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More realistic treatment of long-term cement degradation: support from ancient natural cements

W. Russell Alexander

Bedrock Geosciences, Auenstein, Switzerland

(russell@bedrock-geosciences.com)

Driving force

- **Recently, national regulators have been calling for a less conservative approach to the assessment of engineered barrier degradation**

- **For example, in 2009, the Swedish regulator, SSM, noted that it would like to see the long-term degradation of cementitious materials (waste, containers, backfill, tunnel liners) treated in a more realistic manner**

Driving force

- **Current treatment is highly simplistic in most national programmes, utilising simple mixing tank approaches with emphasis on over-prediction of consequences (i.e. relatively rapid degradation of the cement leading to release of radionuclides to the surrounding host rock)**

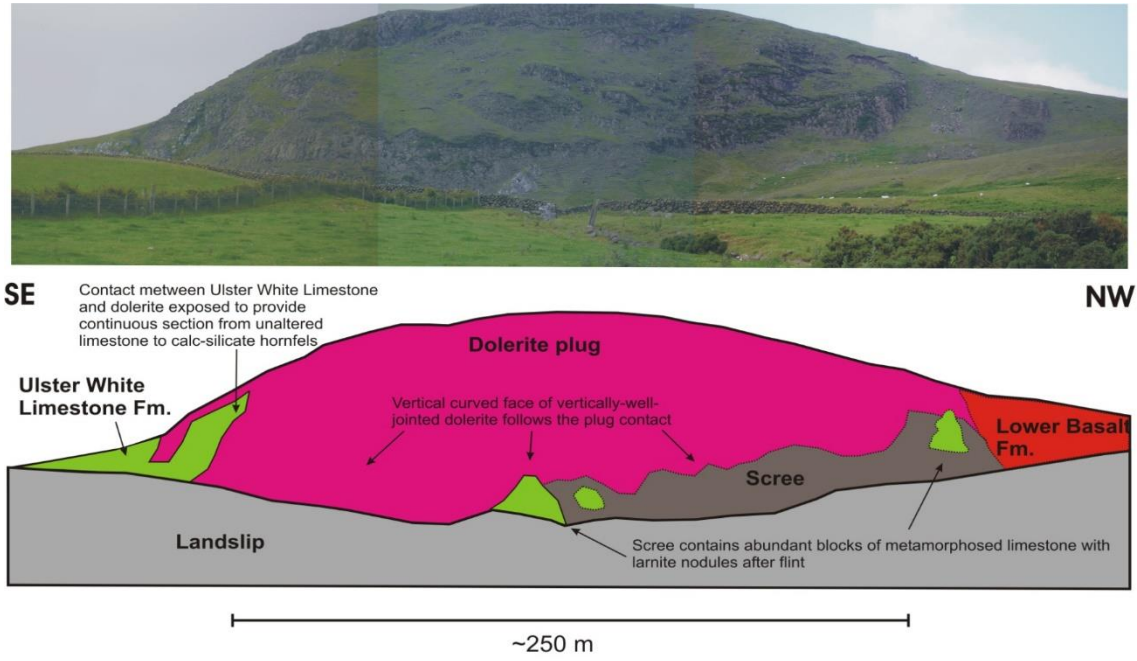
- **Even when more sophisticated reactive transport codes are used for these assessments, they are generally supported by only short-term laboratory experiments, so it is perhaps not surprising that longer-term processes are treated in an over-conservative manner (due to a lack of relevant data)**

Driving force

- **Most assessments of long-term concrete degradation to date focus on leaching of the cement, with concomitant loss of the flow barrier and loss of the radionuclide retardation capacity of the material. However, this approach ignores the fact that:**
  - **very old cements exist: e.g. Scawt Hill in Northern Ireland is ca. 58 Ma**
  - **they are very widespread: e.g. the natural cements in the Middle East cover an area of around 500,000 km^2**
- **suggesting that this 'leaching' approach is fundamentally flawed**

