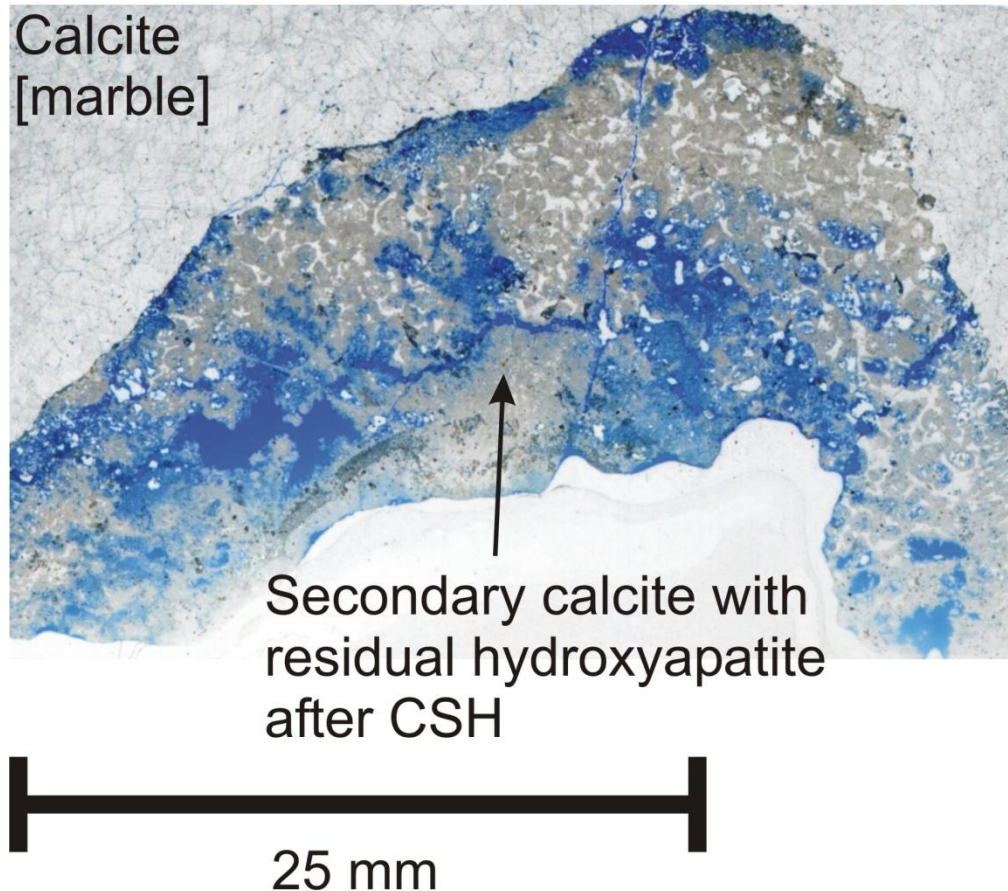
Zone 1: tight, coarsely crystalline intergrowth of calcite, larnite, spurrite, paraspurrite, and scawtite

Reaction front finely crystalline intergrowth of calcite, quartz and scawtite

50 mm

Section through an altered calcsilicate nodule from Scawt Hill

# Calcium silicate nodule alteration – Scawt Hill



Optical petrography of an altered calcsilicate nodule from Scawt Hill

# Calcium silicate nodule alteration – Scawt Hill



Zoned alteration:

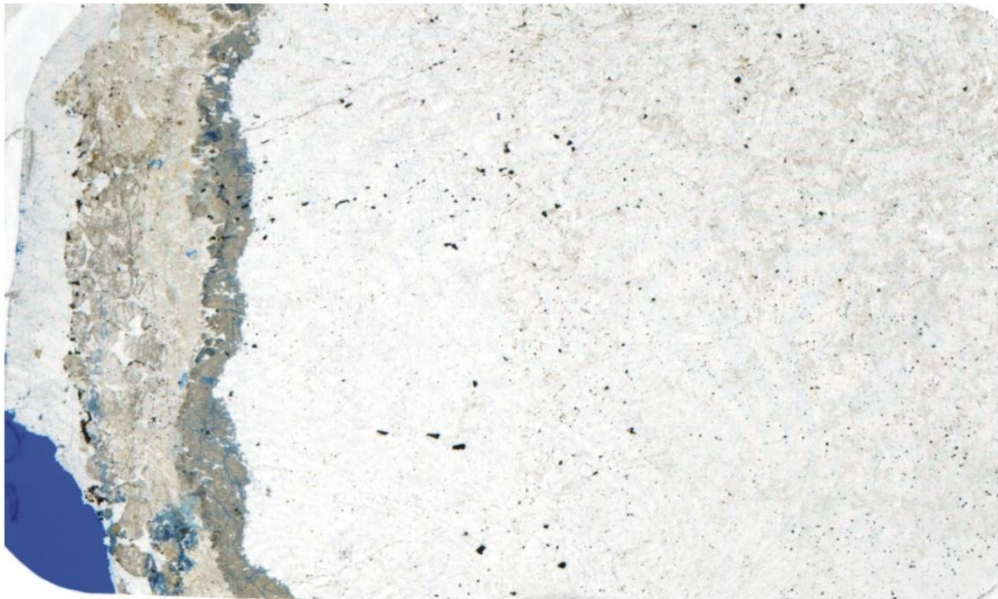
A - quartz-rich zone with minor larnite;

