



Nuclear Waste
Services

Analogue Studies of Rock Matrix Diffusion in Higher Strength Rocks

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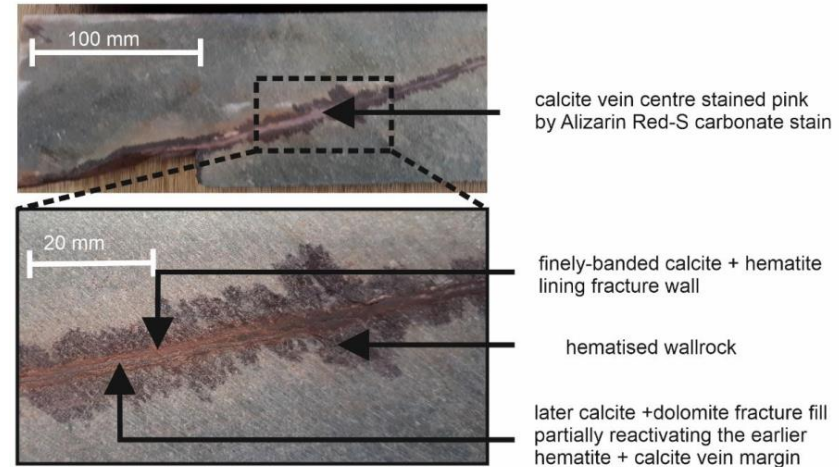
1. Quintessa Limited 2. British Geological Survey 3. University of Leeds 4. Georg-August-Universität Göttingen 5. University of Manchester, 6. Nuclear Waste Services Ltd 7. NSG Environmental Ltd

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Introduction

- Higher strength rocks (HSR) are igneous, metamorphic or sedimentary rocks that:
 - have low matrix porosities and permeabilities
 - allow groundwater advection only through transmissive discontinuities, e.g. fractures
- Water / solutes may diffuse from these discontinuities into the rock matrix (“Rock Matrix Diffusion”, RMD)
- Solute migration in the rock matrix is much slower than in transmissive discontinuities because in the matrix:
 - water is effectively stagnant
 - sorption / desorption of solutes may occur
 - co-precipitation of solutes may occur
- This retardation of solute migration may be important in a safety case for a geological disposal facility (GDF)

Borrowdale Volcanic Group (meta-tuff), Northwest England

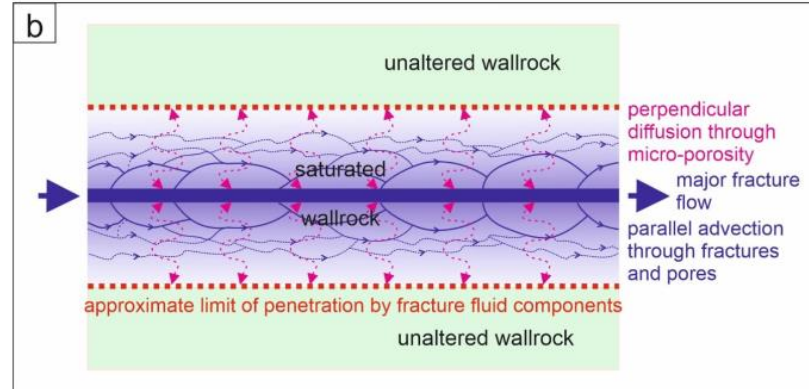
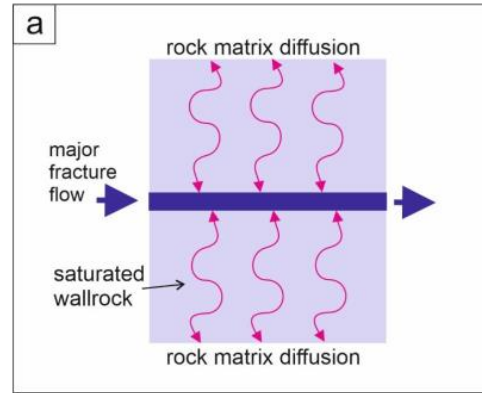


Context

- RMD project commenced in 2016. Phase 2 is now concluded.
- UK GDF siting process has evolved over this period. The siting process is ongoing, with 4 community partnerships now formed.
- A wide variety of HSR could be considered as potential GDF host rocks.
- Project assesses what (if anything) can be stated about the potential effectiveness of RMD in HSR in relation to radionuclide migration.
- Much work on RMD has been done by Waste Management Organizations in a number of countries.
- It is desirable to judge to what extent learning from these investigations can be generally applicable and to what extent it is site-specific.
- As a basis for informing such judgements, a range of different HSR rock types was studied.