Background to cementitious NA

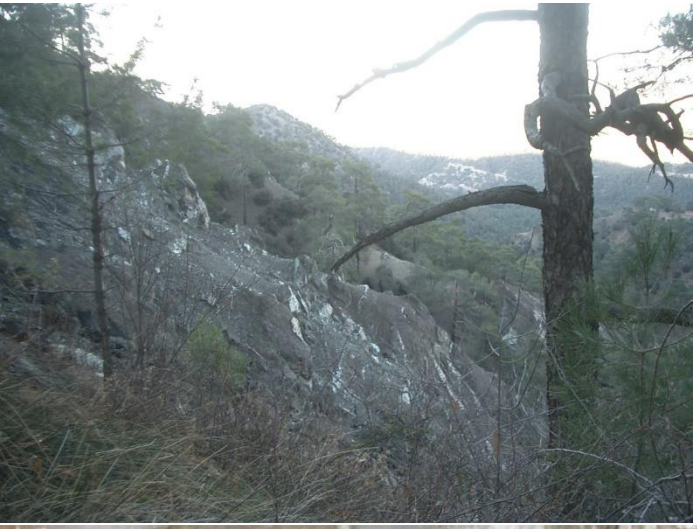
- **There are very few relevant OPC (Ordinary Portland Cement) analogues:**



Mathewson et al. (2006); Posiva (2013)

Background to cementitious NA

- **There are very few relevant low alkali cementitious analogues:**

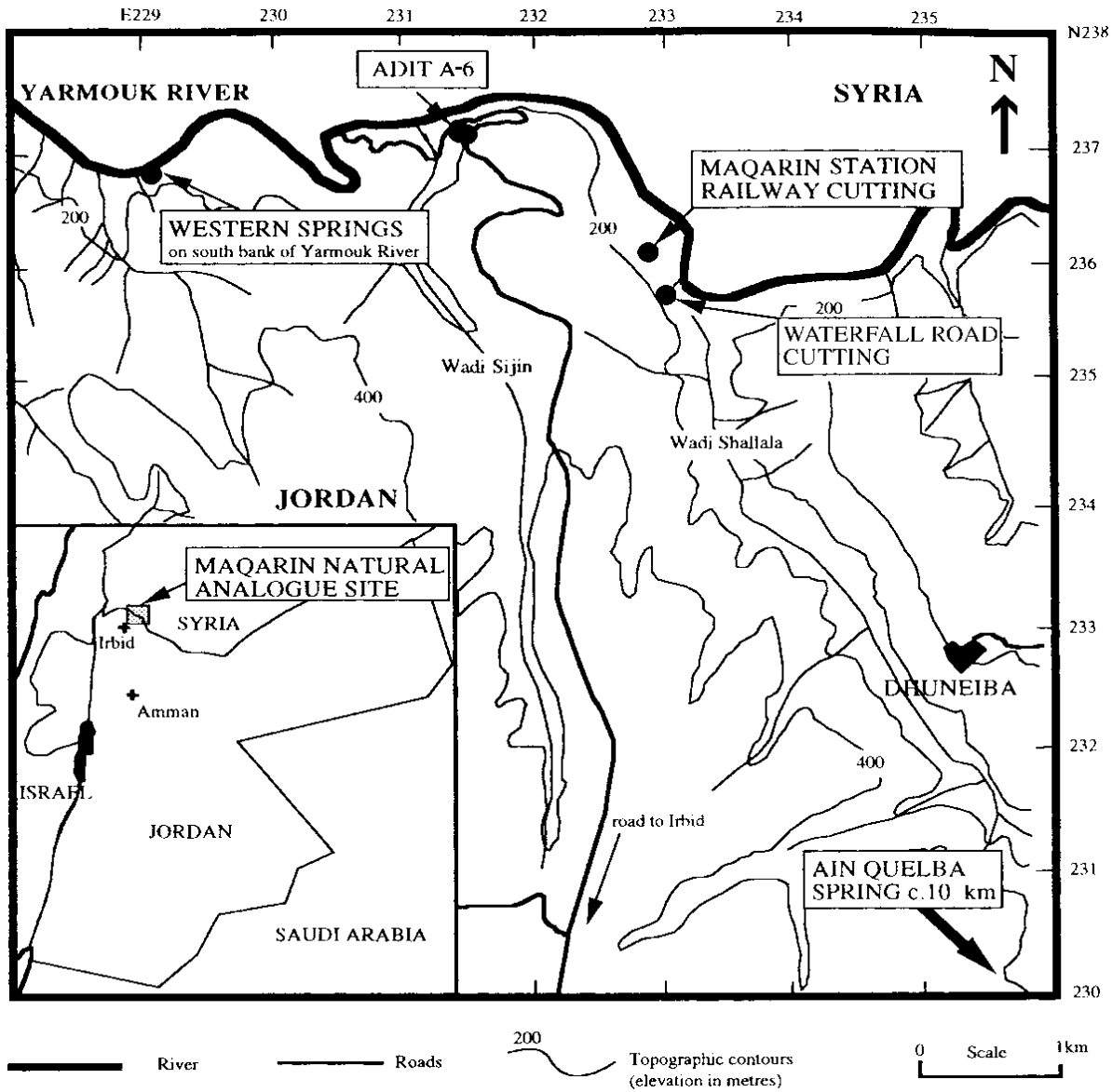


Posiva (2013); Milodowski et al. (2016);
Fujii et al., (this workshop)