B – larnite with minor spurrite or paraspurrite;

C – Inner zone of the late-stage alteration rim, with secondary porosity highlighted by blue resin;

D – zone of carbonation reaction with scawtite, amorphous silica and calcium carbonate;

E – host marble.



2.5 mm

Optical petrography of an altered calcsilicate nodule from Scawt Hill

# Summary mineralogy and alteration sequence

## **1. Unaltered cores:**

***Primary metamorphic assemblage [1050-1100°C, about 200 bars]***

- Quartz,
- Larnite, wollastonite
- Bredigite
- Brownmillerite
- Spurrite, paraspurrite

## **2. Early hydrothermal alteration:**

- Xonotolite
- Magnetite

## **3. Late hydration**

***[<100°C for CSH gel and probably <160°C for tobermorite]***

- Tobermorite, CSH gel, ettringite, gypsum

## **4. Carbonation – Replacement of tobermorite, CSH, ettringite**

- Scawtite
- Calcite, aragonite, vaterite
- Silica

# Comparison with flow-through experimental conditions

## **Experiment Run 1236 (Cement Plug “T2”)**

- Sleipner-type oil well cement
- Reacted with dry CO<sub>2</sub>
- 30 C, 80 bar [8 MPa], 62 days reaction time

## **Experiment Run 1237 (Cement Plug “T3”)**

- Sleipner-type oil well cement
- Reacted with synthetic Utsira (saline) formation water saturated with CO<sub>2</sub>
- Fluid : cement ratio = 2:1
- 30 C, 80 bar [8 MPa], 63 days reaction time

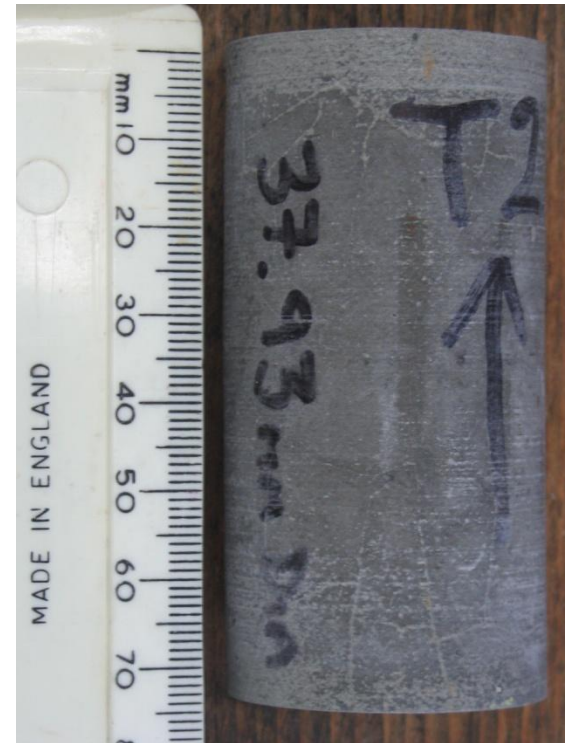
## **Experiment Run 1237 (Cement Plug “T3”)**

- High-temperature (IFP) oil well cement
- Reacted with dry CO<sub>2</sub>
- Fluid : cement ratio = 2:1
- 130 C, 300 bar [30 MPa], 62 days reaction time