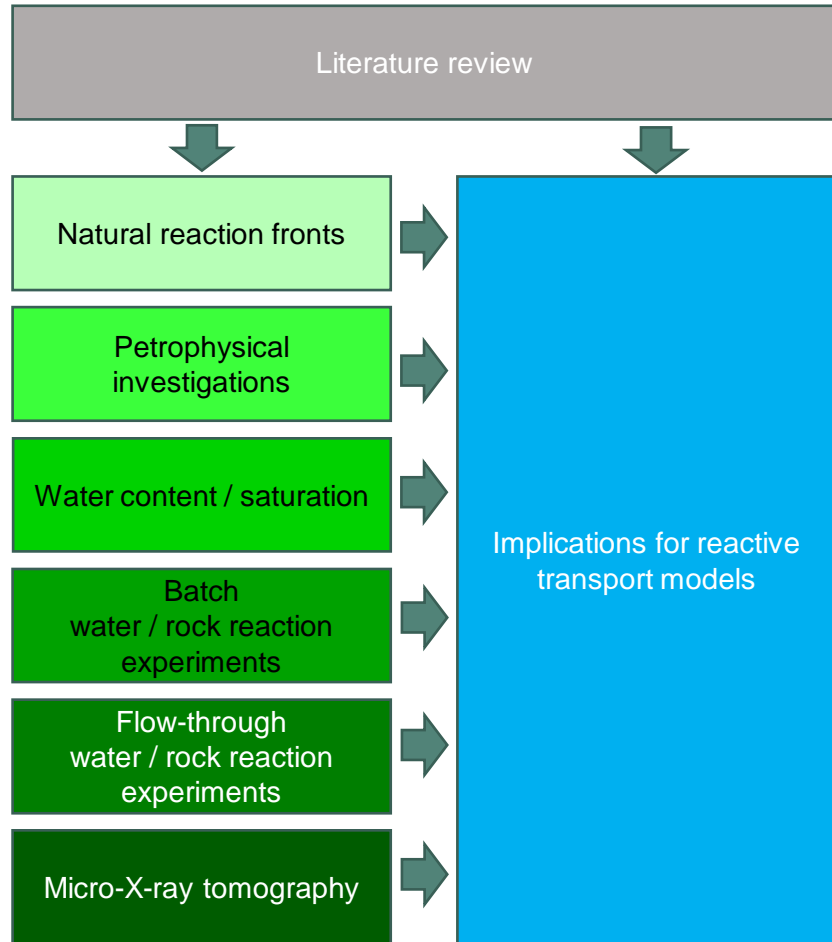
Questions

- RMD has been studied extensively in the last c. 40 yrs
- Two alternative models have been proposed / applied:
 - a) all rock matrix accessible to water/solutes
 - b) only a localized zone of rock matrix near to conductive fractures is accessible
- Role of water / rock reactions as a control on rock matrix accessibility has been debated
- Key questions:
 - How generally applicable are results from site-specific studies?
 - Are there circumstances when model (a) applies and circumstances when model (b) applies?
 - How can RMD be treated conservatively in assessment models?



Approach

- Complementary evidence from different kinds of investigation
- Learn from sectors besides radwaste (especially hydrocarbons)
- Study natural reaction fronts (analogues)
- Study effects of sample perturbation on measured petrophysical properties
- Conduct lab experiments to study
 - accessibility of unaltered rock matrix to water / solutes
 - how water / rock reactions are coupled to this accessibility
- Assess prospects for representing process couplings realistically in numerical models



HSR Sample Requirements

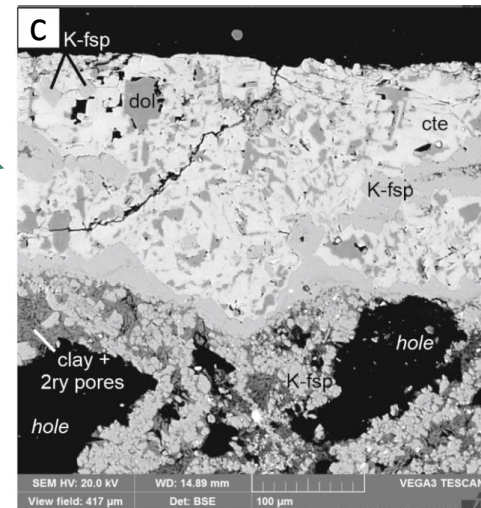
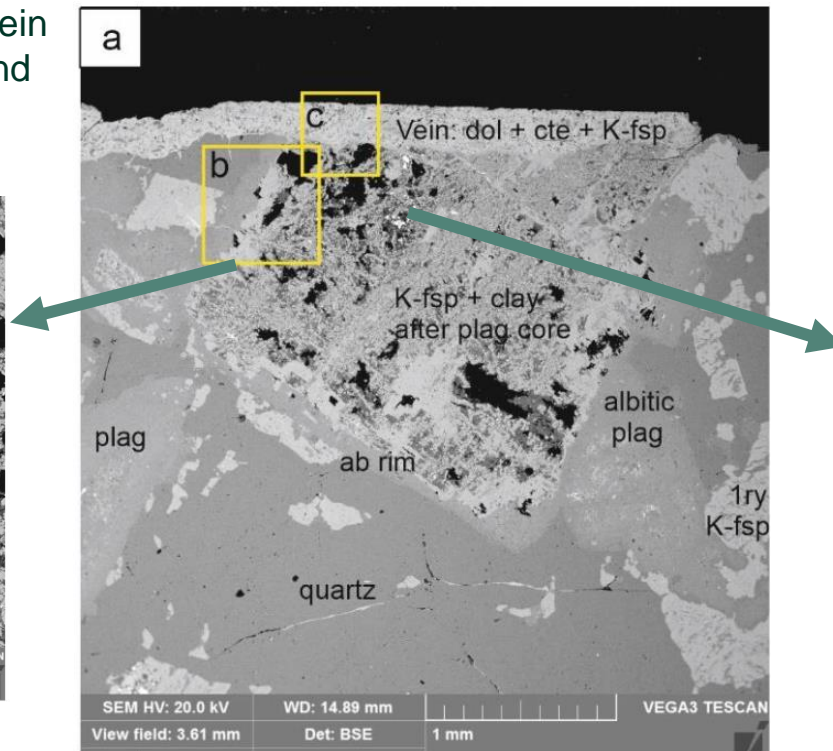
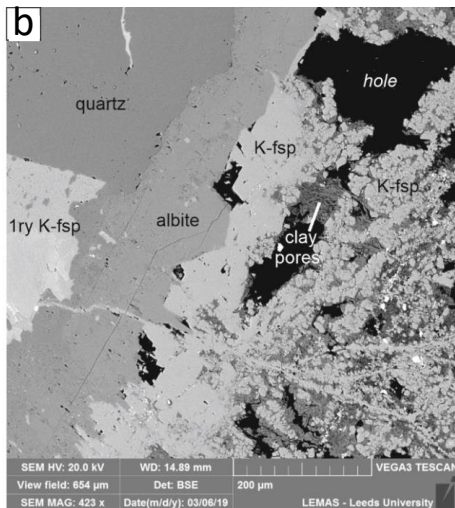
- Natural reaction front studies:
 - sufficiently fine grained so heterogeneities in primary minerals and textures do not mask spatial variations in secondary mineralogy
 - alteration in fracture wall rocks over small spatial scales (mm to 10's of mm) so transitions between altered and fresh rock can be studied in thin section
 - unaffected by near-surface weathering unrelated to circulation of water in the deep sub-surface
- Investigations of porosity and water saturation, and their perturbation during sampling
 - sample obtained underground with as little disturbance as possible, preserved to prevent drying
- Experiments to investigate water/rock reaction influences on porosity / mineralogy, and solute uptake
 - samples sufficiently uniform and fine-grained for water/rock reactions at small laboratory scales

