Palaeohydrogeology of a deep groundwater system in west Cumbria, UK: An analogue of the impact of Quaternary glacial cycles on salinity and redox evolution

Antoni Milodowski[1], Adrian Bath[2] and Simon Norris[3]

*[1]British Geological Survey
Environmental Science Centre,
Nottingham, UK*

*[2]Intellisci
Loughborough,
Leicestershire, UK*

*[3]RWM Ltd
Harwell
Oxfordshire, UK*

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- A thought to consider – is all glacially-recharged groundwater oxidising?

Introduction

- Safety assessment may analyse containment by the engineered and natural barriers for a reference scenario which assumes that present-day groundwater conditions are in equilibrium and will persist for long times into the future.

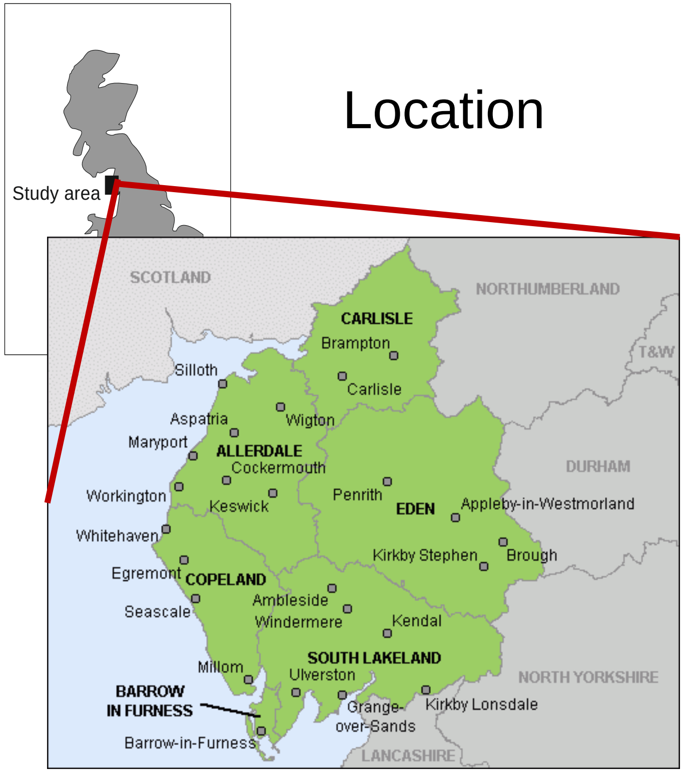
- The credibility of this approach depends on understanding what changes occurred in the past, and how similar changes in the future might influence the hydrogeological setting.

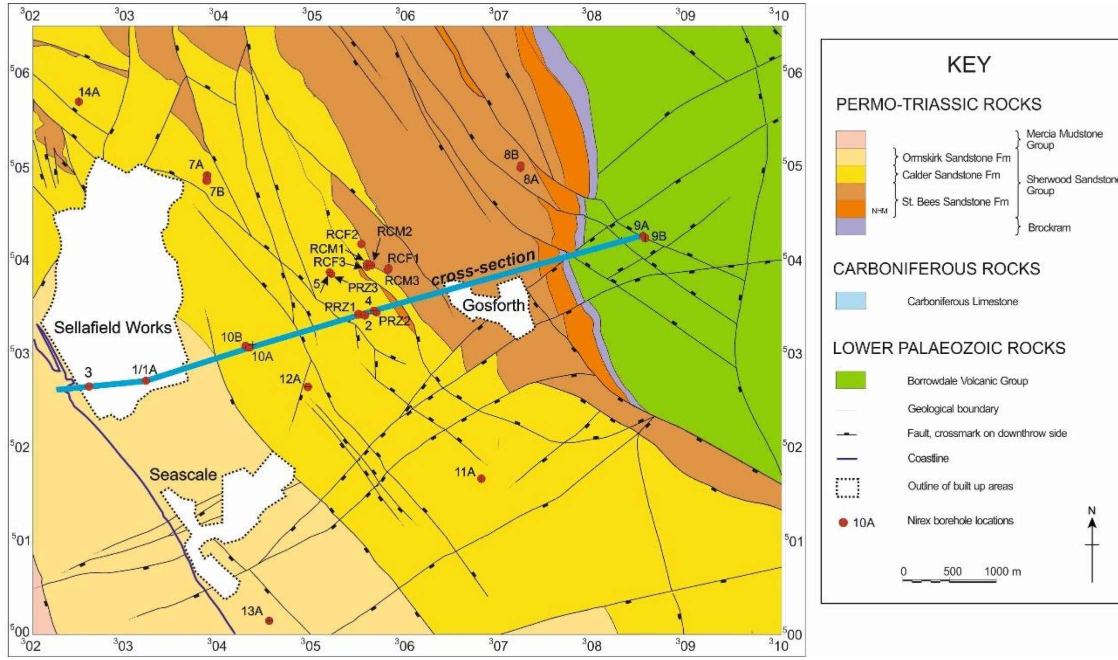
- The timescale for safety projections of up to a million years means that changes of climate and sea level at the surface, and neo-tectonic changes within rock formations, might be significant processes that must be considered.

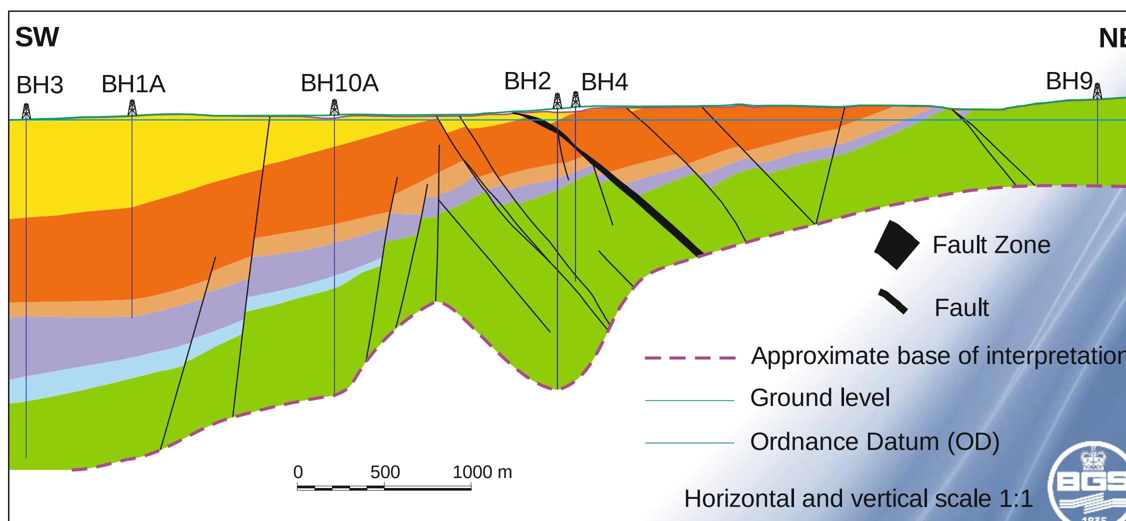
- Of particular concern is the potential impact that the sub-glacial recharge of meltwater, enriched in dissolved oxygen may have in future, on redox conditions at repository depth