# Experiment Run 1236 (Cement Plug "T2")



Initial cement plug

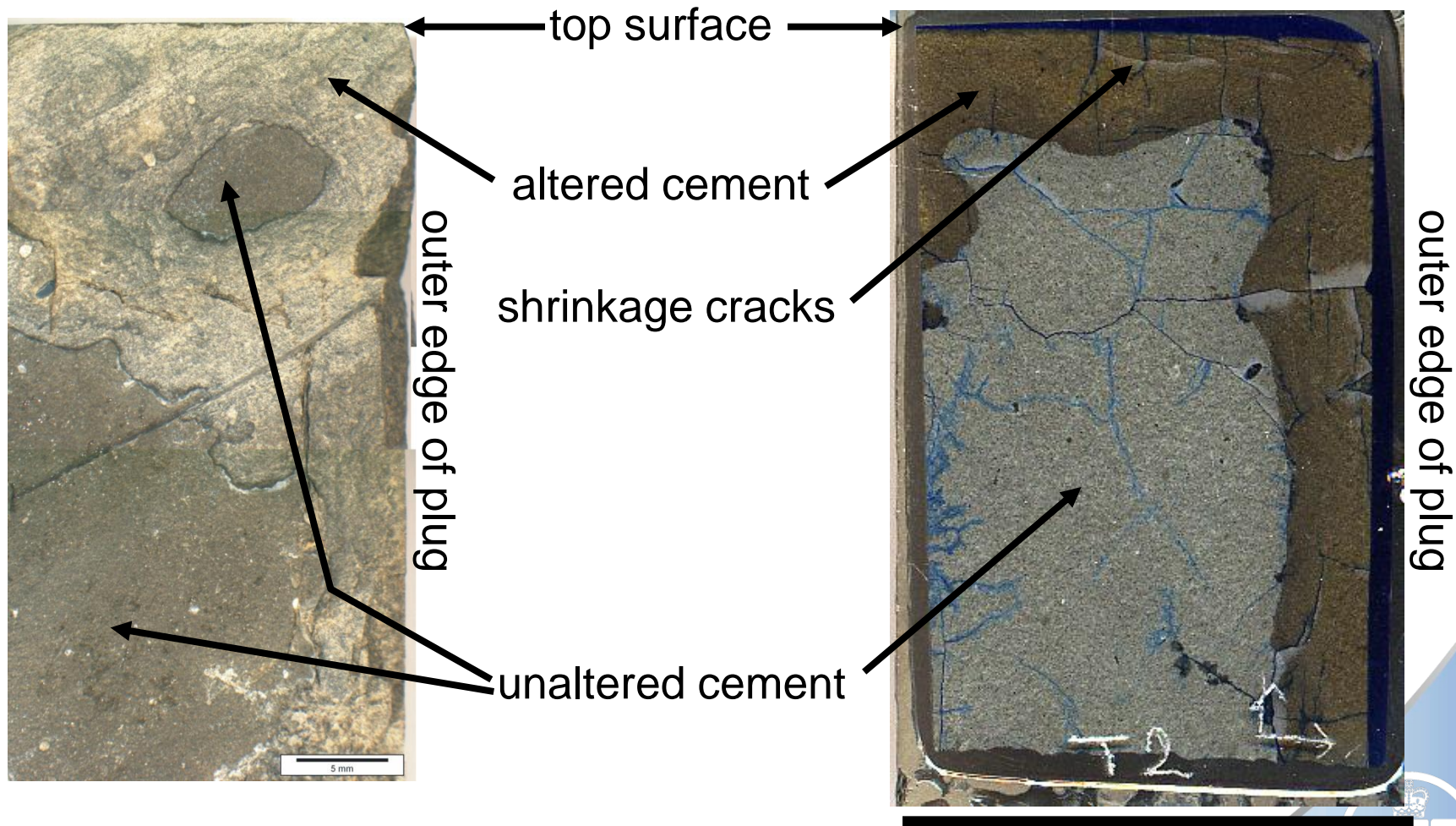


Reacted cement plug

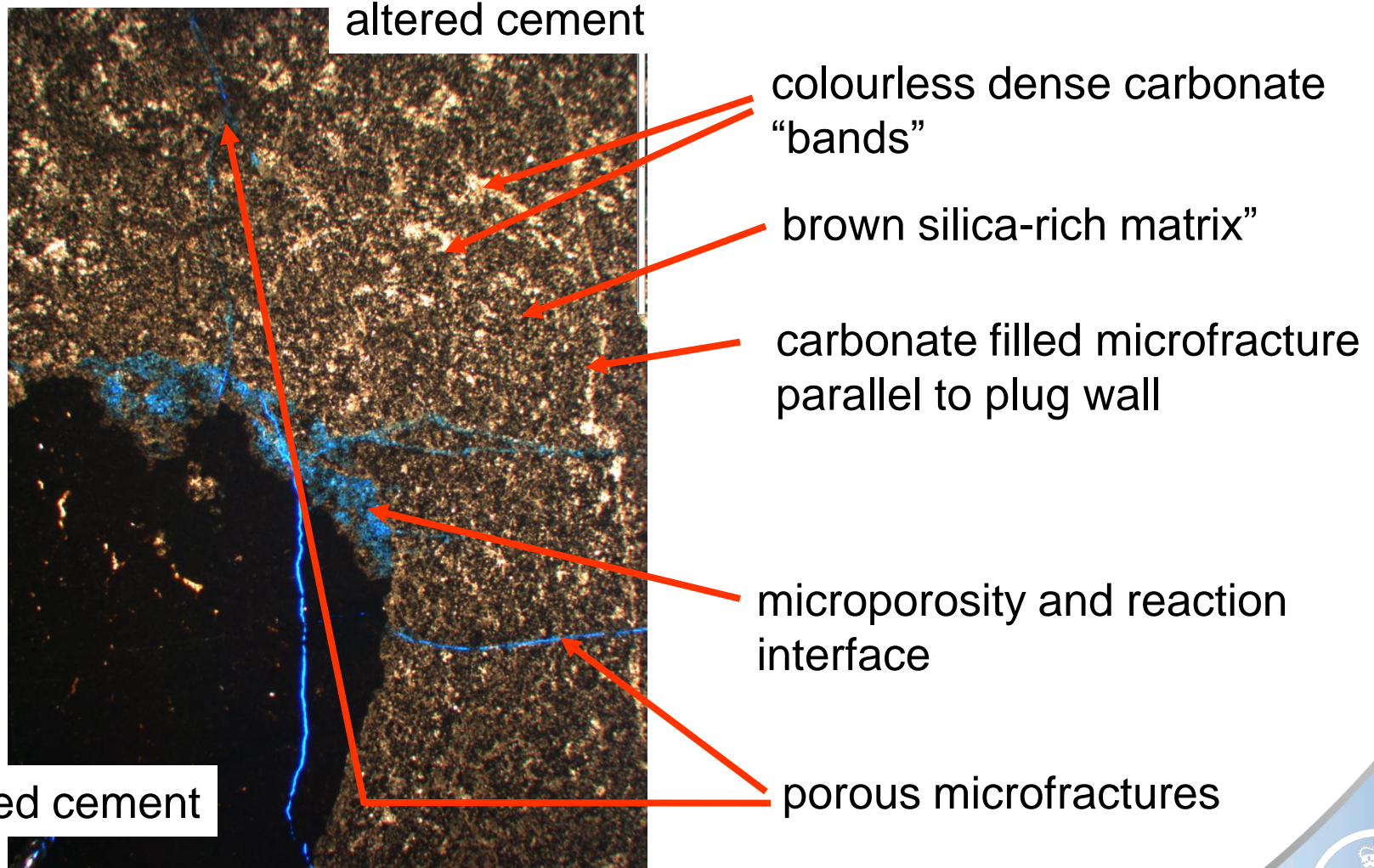
# Experiment Run 1236 (Cement Plug "T2")

Fractured surface through reacted plug  
[binocular microscope]

Thin section through reacted plug  
[transmitted light]