HSR Samples

- Borrowdale Volcanic Group (BVG) NW England
 - NSF-9A, very fine-grained metavolcanic rock cut by thin planar fractures, typically c. 0.5 mm wide width, filled by calcite and dolomite, often rimmed by a reddened zone c. 1-2 mm wide
 - RCF-1, foliated metavolcanic rock with a complex iron oxide-carbonate vein with interlayering of dolomite, calcite and iron oxide zones
- Mountsorrel Granodiorite, MSG-1, central England
 - coarse-grained (grains several mm across) granodiorite
 - a vein a few mm thick occurs along one side composed of calcite, dolomite and K-feldspar
- Karin Grey granite, south-central Finland
 - Fine-grained granite with grains between 0.5 mm and 2 mm across
 - Very little alteration
 - No veins
- Central Aar Granite, Grimsel, southern Switzerland
 - Coarse-grained (grains up to 10 mm across) granite
 - Sample cut by mylonitised shear zone

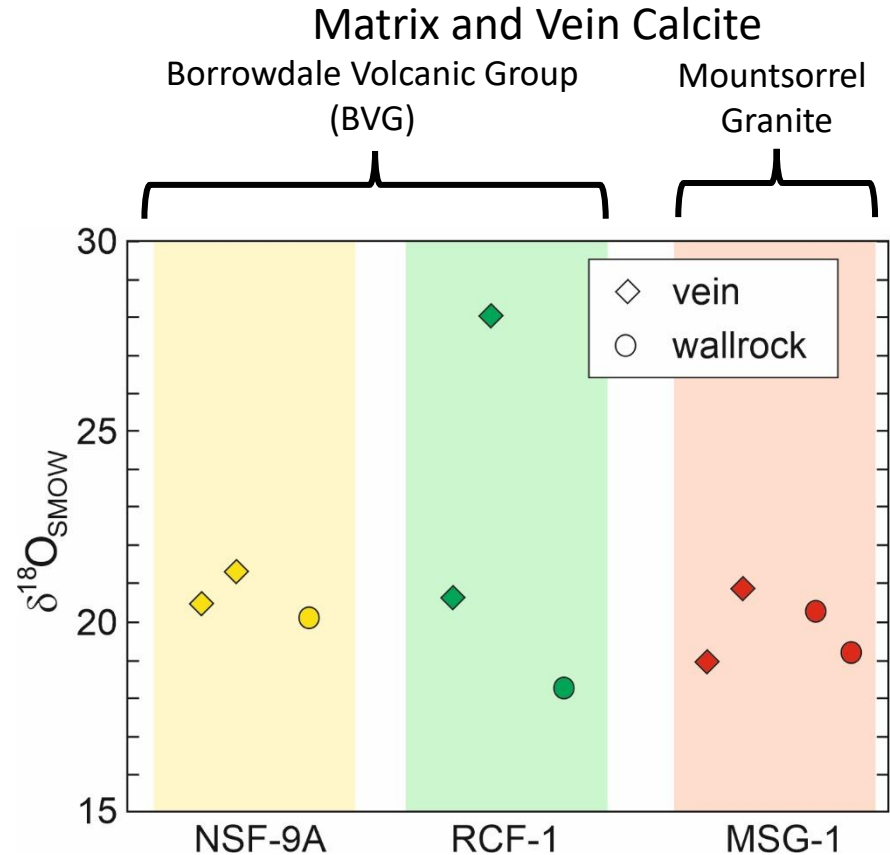
Natural Fronts – Mountsorrel Granodiorite (MSG-1)