Geological setting

Location



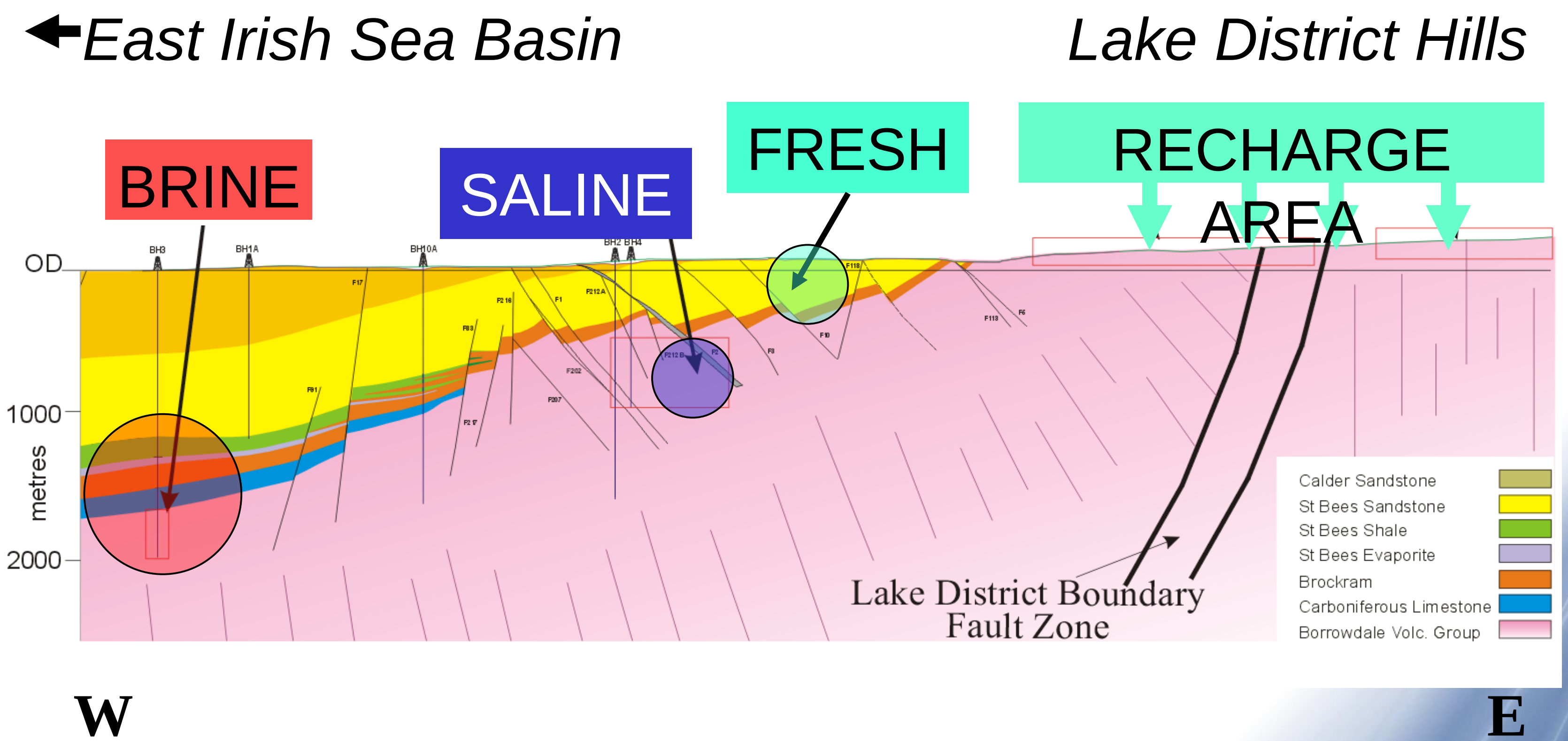




Carboniferous to Permo-Triassic sedimentary cover

Fractured Lower Palaeozoic basement

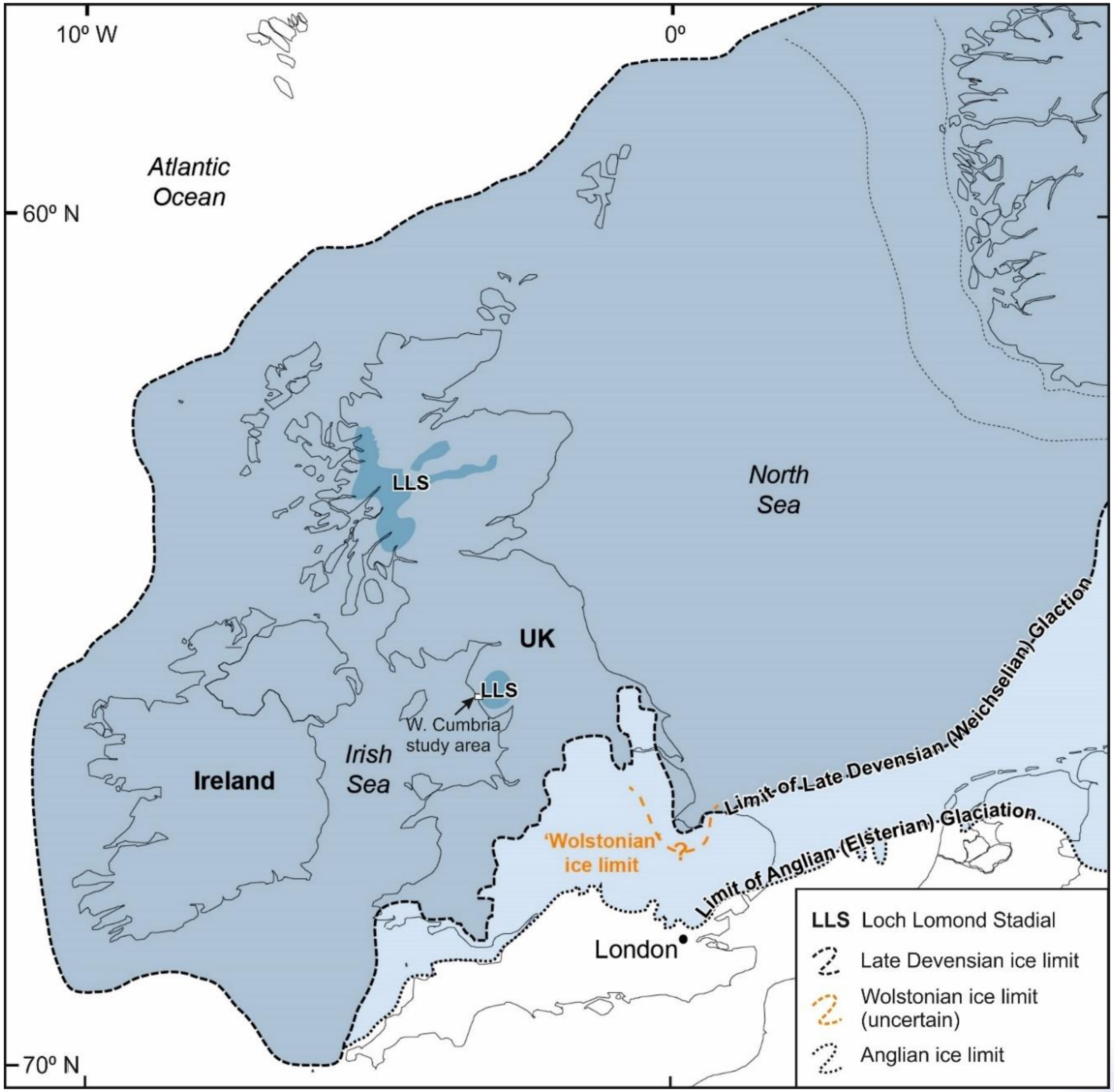
Hydrogeological setting



Quaternary history and glaciation

- Experienced multiple glaciations during the Quaternary (2.6 Ma)
- Onshore record poorly preserved: 4 major glaciations recognised:
    - Loch Lomond Stadial (Younger Dryas) 10-11 ka
    - Late Devensian (Weicheselian) 26-13 ka
    - Wolstonian 186-128 ka
    - Anglian 480-430 ka
- Late Devensian glaciation largely destroyed evidence of earlier Pleistocene climate states.
    - Dominates the glacial deposits and erosional landforms

Extent of ice sheets



Chronostratigraphy & Climate State

Age (ka bp)	British Stadial or Interstadial name	Climate state
10–0*	Holocene (or Recent)	Temperate
26–10*	Late Devensian	Glacial to temperate
11–10*	Loch Lomond Stadial (or Younger Dryas)	Periglacial
13–11*	Late glacial Windermere Interstadial	Boreal to temperate
26–13*	Dimlington Stadial (Main Late Devensian glaciation and deglaciation)	Glacial
?15–14**	Scottish Readvance	Glacial
?17–?15**	Gosforth Oscillation	Glacial
26–?17**	Main Late Devensian Glaciation	Glacial
50–26**	Mid Devensian	Periglacial or boreal
59–50**	Mid Devensian	Temperate or boreal
70–59**	Early Devensian	Glacial
116–70*	Early Devensian	Periglacial or boreal
128–116*	Ipswichian interglacial	Temperate
186–128*	Wolstonian	Glacial

Note: * based on Ackhurst et al., 1997, modified after Merritt et al. 2003; **based on Heathcote and Michie, 2004.

- Glaciation prevailed for about 100 ka of the last 700 ka

- Climate variations would have caused fluctuations in freshwater recharge:
  - *Topographic-driven recharge would restart during interglacials*
  - *Permafrost would have inhibited recharge through the ground surface*

Present-day groundwaters

Geological location of water samples	**Approx depth range**	**TDS mg/L**	**$\delta^{18}O$ & $\delta^{2}H$ ‰**	**Noble gas recharge T °C**	**^{4}He content $\mu cm^3/cm^3$**	**$^{87}Sr/^{86}Sr$**
Sandstones and outcropping basement	75 to 570 m	165 to 3730	-6.8 to -6.0 ‰ -45 to -36 ‰	3.7 to 18.6 °C	0.11 to 146	0.7130 to 0.7131
Deeper sedimentary cover rocks	440 to 1110 m	722 to 68000	-8.1 to -7.1 ‰ -51 to -44 ‰	1.0 to 5.6 °C	30.6 to 823	0.7120 to 0.7138
Basement under cover rocks	350 to 1590 m	5850 to 67600	-8.0 to -7.0 ‰ -55 to -39 ‰	2.4 to 10.8 °C	197 to 677	0.7145 to 0.7152
Deep sedimentary and basement rocks below coast	690 to 1670 m	84900 to 188000	-6.9 to -5.1 ‰ -44 to -31 ‰	4.5 to 20.3 °C	38 to 755	0.7100 to 0.7146

Present-day groundwaters

- $^{87}Sr/^{86}Sr$ ratios highest in saline groundwaters in basement covered by sedimentary rocks
The same groundwaters have higher Br/Cl ratios.

- High Sr isotope ratios and high Br/Cl indicate a greater extent of water-rock reaction and long residence times (Bath et al. 2006).

- Lower $^{87}Sr/^{86}Sr$ ratios in sedimentary cover rocks, especially in deep brines in the thick sedimentary sequence below the coast - explained by the lower production of radiogenic ^{87}Sr in sandstones and in offshore evaporites from which the brines derive their high salinity.