Proposed approach

- The approach proposed here is to examine evidence for long-term sealing of cementitious materials
- Although sealing processes such as carbonation and ettringite development can be viewed as mainly a favourable phenomenon in a safety assessment (SA), they have generally been neglected to date
- once again, due to a lack of relevant data on the long-term evolution of cementitious materials

Jordan – 2 Ma old cements

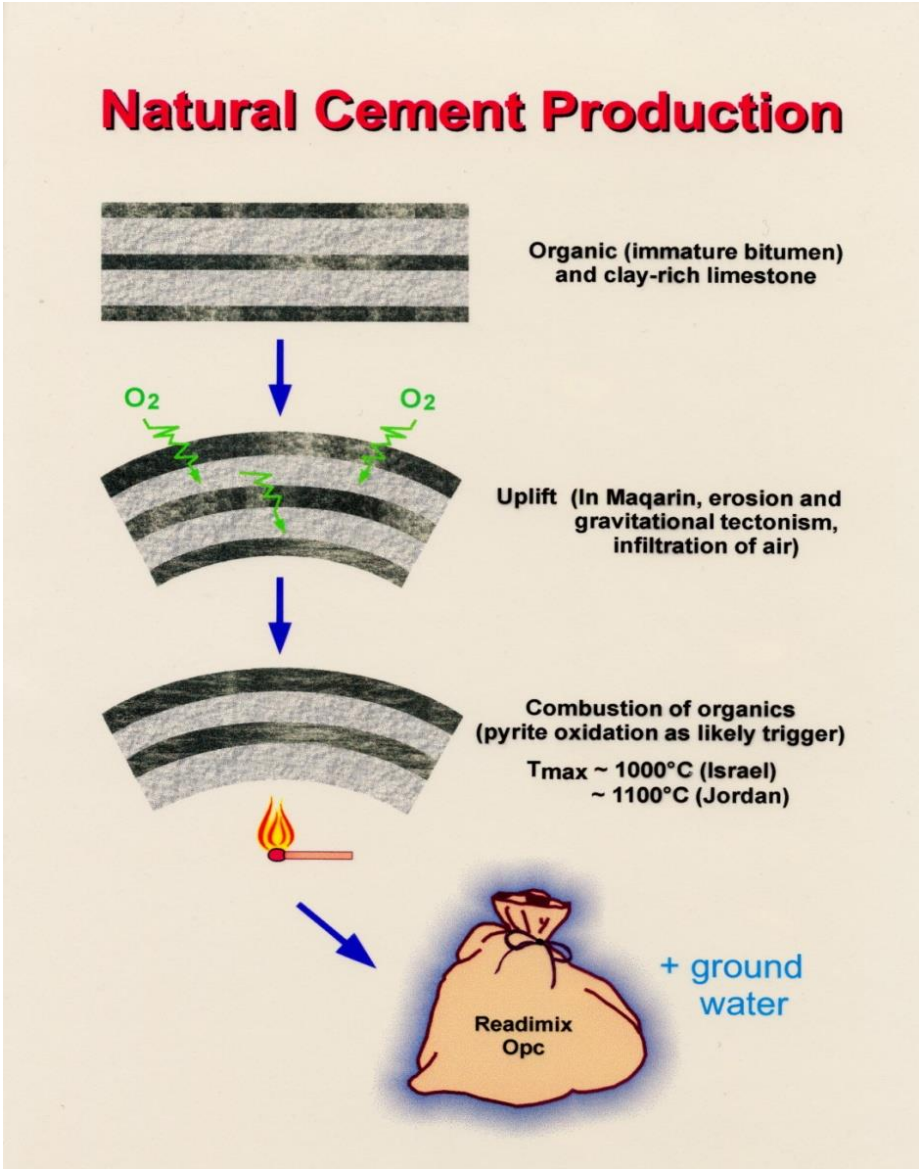


Khoury et al. (1998)