- Alteration localized near vein
- Feldspar altered to clay and carbonate



Natural Fronts – O isotopes

- O-isotopes were analysed by ion probe in:
 - Late-stage calcite veins
 - Calcite in the immediate wallrocks
- Each point shows the mean O-isotopic composition of a distinct sample area
- Vein and matrix compositions are closely related, (except one (+28‰) reflecting precipitation at lower T or from fluid with heavier O-isotopic composition)
- O-isotopic composition of secondary calcite is consistent with growth from surface waters at geologically low temperatures (c. 100 – 150 °C)
- These O-isotope data indicate growth of calcite in late-stage veins, and in their immediate wallrocks due to infiltration of deep groundwater
- No need for interaction with wallrock pore waters



Petrophysical Investigations – Samples (1)

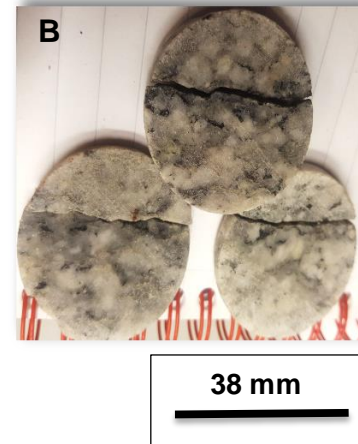
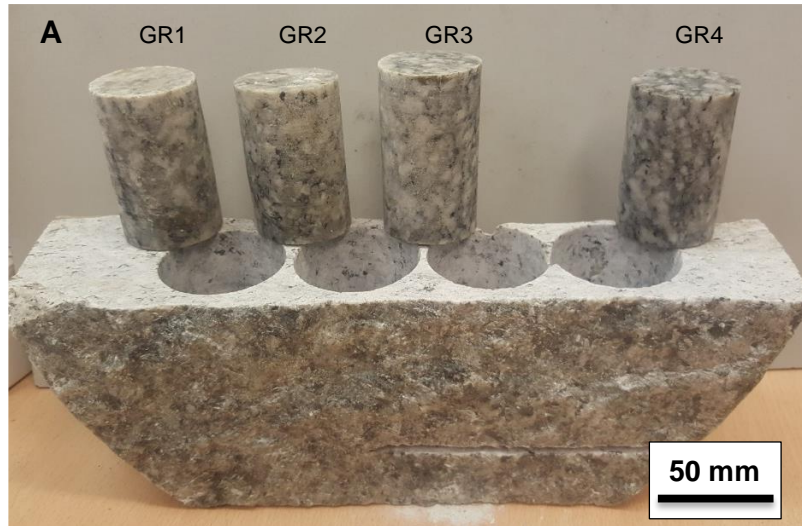
Central Aar Granite – Core

- Core specially obtained by Nagra and from the Grimsel Test Site (GTS) in the Swiss Alps
- Sampling location c. 450 m below the Juchlistock mountain at an altitude of ca. 1730 m
- Horizontal borehole 5.75 m long, diameter 300 mm
- Core preserved in resin immediately on sampling



Petrophysical Investigations – Samples (2)

Central Aar Granite – Core Plugs



Water Content Measurements

Central Aar Granite Core 4.85 - 5.15 m from tunnel											
Broken into chips				Sawn to plug shape		Sawn, dried, cored (37.7mm) c. 5.00 m					Cored (25mm, 5.1 m from start of core)
A		B (chl-rich)		C		GR1	GR2	GR3	GR4	Mean (Excl chl)	
1	2	1	2	1	2 (chl)						
Initial pore water content by NMR (vol %)											
0.62	0.54	1.04	1.06	0.61	1.35	0.90	0.88	0.76	0.75	0.72	
Total porosity by NMR after re-saturation(vol %)										Porosity (MICP)	
										0.80	
Pore saturation of extracted core (%)											
										57.7	
										56.0	
										65.9	
										64.3	
										59.4	
										51.4	

- Various methods used to determine water content / porosity / water saturation
- All show porosity of preserved (resin) core is under-saturated

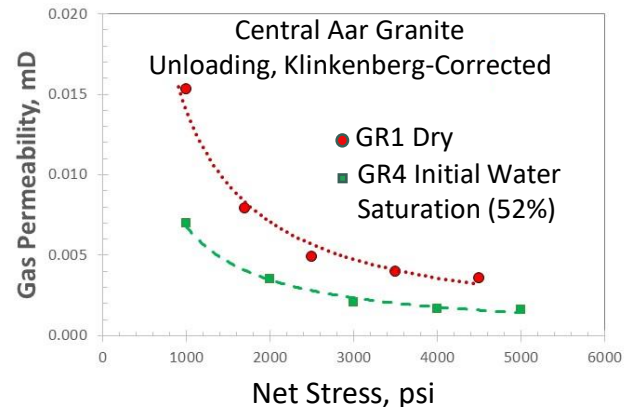
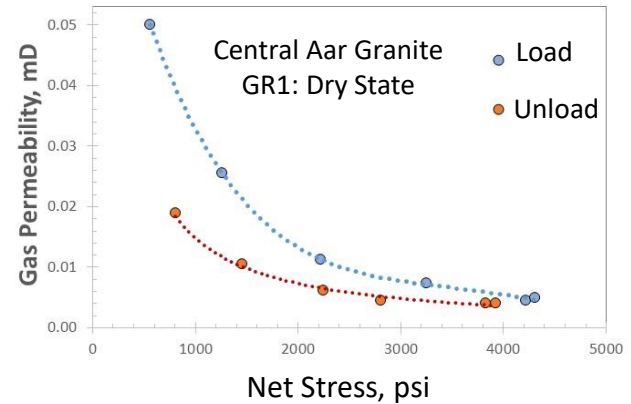
Central Aar Granite Core, 5.30 - 5.75 m from tunnel						
Sample sawn, dried and split by jaw crusher						
A		B		C		Mean
A1	A2	B1	B2	C1	C2	
Initial pore water content by Gravimetry (vol %)						
0.76	0.74	1.05	0.63	0.53	0.60	0.72
Total porosity by Gravimetry after re-saturation (vol %)						
2.22	2.22	2.47	2.19	1.94	1.89	2.16
Pore saturation of extracted core (%)						
34.2	33.3	42.5	28.8	27.3	31.7	32.99