- **Freshwater** in sandstones similar isotopically present-day recharge

- **Saline** groundwaters in basement to 1000 m are lighter $\delta^{18}O$ - indicative of colder climate than now but not as extreme as glacial meltwater : Interpreted as possible mixing of waters recharged under different glacial - interglacial cycles

- **Brines** in deeper sedimentary rocks and underlying basement have heavier isotopes and consistent with recharge under conditions warmer than today (?Tertiary)

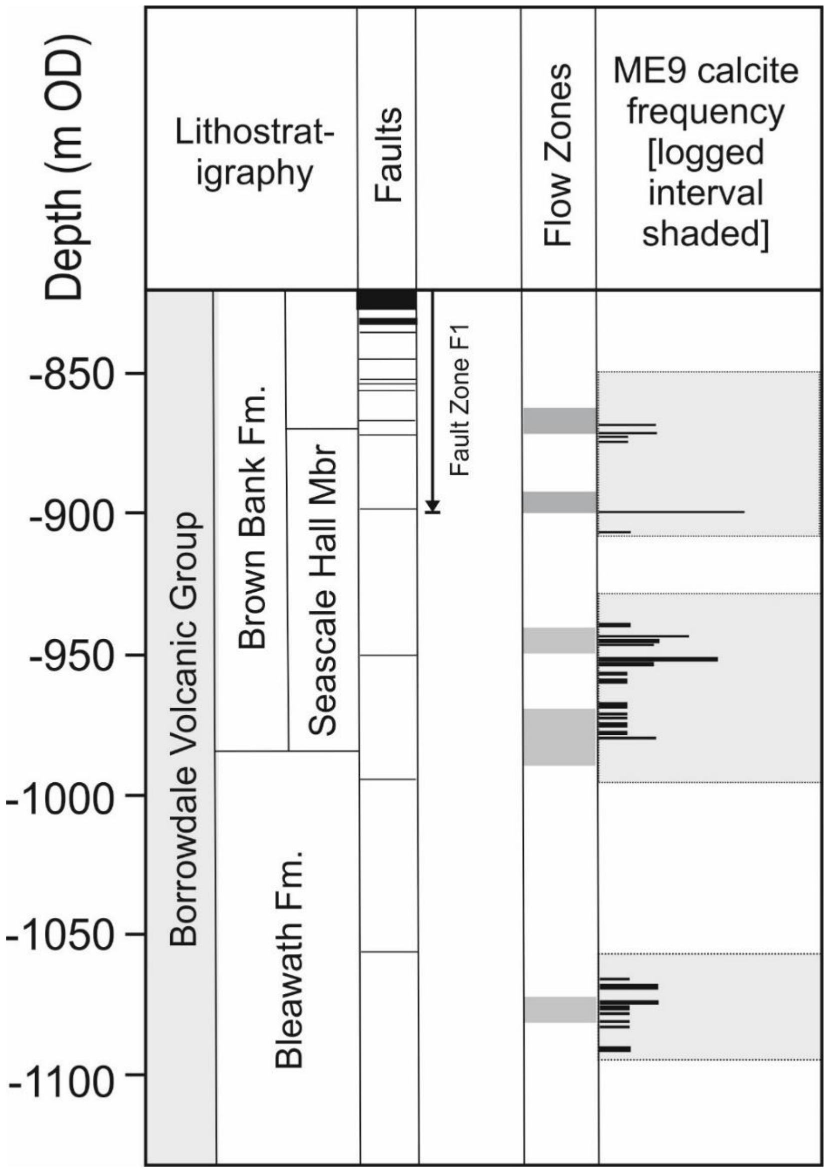
Mineralisation and fracturing history

Mineralization Episode	Principal associated minerals	Dominant type of mineralization
ME1	K-feldspar/ adularia ±quartz, ±chlorite, ±albite, ±hematite	Silicate
ME2	<u>Quartz</u> ±epidote, ±calcite, ±chlorite, ±apatite, ±K-feldspar, ±albite, ±sericite, ±hematite	Silicate (& carbonate)
ME3	<u>Pyrite</u> ± traces of chalcopyrite, arsenopyrite, marcasite, galena, sphalerite, Bi-Se sulphosalts and quartz	Sulphide (& silicate?)
ME4	<u>Anhydrite</u> ±barite, ±fluorite, ±hematite, ±quartz, ±siderite (?), ±K-feldspar	Sulphate
ME5	Albite, K-feldspar, <u>kaolinite</u>, <u>illite</u>, ±hematite	Silicate
ME6 a	*Early ME6a*: ferroan/ manganoan carbonate now replaced completely by specular hematite and <u>calcite</u> with abundant inclusions of Fe- and Mn-oxides. *Late ME6a*: <u>calcite</u> and hematite	Carbonate
ME6 b	Dolomite, <u>ferroan dolomite</u>, ankerite, ±siderite, ±quartz, ±anhydrite, ±ferroan calcite	± sulphate
ME6 c	<u>Calcite</u> (usually ferroan) ±barite, ±fluorite, ±hematite, ±pyrite, ±sphalerite, ±galena	
ME7	<u>Illitic clay</u> and <u>hematite</u>	Silicate & oxide
ME8	<u>Mn- and Fe-oxides/ oxyhydroxides</u>	Oxide
ME9	<u>Calcite</u> ±pyrite, ±anhydrite, ±gypsum	Carbonate ± sulphate ± sulphide

Long and complex fracturing and mineralisation history

- <u>ME1-ME3</u> – silicate dominated old epithermal to mesothermal mineralisation
- Affect only Lower Palaeozoic strata [PALAEOZOIC]
- <u>ME4-ME7</u> – carbonate-sulphate-fluorite-hematite-barite dominated.
- Derived from warm brines expelled during burial and diagenesis of thick Carboniferous and evaporite-bearing Permo-Triassic strata in the East Irish Sea Basin
- Affects all strata
  (*Early ME6a is now recognised to be Pre-Permian*)
- <u>ME8-ME9</u> – closely related to modern groundwater flow and chemistry
  - ME8 shallow oxidative alteration (weathering)
  - ME9 deeper calcite +/- pyrite/marcasite and barite (anhydrite in west only)

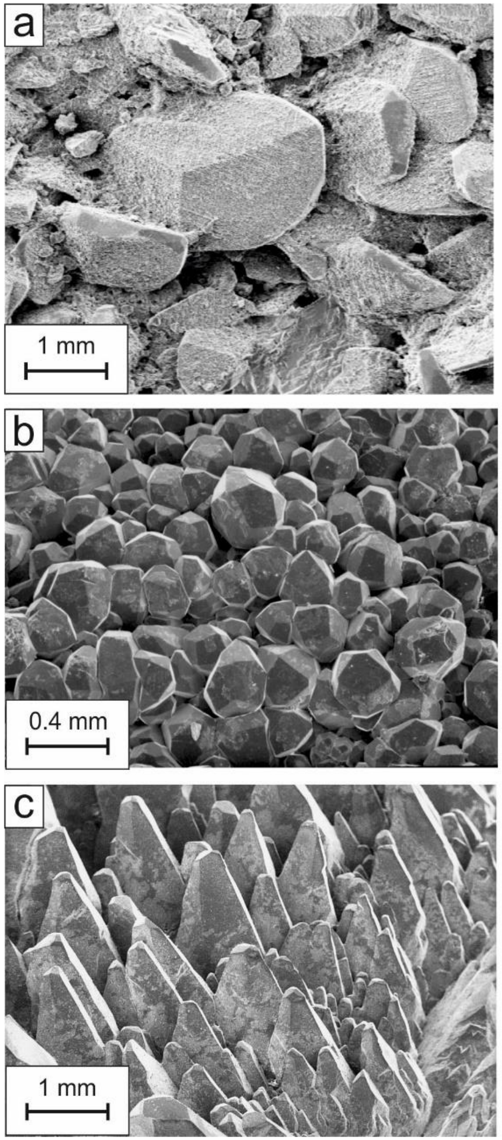
Distribution of late mineralisation and groundwater flow



Distribution of faults, groundwater flow and late mineralisation in part of Nirex borehole 2

- ME8 and ME9 mineralisation correlate closely with present-day groundwater flow in deep boreholes
- ME8 found at shallow levels near-surface weathering

Morphology variations in ME9 calcite



c-axis flattened crystal form
['nailhead' morphology]