# Experiment Run 1236 (Cement Plug "T2")

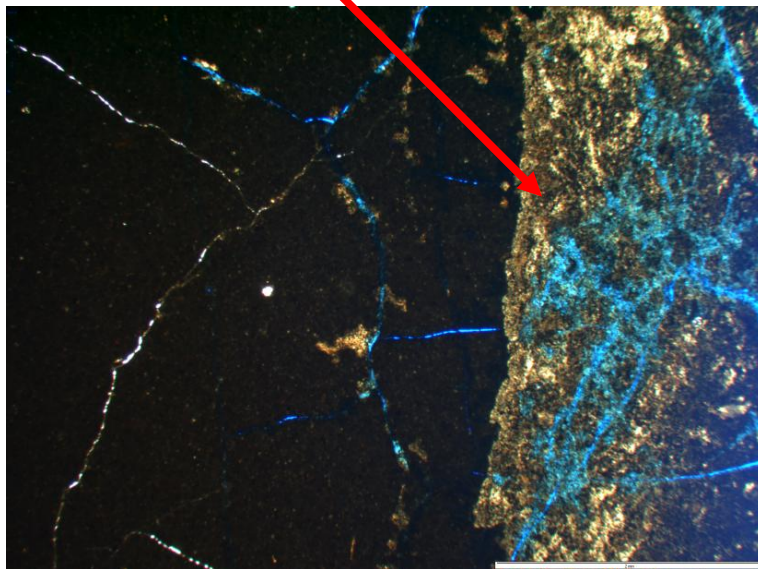


*Thin section through reacted plug  
[transmitted light]*

# Reaction fronts and cracking (Cement Plug “T2”)

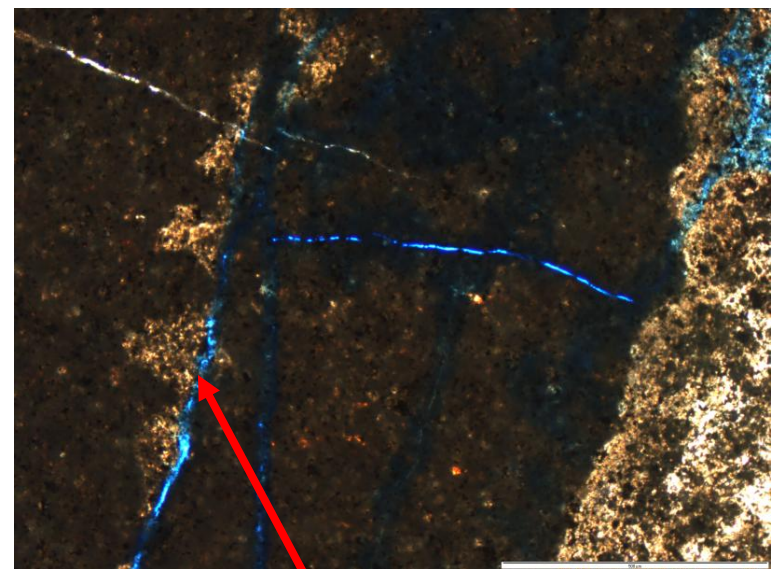
Porosity generation at the interface between carbonated cement and residual cement core

CaCO<sub>3</sub> replaced CSH matrix



2 mm

Enhanced matrix CSH dissolution  
microporosity locally associated with  
carbonation and shrinkage microfractures



500 µm

CaCO<sub>3</sub> replaces cement along  
margins of shrinkage fractures in  
residual cement core

# Conclusions 1

- That moderately-sized nodules of CSH phases do not undergo total carbonation even after several thousand years is important. Supports the idea that similar minerals in well cements may possibly have significant longevity under certain subsurface conditions.
- Caution is noted however, as the carbonation of these natural CSH materials has clearly occurred under different conditions to those anticipated for supercritical CO<sub>2</sub> storage within a deep saline aquifer or depleted hydrocarbon reservoir.
- Closer analogies could perhaps be drawn with lower CO<sub>2</sub> concentrations at the outer margins of any dissolved CO<sub>2</sub> 'plume'.
- Emplacement of Carneal Plug and Scawt Hill, and the observed contact metamorphism of the Ulster White Limestone occurred at <700 m depth.
- Late-stage hydration and alteration of the contact metamorphic assemblage has probably occurred at shallower depths, following significant post-Tertiary and Quaternary uplift and erosion which affected the region

# Conclusions 2

- The natural CSH minerals will not have reacted with supercritical CO<sub>2</sub> at a high concentration.
- Carbonation occurred under very low CO<sub>2</sub> concentrations either by direct interaction with atmospheric CO<sub>2</sub> during exposure and weathering, or by interaction with HCO<sub>3</sub><sup>-</sup> dissolved in dilute shallow groundwaters (i.e. more analogous to groundwaters at the very periphery of a dissolved CO<sub>2</sub> front around a store of CO<sub>2</sub>).
- Despite these differences, the observations from Scawt Hill and Carneal Plug may provide an insight into some aspects of the interaction of CO<sub>2</sub> with well cements.
- Natural CSH gel from Scawt Hill/Carneal Plug is very similar to the CSH gel encountered in Portland type cement, and has reacted with CO<sub>2</sub> to form secondary calcium carbonates and silica.

# Conclusions 3

- Calcite is the dominant secondary calcium carbonate mineral, but vaterite and aragonite are also formed.
- The carbonation produces a reduction in volume, accompanied by shrinkage and microfracturing of the residual poorly crystalline CSH gel and its silica-rich alteration product. This has created significant secondary porosity in the altered material.
- Although some secondary calcium carbonate reaction products may partially mineralise the fractures, they do not seal the fractures completely.
- Uncertainties remain about these natural samples, not least quantification of the rates of the carbonation reactions and the  $\text{CO}_2/\text{HCO}_3^-$  flux. However, further studies of these unusual natural analogues could provide much relevant information to aid our understanding of the long-term stability of borehole cements in  $\text{CO}_2$ -rich environments.