Possible Explanations for Partial Saturation

1. The in-situ Central Aar granite could be only partially water saturated
2. The stress release during coring and sub-sampling could have produced the opening of grain boundaries and microfractures along preferential stress directions
3. Despite efforts to preserve the core and prevent drying, some water loss may nevertheless have occurred post-sampling

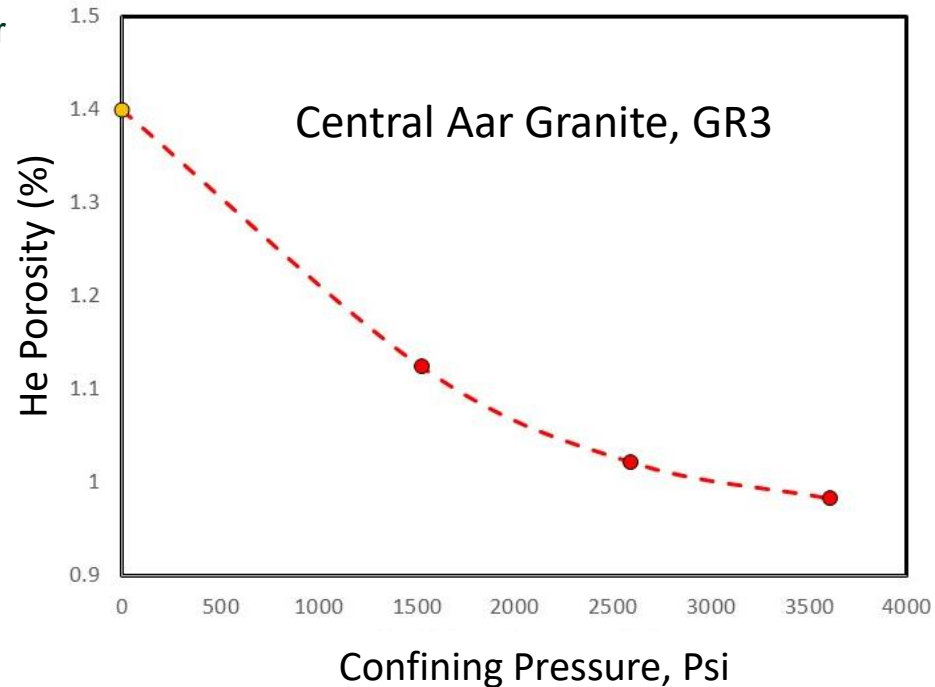
Petrophysical Investigations – Gas Permeability at Stress

- Hysteresis observed for gas permeability during loading / unloading
- Even at 4000 psi (27.58 MPa) the gas permeability is 4 μD :
 - high for this type of matrix
 - suggests flowpaths dominated by microfractures
- During destressing, GR4 (initial water saturation 52%) has lower Klinkenberg-corrected gas permeability than GR1 (dry)
- Within the stress range tested, relative gas permeability varies between 0.51 and 0.64 (Klinkenberg-corrected 0.46):
 - evidence for a gas flow path even at higher stresses
 - suggests sample only partially water saturated even at in situ stress



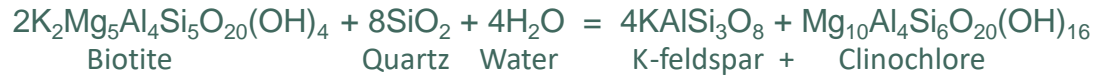
Petrophysical Investigations – Porosity at Stress

- As porosity decreases with increasing stress, water saturation increases
- GR3 water saturation at ambient condition is 60%
- Water volume is constant so at stress of 3600 psi (24.80 MPa) saturation 86%
- 24.80 MPa is within range of measured horizontal principal stress at Grimsel
- Suggests sample may have been only partially saturated in situ
- Conclusion may hold even if actual in situ stress is higher, since the curve flattens at higher stress



Accessibility of Water – Thermodynamic Arguments

- Primary minerals igneous minerals (biotite, hornblende, plagioclase) commonly occur in granite, even with ages of billions of years
- These minerals react in the presence of water at low temperatures to produce chlorite, clays, calcite, or other secondary products, e.g.