Shallow fresh groundwater
St Bees Sandstone Formation, borehole PRZ2

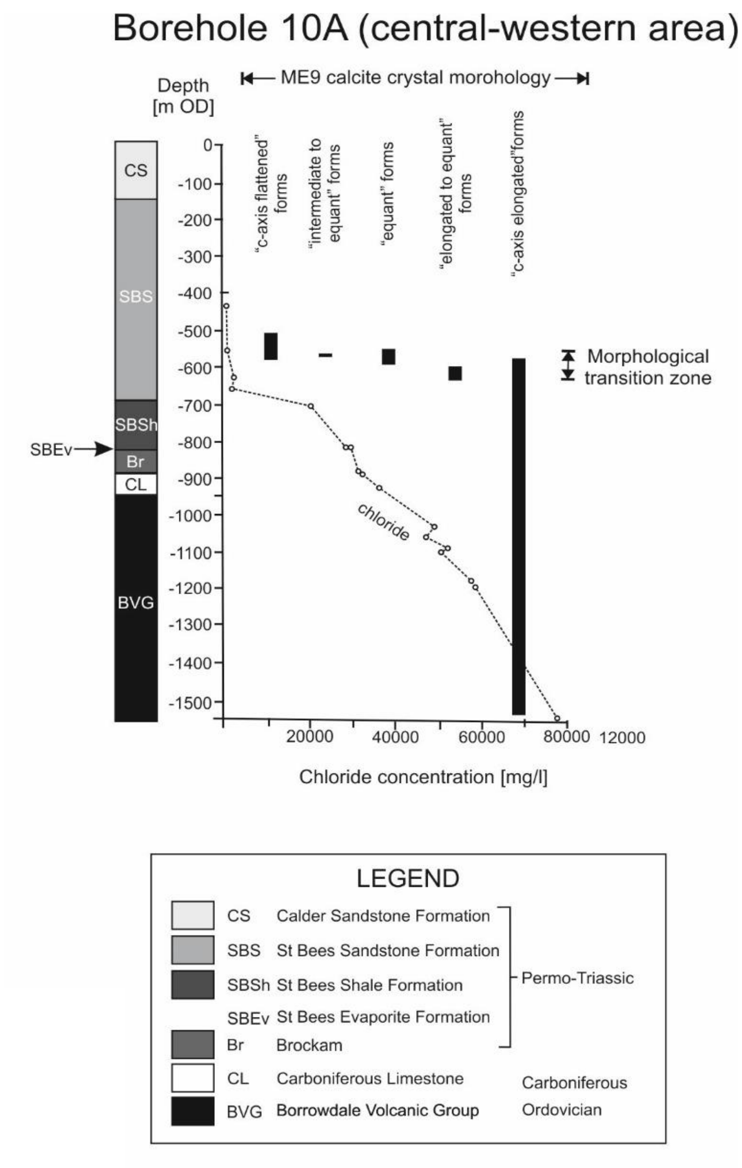
Equant crystal form

Deeper fresh to weakly brackish groundwater
St Bees Sandstone Formation, borehole PRZ2

c-axis elongated crystal form
['dog-tooth' morphology]

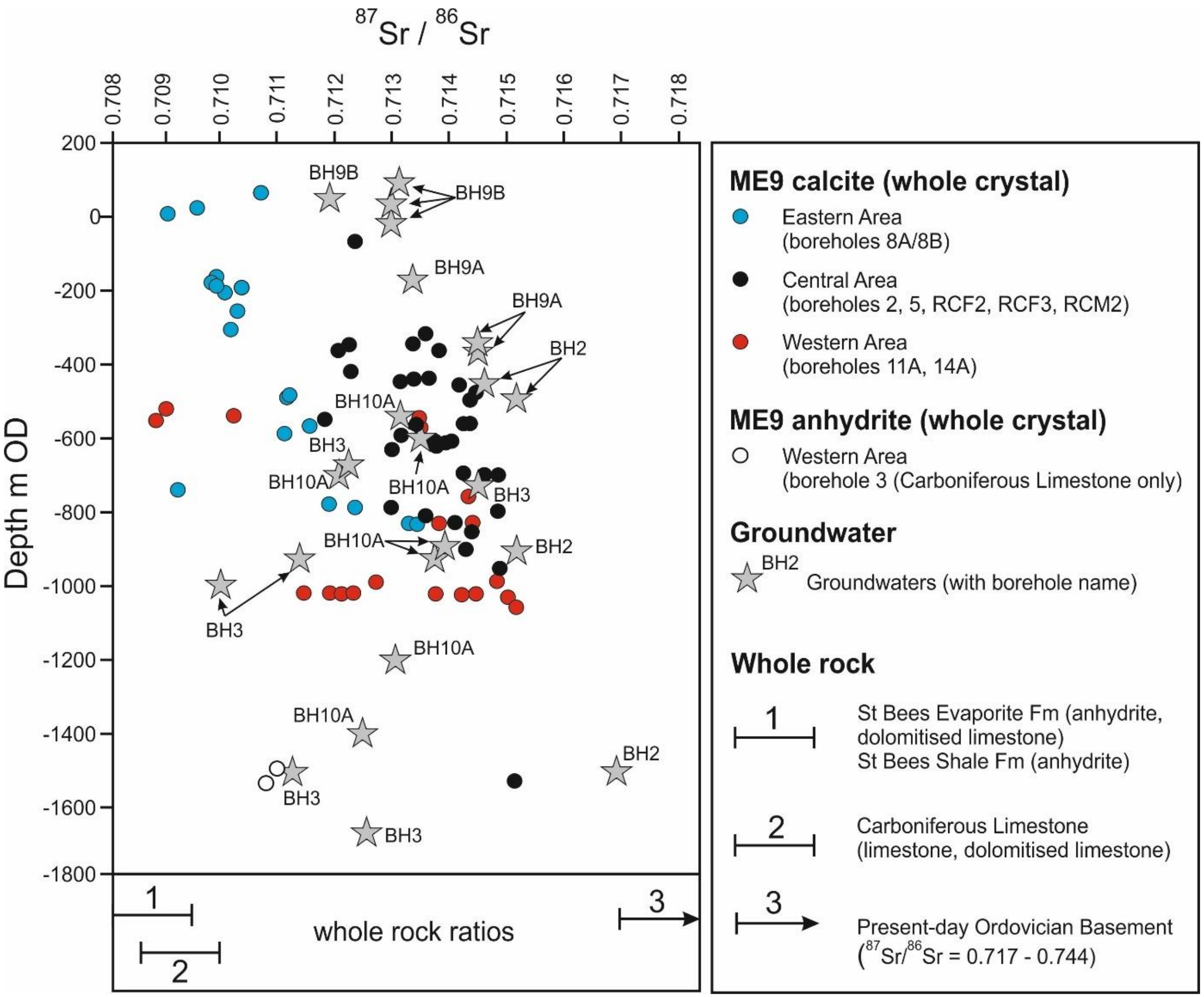
Deep, saline groundwater
Borrowdale Volcanic Group, borehole 8A

ME9 calcite morphology and groundwater salinity



- Systematic variation in crystal morphology and salinity
- Salinity and chemistry (principally Mg, Sr, SO_4,Cl influence kinetics of crystal nucleation on different crystallographic faces *(e.g. Folk.1974; Kiven & Wilkinson, 1985)*

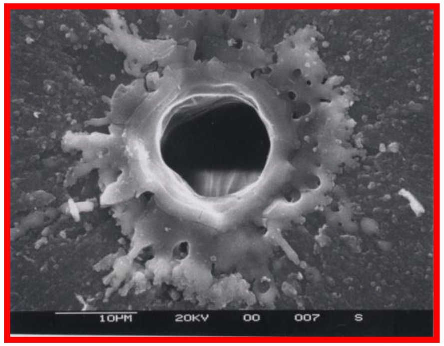
Strontium $^{87}Sr/^{86}Sr$ isotope ratios in ME9 calcite



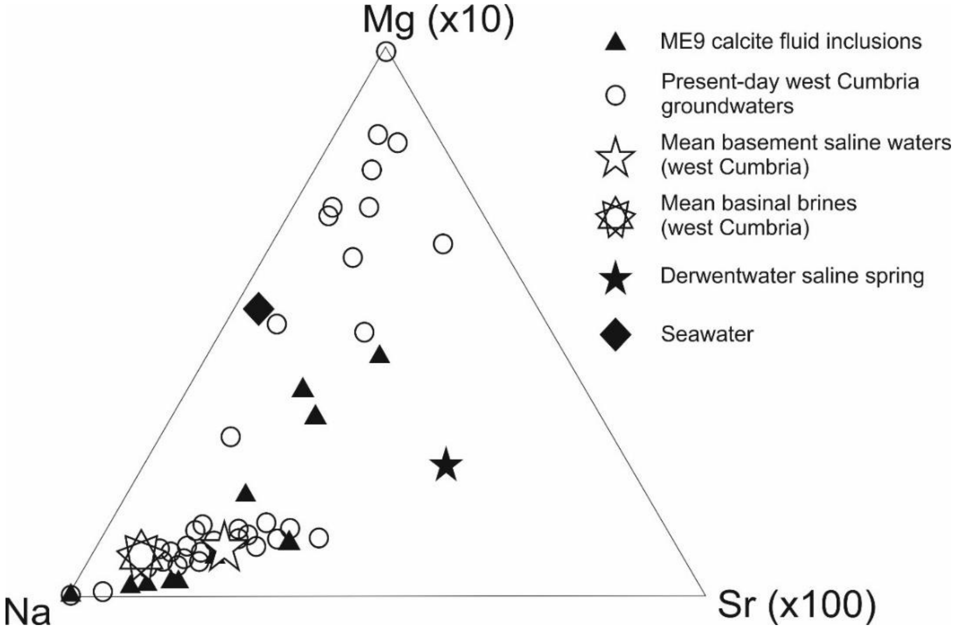
- Within the range of present-groundwater values
- Variation from west to east, reflects interaction of groundwaters with local bedrocks

Fluid inclusions in ME9 calcite and groundwater chemistry

Laser ablation microprobe ICP-MS analysis of individual fluid inclusions



- Microthermometry:
  - Rare inclusions
  - Single phase
  - Low T <80 °C
  - Range in salinities similar to range of present-day groundwaters



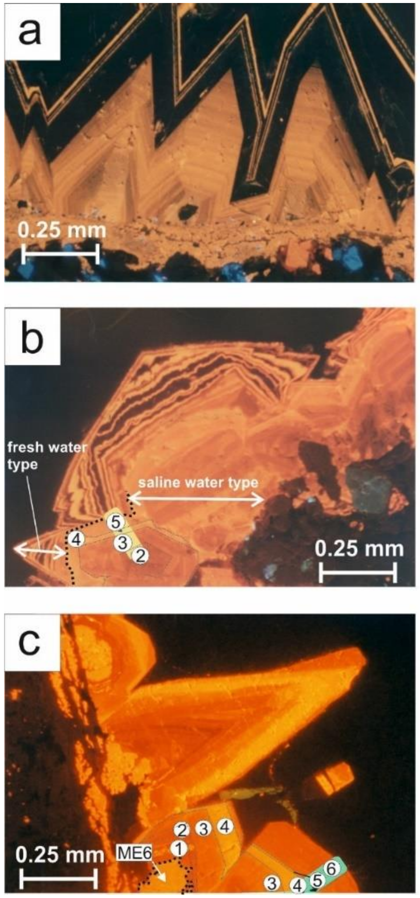
- Chemistry
  - Similar to that of present-day deep basement brines and saline groundwaters
  - Dilute (freshwater) inclusions difficult to analyse – below detection

Age of ME8 Mn-Fe oxyhydroxide and ME9 calcite

Mineral	Sample No	Nirex borehole	Depth (m OD)	Host rock	Age	Dating method
ME8 Mn oxyhydroxide	NSF2/1307/P4	2	60*	Calder Sst	26.39 Ma	^{40}Ar-^{39}Ar total gas age
ME8 Mn oxyhydroxide	NSF2/1307/P4	2	60*	Calder Sst	14 – 21 Ma	^{40}Ar-^{39}Ar plateau age
ME8 Mn oxyhydroxide	*PRZ2/5/P4*	*PRZ2*	*-321**	*St Bees Sst*	*276 Ma**	*^{40}Ar-^{39}Ar total gas age***
ME9 calcite	RCF1/86/P4	RCF1	-536	BVG	74 ka (+48 / -33)	$^{230}Th/^{234}U$ HRICPMS pseudo-isochron pure and impure calcite
ME9 calcite	NSF2/1321/P4	2	-878	BVG	105ka (+104 /-55)	$^{230}Th/^{234}U$ HRICPMS pseudo-isochron
ME9 calcite	NSF5/672/P4	5	-295	St Bees Sst	267 ka (+32 / -24)	$^{230}Th/^{234}U$ HRICPMS total dissolution
ME9 calcite	NSF5/672/P4	5	-295	St Bees Sst	300 ka (+45 / -33)	$^{230}Th/^{234}U$ HRICPMS total dissolution [duplicate]
ME9 calcite	NSF5/672/P4	5	-295	St Bees Sst	245 ka (+26 / -21)	$^{230}Th/^{234}U$ HRICPMS calcite leachate
ME9 calcite	NSF5/672/P4	5	-295	St Bees Sst	289 ka (+25 / -22)	$^{230}Th/^{234}U$ HRICPMS calcite leachate [duplicate]
ME9 calcite	PRZ2/16/P4	PRZ2	-274	St Bees Sst	70 ka (+300 / -70)	$^{230}Th/^{234}U$ HRICPMS pseudo-isochron pure calcite
ME9 calcite	NSF2/1301/P4	2	-1531	BVG	21 ka (±9)	$^{230}Th/^{234}U$ Alpha spectrometery
ME9 calcite	RCF3/303/P4	RCF3	-901	BVG	>300 ka	$^{230}Th/^{234}U$ HRICPMS calcite leachate
ME9 calcite	NSF10A/1/P4	10A	-633	St Bees Sst	17 - 65	$^{230}Th/^{234}U$ TIMS corrected for ^{230}Th from wallrock and hematite impurities

- ^{40}Ar-^{39}Ar dating of ME8:14-21 Ma consistent with regional Miocene uplift, meteoric invasion and weathering
- ME8 also found in Quaternary glacial deposits and present-day surface
- $^{230}Th/^{234}U$ dating of ME9 calcite: 17-300 ka
- Whole crystal age
- Large errors but consistent with Quaternary formation

Evolution of salinity:
ME9 calcite growth history



Fresh groundwater

St Bees Sandstone Formation
-147 m OD, borehole PRZ2

Morphological Transition Zone

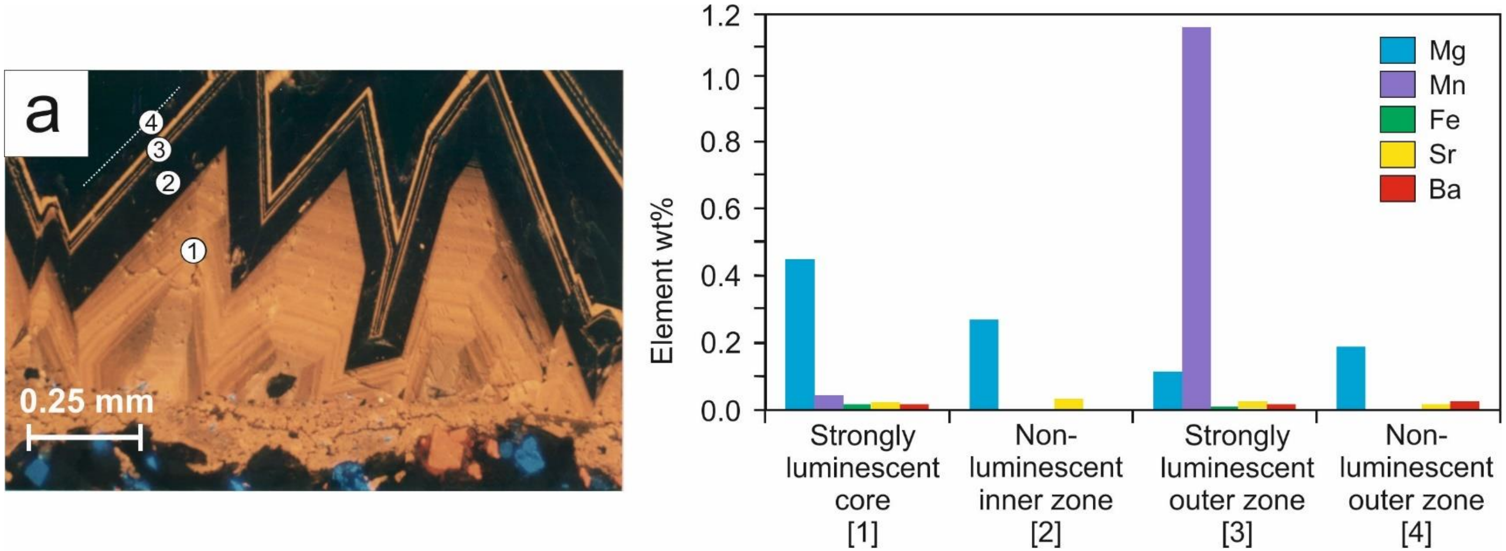
St Bees Sandstone Formation
-635 m OD, borehole 10A