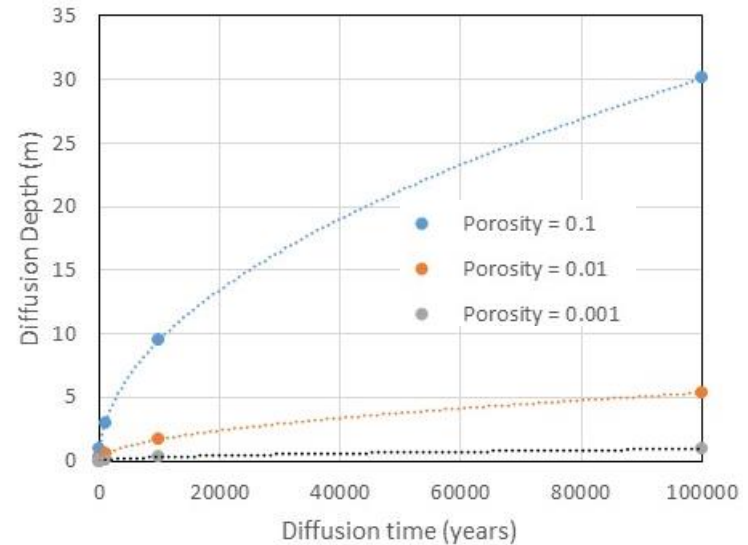
- Using the Thermoddem data $\Delta G^0_r = -122.5 \text{ kJ}$, so
 - the right hand side of (chlorite present) is stable relative to the left (biotite present)
 - activity of water is extremely small (4.3×10^{-6})
- Preservation of primary minerals implies that water does not freely access the rock matrix

Accessibility of Water – Diffusion Arguments

- Diffusion depth can be calculated approximately by:

$$L = 2 \sqrt{D_{eff} \times t}$$

- D_{eff} is effective diffusivity (m²/s)
- t = time (s)
- L = diffusion depth (m)
- If D_{eff} was as low as 10⁻¹⁵ m²/s, L is c. 0.3 m in 1 Ma
- Measured values for granitic rock suggest D_{eff} could be much larger (e.g. Yoshida et al., 2009, Eng. Geol., 106, 116–122).
- Implies whole rock mass readily accessible to water
- If so how are primary minerals preserved over very long timescales?

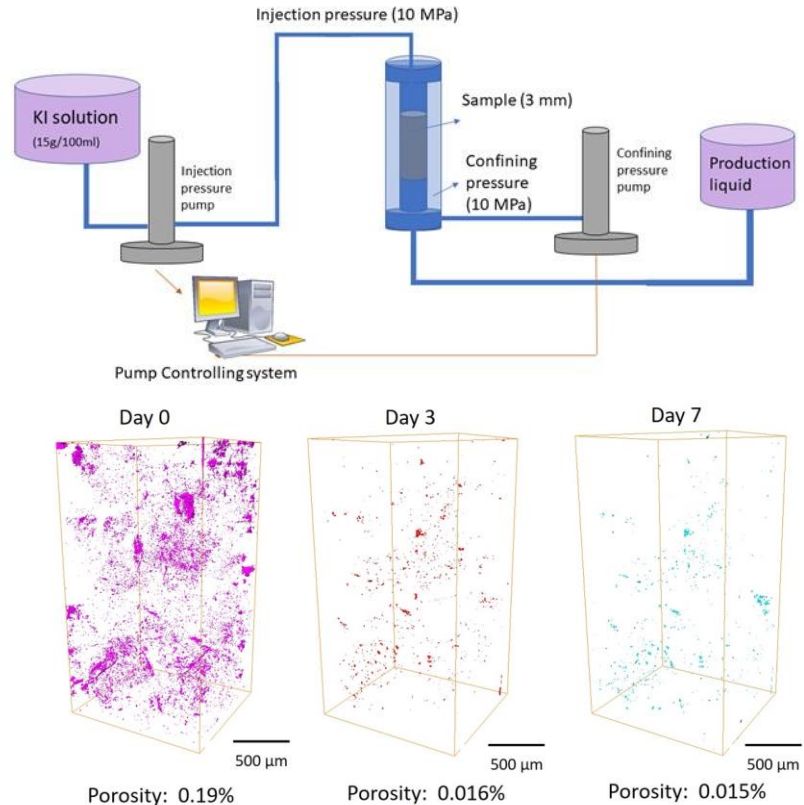


Investigations of Fresh Granite - Rationale

- Investigations of RMD have tended to focus (reasonably) on wallrocks of natural fractures
- This has been done in this study for:
 - Mountsorrel Granodiorite
 - BVG
 - Central Aar Granite
- Natural fracture wallrocks tend not to be fresh, so
 - Difficult to elucidate how / degree to which water and solutes can access rock matrix far from fractures
- To complement these studies, investigate fresh rock:
 - Karin Grey Granite

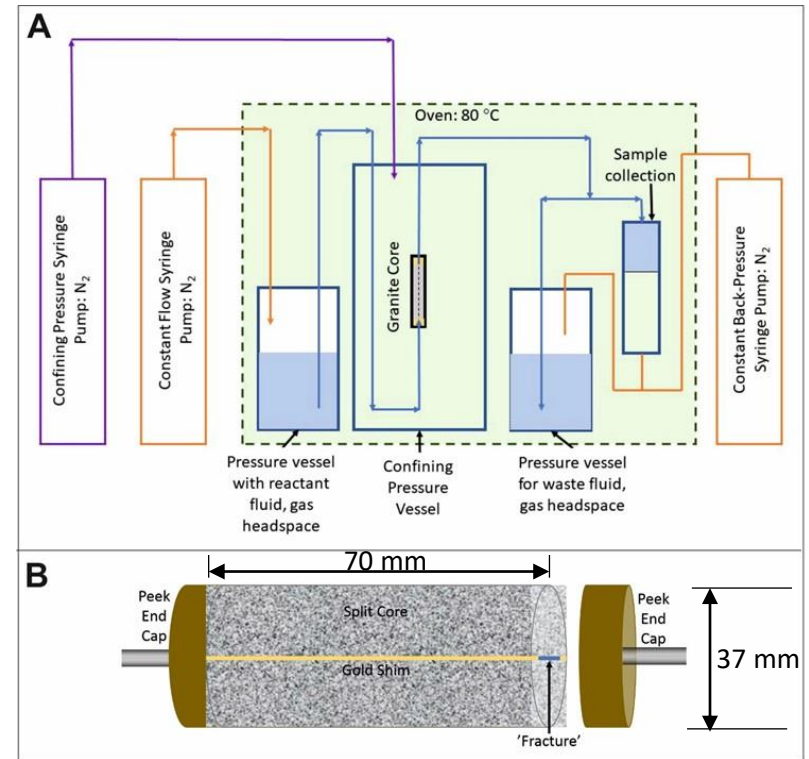
XCT Investigation of Water Access to HSR