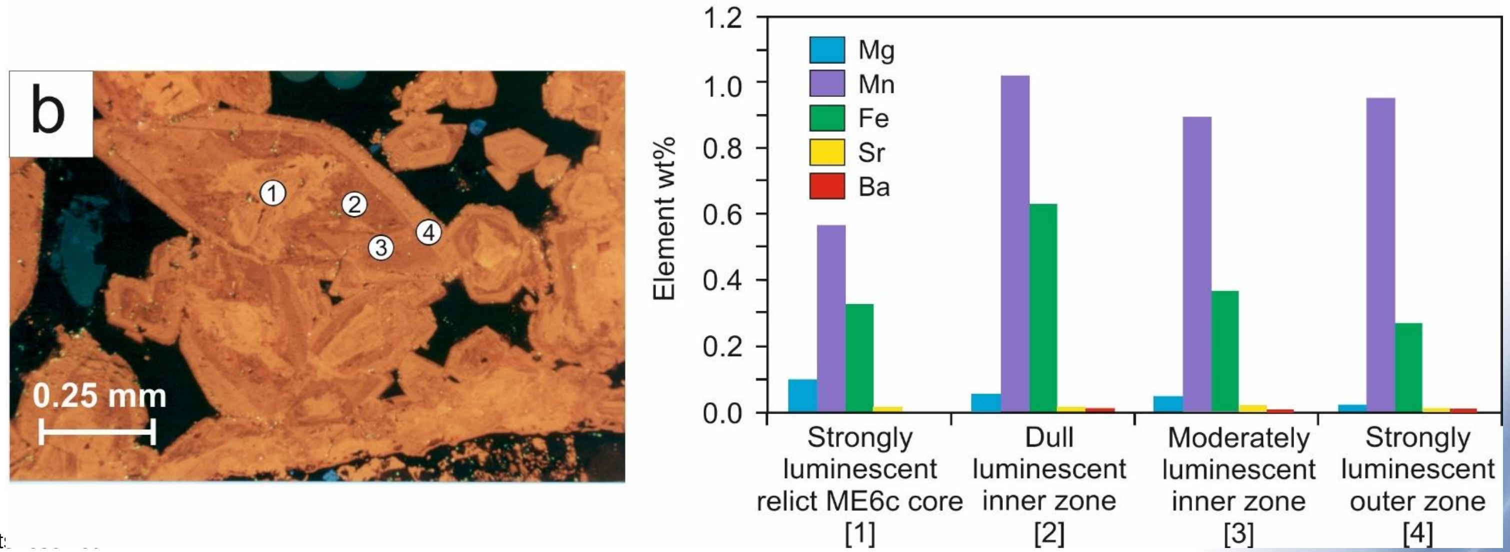
Saline groundwater

Borrowdale Volcanic Group
-809.12 m OD, borehole RCF3

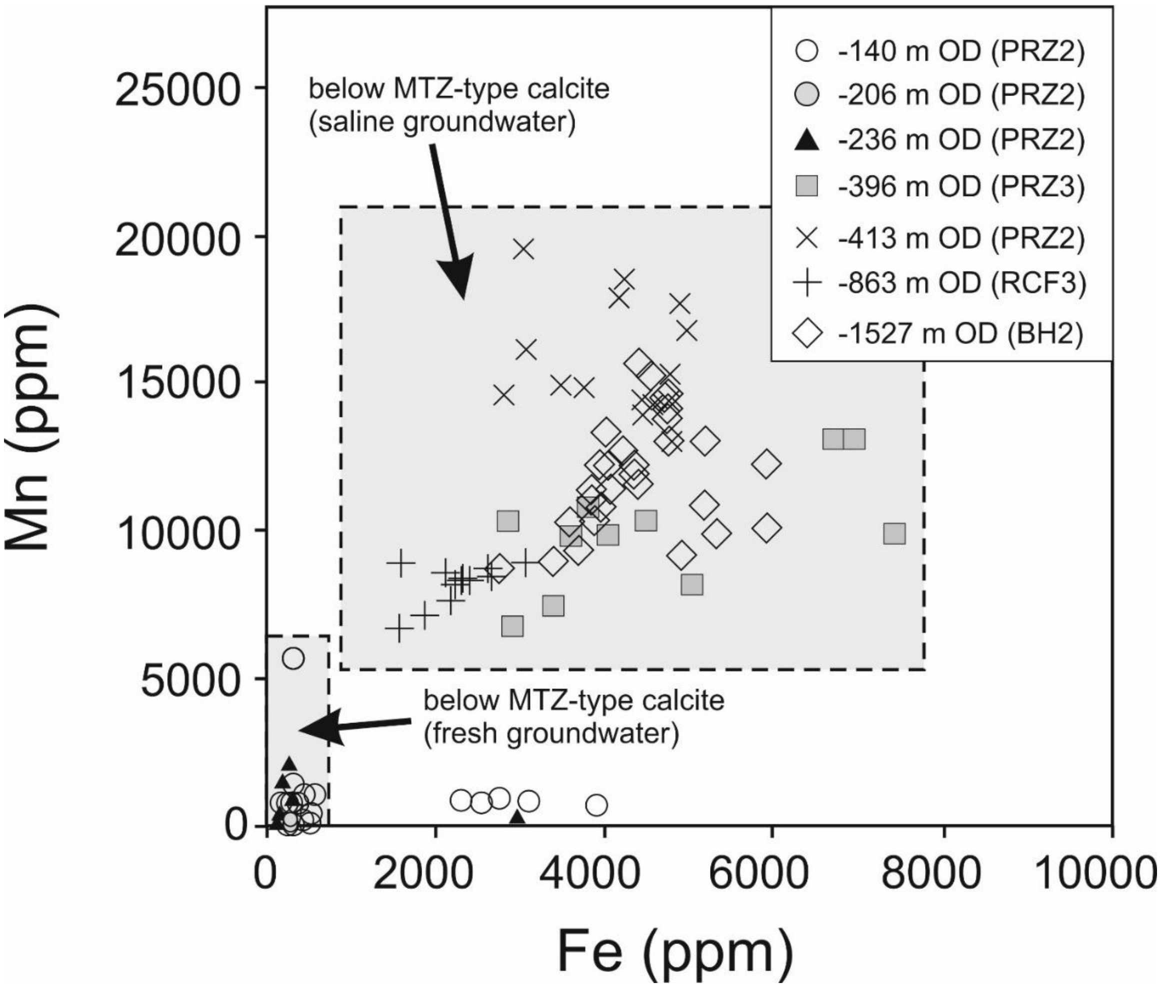
- Cathodoluminescence (CL) microscopy reveals detailed growth zoning of calcite crystals
- Luminescence characteristics vary systematically with groundwater composition
- Crystal zoning patterns show evidence of change in growth morphology with time in zone of freshwater – saline groundwater mixing. Reverse pattern is not seen
- Indicates progressive downward-movement of freshwater – saline groundwater interface with time but over <50 m interval

REDOX: calcite growth zoning: major element behaviour



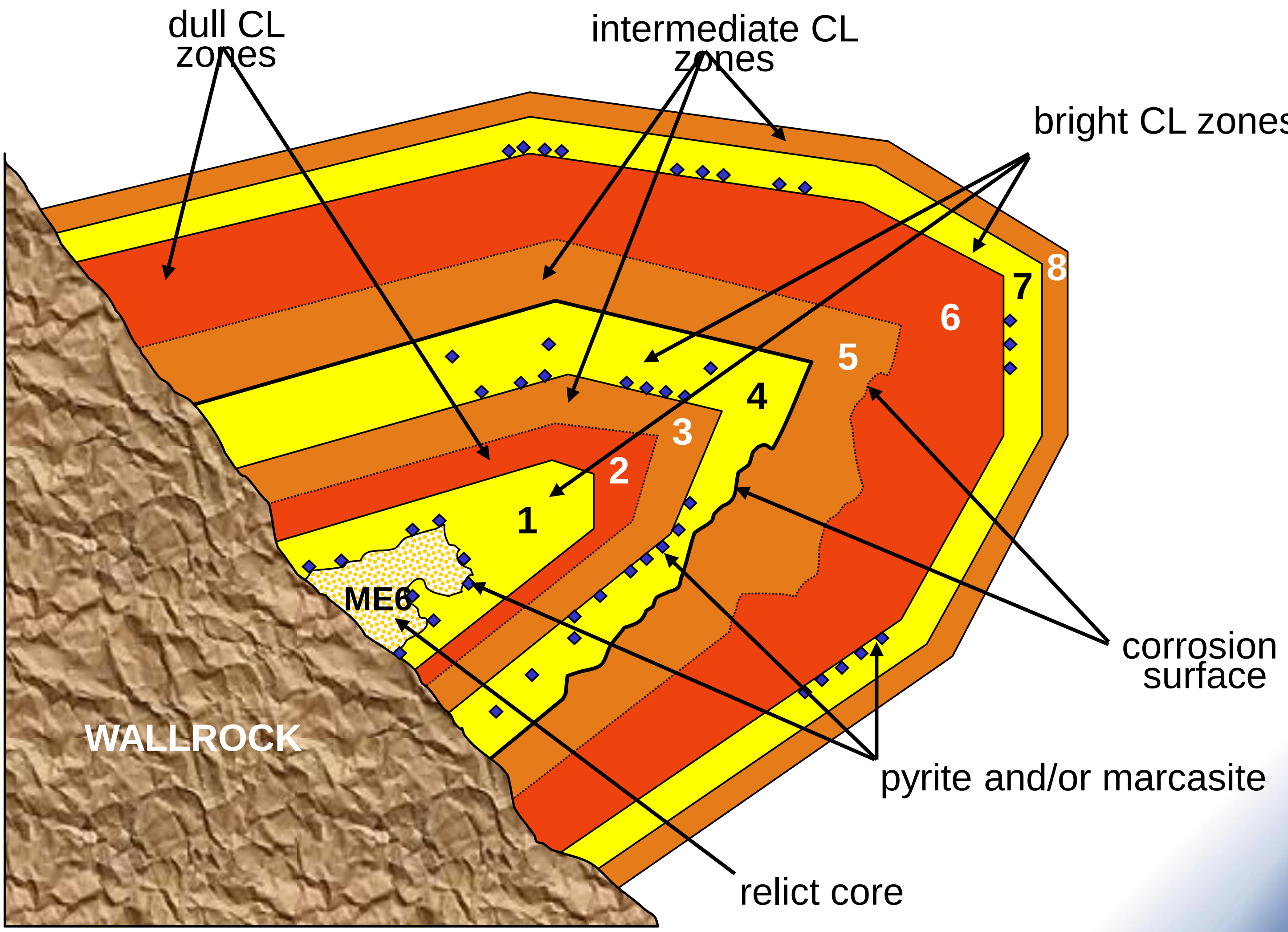


REDOX: : Fe and Mn in ME9 calcite



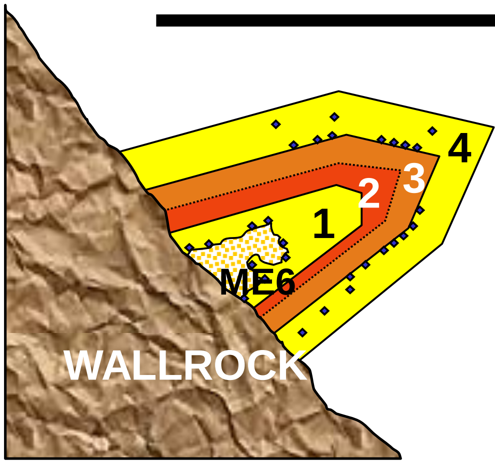
- Constantly reducing conditions maintained for co-precipitation of Fe(II) and Mn(II) during growth of ME9 calcite in deep saline groundwaters
- Variation in Fe:Mn could be due to periodic sulphate reduction