- Use XCT to investigate how water gains access to Karin Grey Granite
- Done without applied stress (maximise accessibility of porosity)
- Central Aar Granite not used since too coarse grained
- Real time KI solution access observed
 - 92% of pores filled after 3 days
 - only 0.5% more pores filled between day 3 and day 7
 - well-connected pores filled first (day 0-3), then smaller pores (5-10 μm)
- Empty pores identified on day 7 might not be connected to the overall pore network



Flow-Through Experiment

- Karin Grey Granite core investigated
- As shown by XCT, expect porosity accessible at least over mm scale
- 38 weeks (planned for much longer, but curtailed by COVID-19 pandemic)
- Residence time of water in fracture is 0.89 hours
- Temperature 80 °C
- Water composition specified to have:
 - Similar salinity to seawater (i.e. plausible for a GDF host rock, but not so saline that the Pitzer approach has to be used for modelling)
 - close to equilibrium with granite phases
 - dosed with Cs, I, Ni, Co tracers

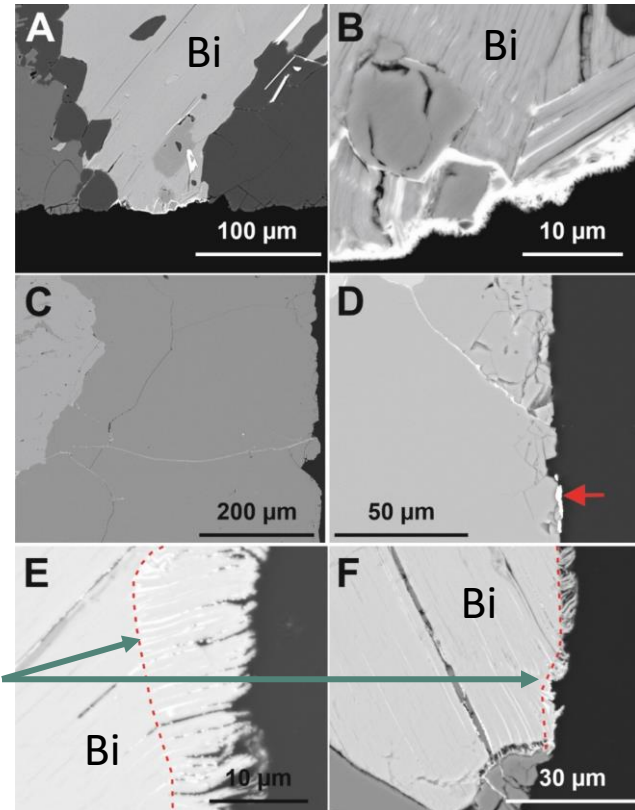


Example Flow-Through Experimental Results

BSEM images:

- A) Image from the inlet end showing Fe (bright) along edge of biotite
- B) High magnification image of part of A
- C) Infilled microfractures in quartz penetrating from the core surface into the rock
- D) Another infilled fracture penetrating the sample from the core surface (red arrow indicates gold particles which originated from the gold sinters in the apparatus)
- E) Biotite crystal near the core surface
- F) Biotite crystal near the core surface

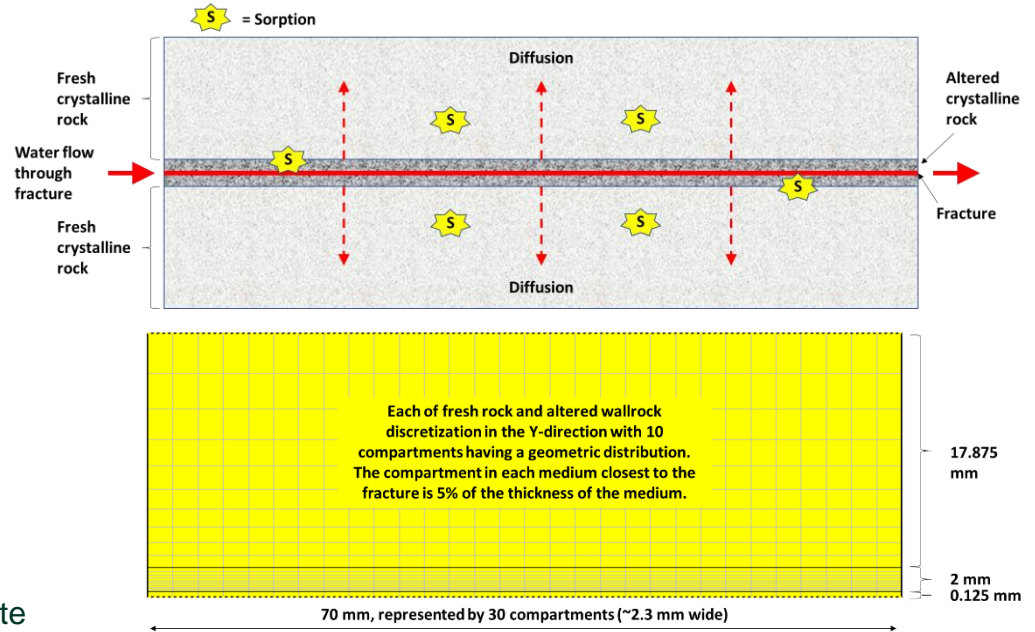
In E) & F) biotite crystals are delaminating and have Fe-oxide (bright) between the laminae extending beyond the region of mechanical damage (extent of mechanical damage indicated by red dotted lines)