Pyrite formation controls Fe:Mn in saline zone calcite



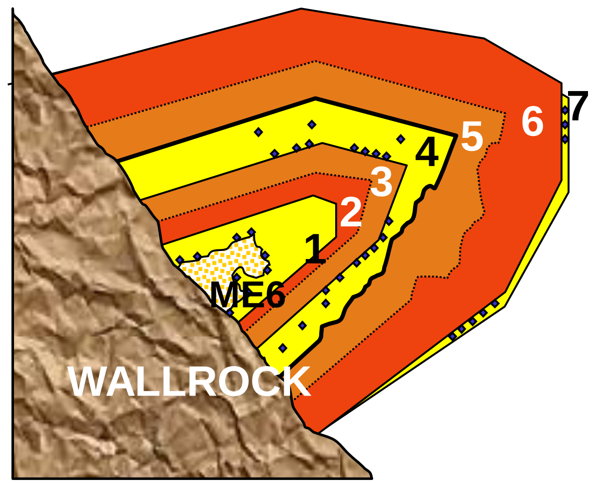
East to West evolution of the flow path system

Evolution with time →



Western Area
Zones 1 to 4
typically present

YOUNGEST HISTORY
[least evolved]

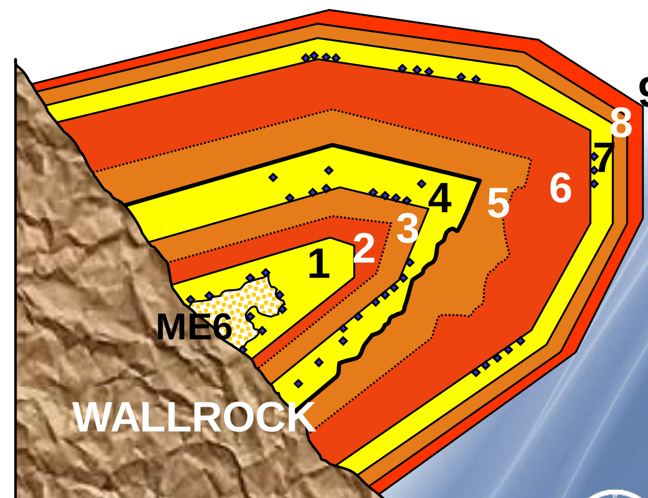


Central Area
Zones 1 to 6 typically
present
Zone 7 rarely present

INTERMEDIATE

Eastern [recharge] Area
Zones 1 to 9 present

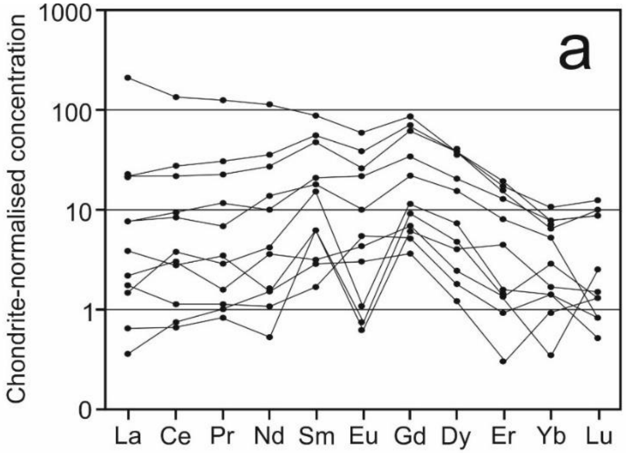
LONGEST HISTORY
[more evolved]



REDOX: calcite growth zoning rare earth element behaviour

<u>Saline zone calcites (a):</u>

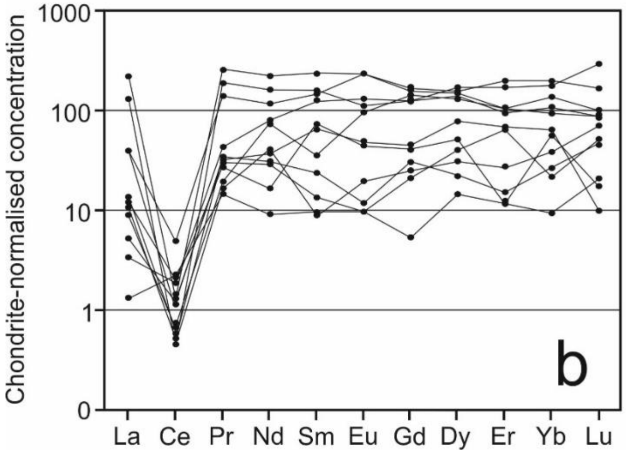
- *REE's behave as REE3+*
- *No Ce anomaly*
- *No evidence of oxidising conditions within saline groundwaters*

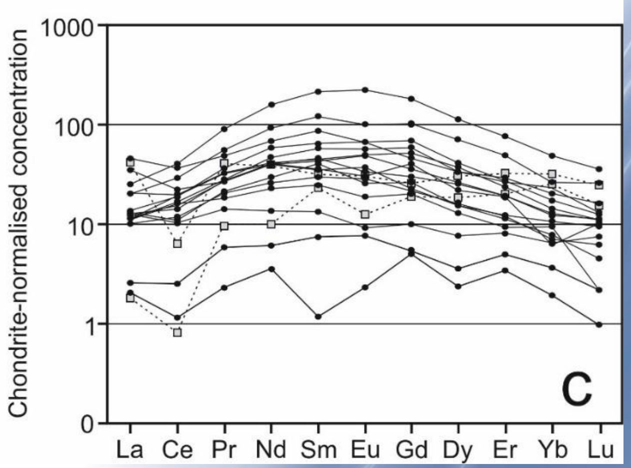


<u>Freshwater zone calcites :</u>

- Non-luminescent calcite (b)
  -ve Ce anomaly (Ce^{4+})
  No Fe / No Mn

- Luminescent calcite (c)
  No Ce anomaly
  Mn-rich but no Fe





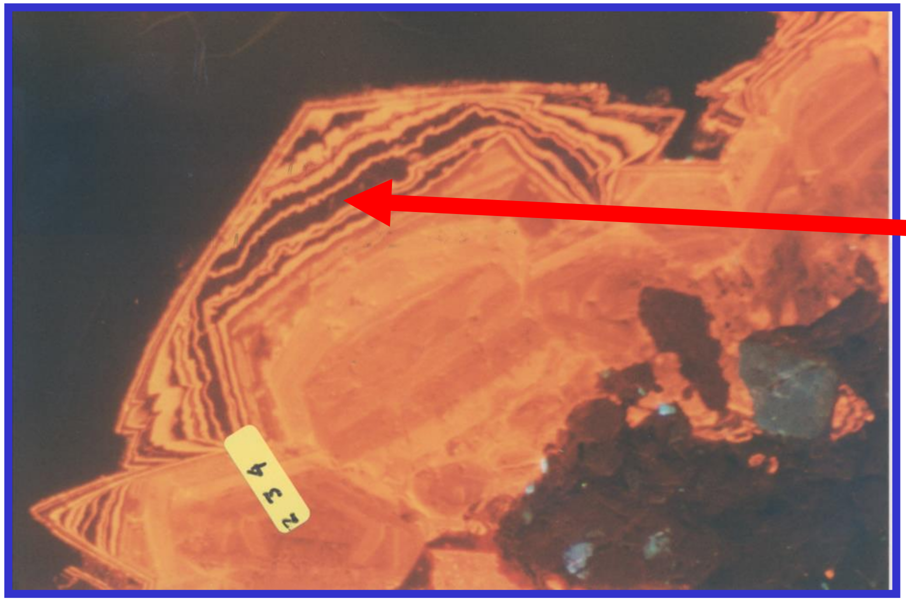
REDOX: calcite growth zoning rare earth element behaviour

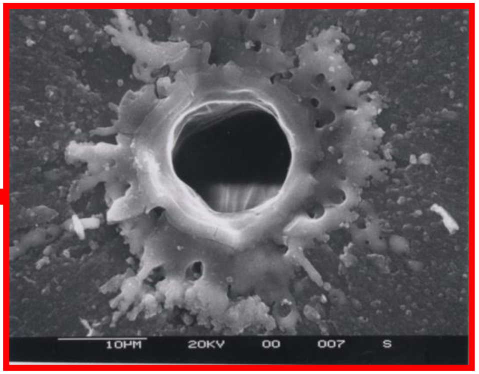
Borehole	Depth (m OD)	Lithology	Above MTZ calcite growth zone CL characteristics		Below MTZ calcite growth zone CL characteristi	
			Non Lum.	Bright Lum.	Bright Lum.	Dull Lum
PRZ2	-147	St Bees Sandstone	-ve Ce anomaly	No Ce anomaly	BELOW MTZ TYPE CALCITE ABSENT	
PRZ2	-206	St Bees Sandstone	-ve Ce anomaly	No Ce anomaly		
PRZ2	-221	St Bees Sandstone	No Ce data			
PRZ2	-236	St Bees Sandstone	-ve Ce anomaly	No Ce anomaly		
PRZ2	-243	St Bees Sandstone	No Ce data			
PRZ2	-278	St Bees Sandstone	ABOVE MTZ TYPE CALITE ABSENT		No Ce anomaly	No Ce anoma
RCF1	-399	Brockram			No Ce anomaly	No Ce anoma
PRZ3	-396	BVG			No Ce anomaly	No Ce anoma
PRZ2	-413	BVG			No Ce anomaly	No Ce anoma
RCF1	-548	BVG			No Ce anomaly	No Ce anoma
RCF1	-837	BVG			No Ce anomaly	No Ce anoma
BH2	-1527	BVG			No Ce anomaly	No Ce anoma