Limit of damage
due to sample
cutting

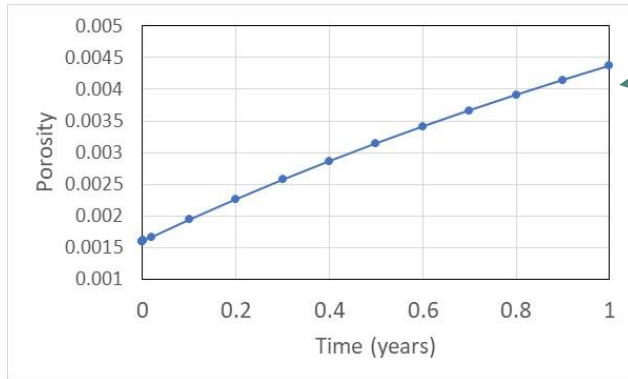
Illustrative Coupled Model Specification

- QPAC software
- *Fully-coupled* (not operator splitting)
- Reaction kinetics:
 - Transition state theory
 - Data from Palandri and Kharaka
- Sorption (k_d)
- Diffusivity coupled to evolving porosity:
 - use Archie's Law, $D_{pore} = D_{water} \times p^n$
 - D_{pore} = Porewater diffusivity (m^2/s)
 - D_{water} = Water diffusivity, $8.6 \times 10^{-8} m^2/s$
 - p = porosity (-), initially 0.16
 - $n = 1.5$
- Simplified water / rock reaction scheme:
 - All primary minerals can dissolve / precipitate
 - Ca-beidellite not present initially, but can precipitate

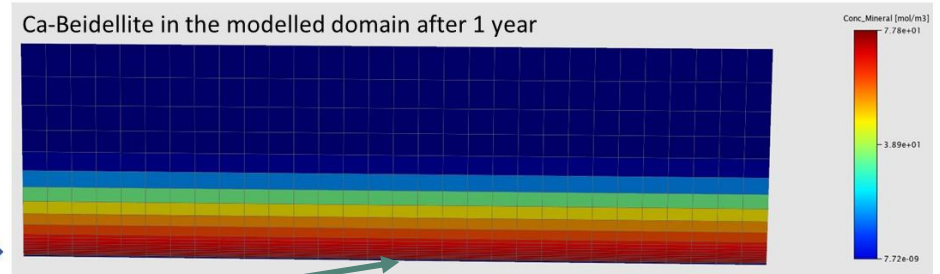


Illustrative Model Results

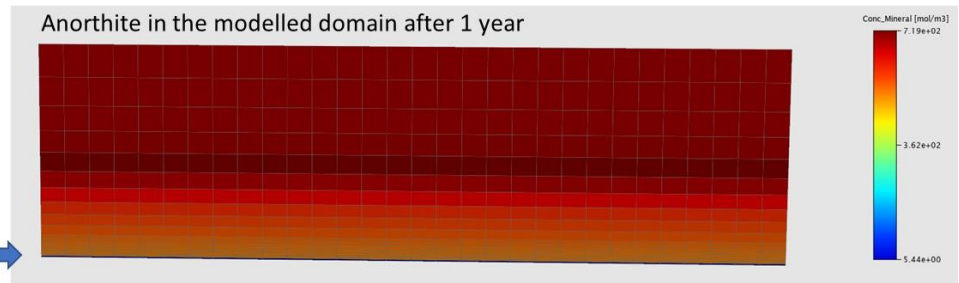
- Water / rock reaction more extensive than observed in experiments
- In this model water / rock reactions
 - increased porosity
 - increased diffusivity
 - accelerating front propagation



Water inflow to fracture



Water inflow to fracture



Conclusions

- It should not be *assumed* that all the matrix of a crystalline HSR is accessible to water / solutes:
 - penetration of water / solutes from transmissive fractures may be only mm to cm;
 - site-specific data are needed to determine the actual distances.
- In our studies, evidence for restricted matrix accessibility includes:
 - spatial distributions of studied natural reaction fronts (Mountsorrel Granite and BVG);
 - petrophysical investigations of Central Aar Granite.
- XCT studies show that pores in the Karin Grey granite are not all equally accessible to water:
 - accessible pores are concentrated along microfractures in the rock, so
 - RMD will be controlled by the spatial distributions and inter-connectivity of these microfractures.
- A variety of evidence suggests that matrix porosity in HSR may not be fully water-saturated.
- If so, this will limit the distance of RMD from major fractures.
- Fully coupled models of all relevant RMD processes must substantially simplify the real system to run in reasonable times, even for length scales of typical lab experiments (cm scale).