He-LACE analyses for stable C and O isotopes

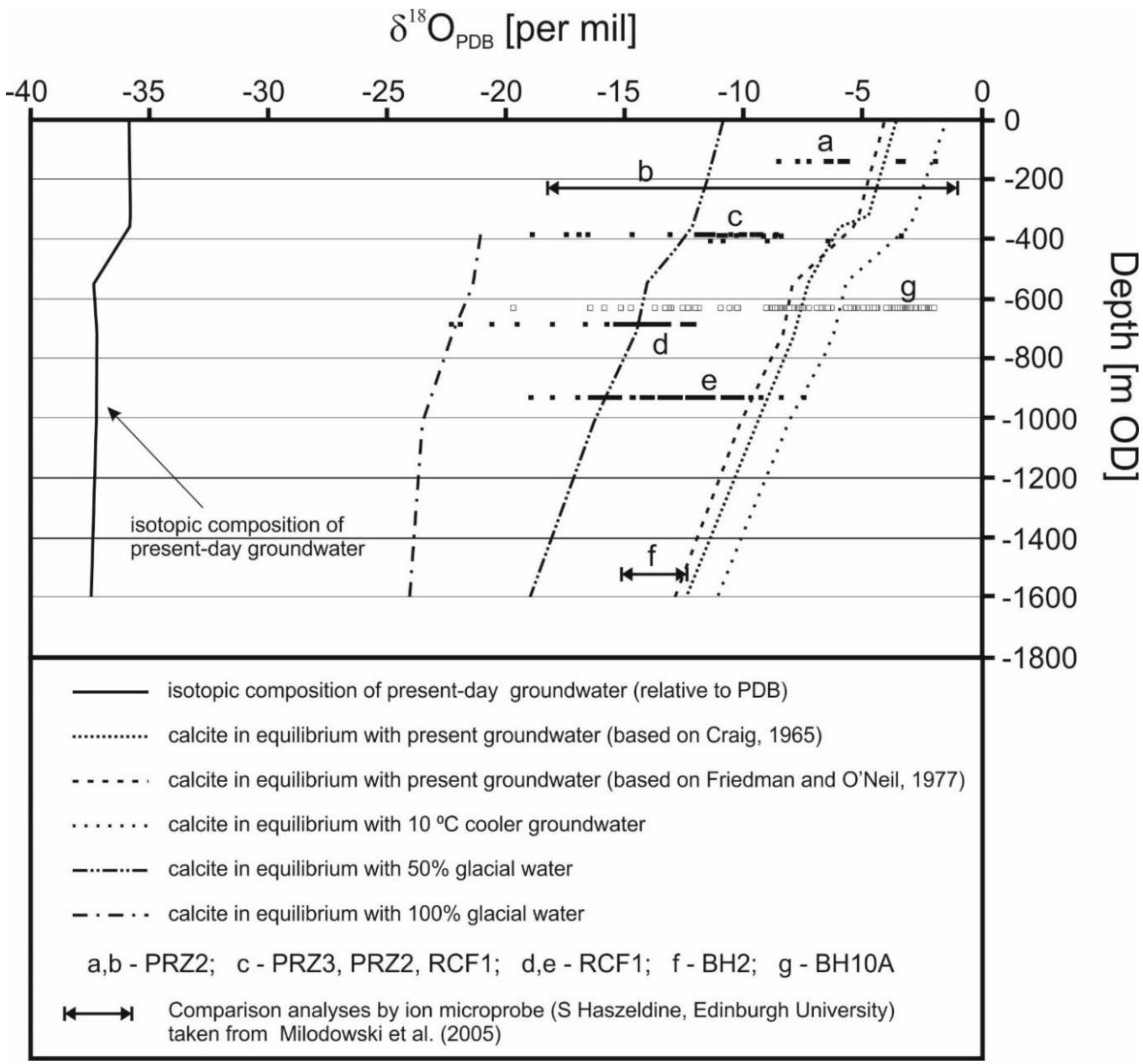
•*Laser and ion microprobe microsampling of individual growth zones in calcite*

•*Indirect indication of age/groundwater process*



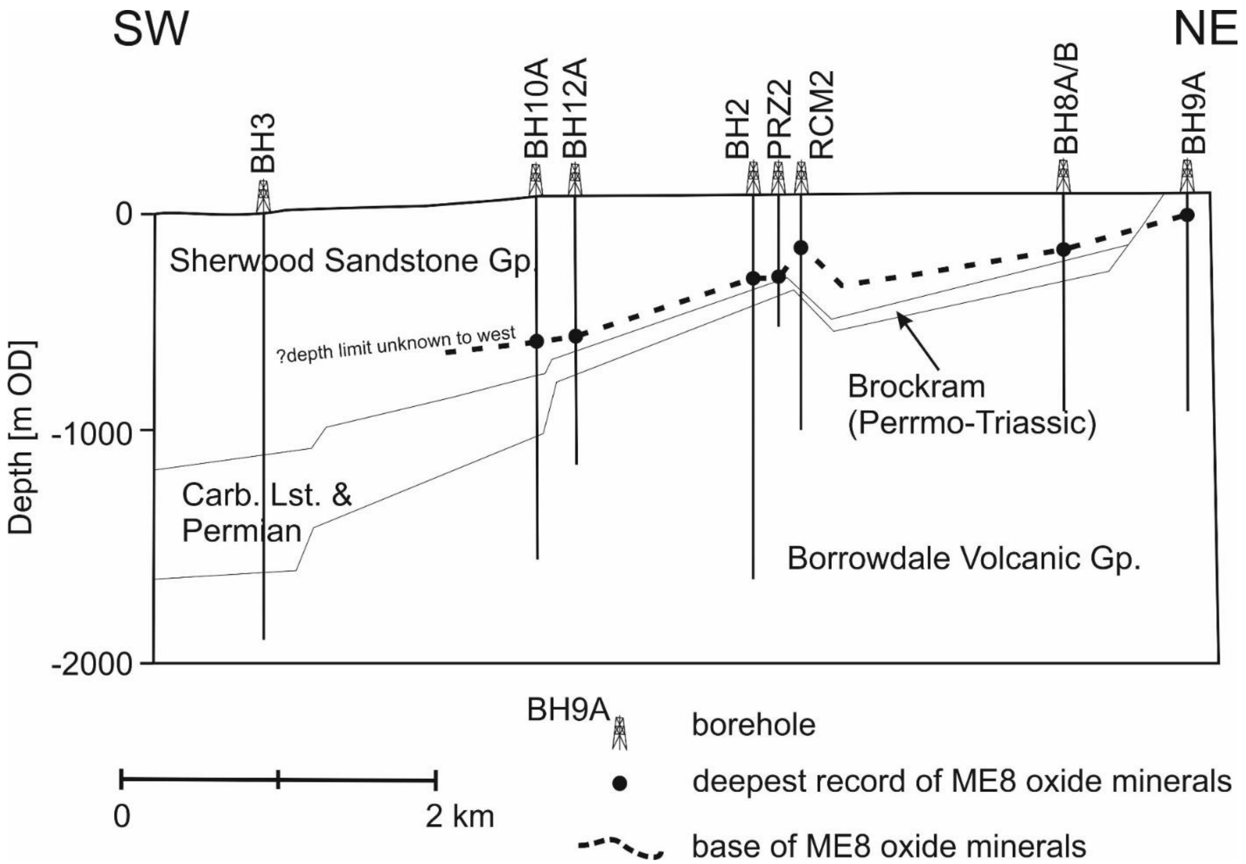


Oxygen isotope composition of ME9 calcite



- *Wide range of $\delta^{18}O$ across individual crystals*
- *Very depleted $\delta^{18}O$ consistent with precipitation from glacially-recharged groundwater*
- *Modelled significant component of glacial-derived water to >1000 m in the saline groundwaters in the basement*

Maximum depth of late (ME8) oxidised minerals



- ME8 Mn and Fe oxyhydroxides produced by weathering and oxidation of earlier Fe-Mn bearing mineralisation (principally earlier carbonate cements
- No evidence of presence in basement below shallow sandstone aquifer

Conclusions

- Review and integration of mineralogical and geochemical studies of fracture minerals and cements, and groundwaters, undertaken as part of a site characterisation programme have identified mineralisation that is closely related to Quaternary groundwater movement.
- Groundwaters may preserve only transient information, but the latest mineralisation in the west Cumbrian groundwater system preserves a record of the Quaternary groundwater history and evolution.
- Past glacially-derived groundwater has penetrated to >1000 m (i.e. potential depth of a deep geological disposal facility) in west Cumbria. However, this has not impacted on the REDOX conditions at depth: Reducing conditions have been maintained despite glacial groundwater penetration
- The late (ME9) calcite records a progressive downwards movement of the freshwater-saline water interface. This is limited (<50 m) and consistent with progressive uplift and meteoric invasion.
- The observations from west Cumbria can provide an analogue for the impact of glaciation on the stability of a deep groundwater system

Not all subglacial water is oxidising!

Blood Falls, Taylor Glacier, Antarctica

© *Photo: Erin Pettit/University of Alaska Fairbanks*

Temperature:	–5.2 °C
pH	6.2
Eh	90 mV
DIC	55 mM
DOC	420 mM
Dissolved inorganic N [100% as NH_4^+]	94 mM
Total iron [>97% as Fe(II)]	3.45 mM

(from: Mikuki et al, 2009, *A contemporary microbially-maintained subglacial ferrous "ocean"* Science, **324**, 397-400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