Maqarin & Khushaym Matruk

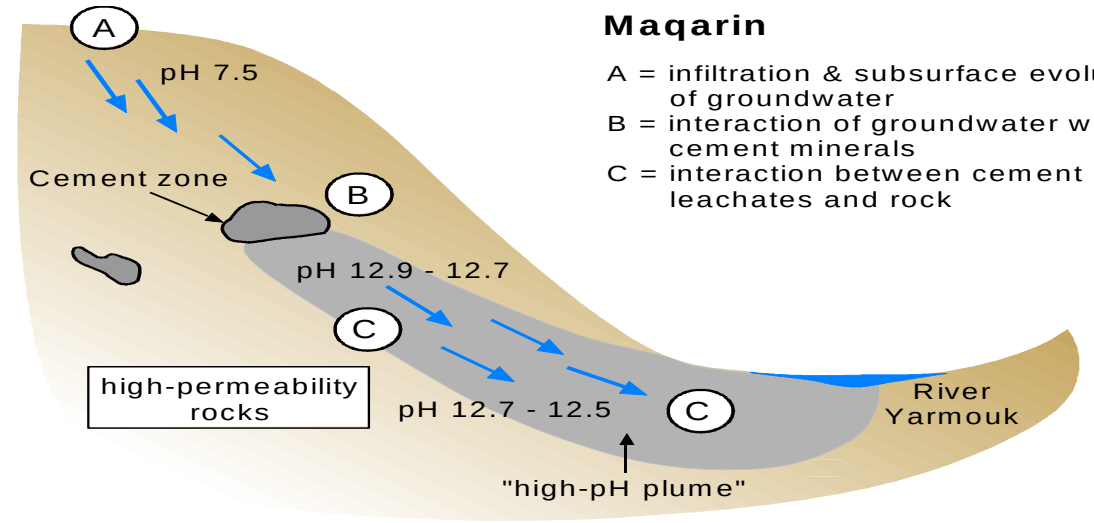
Alexander (1992); Smellie (1998); Pitty & Alexander (2011)

Natural OPC: the basis of the analogy (1)



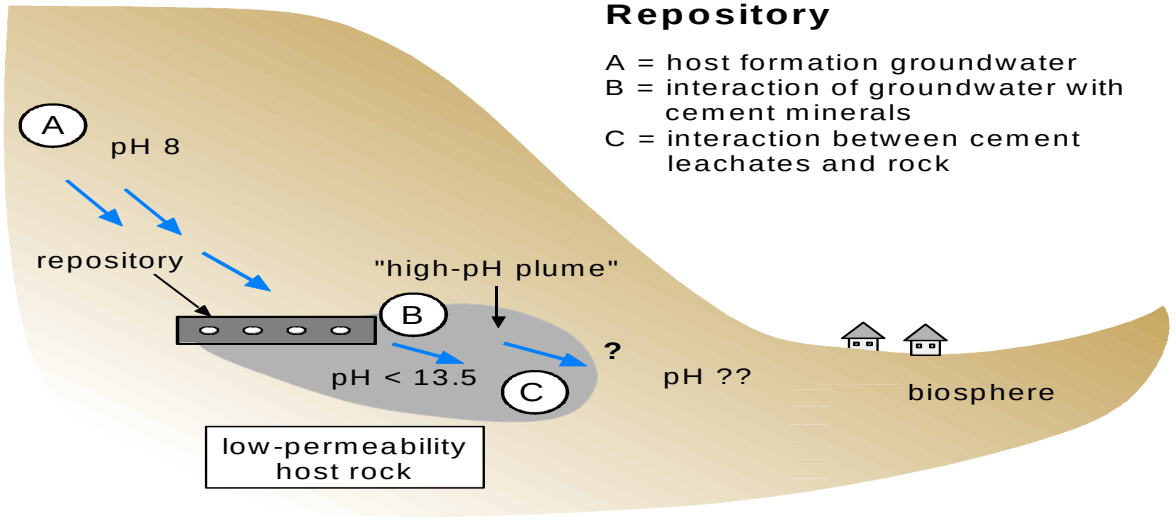
Alexander & Smellie (1998)

Maqarin – the only active site in the world



Maqarin

A = infiltration & subsurface evolution of groundwater
B = interaction of groundwater with cement minerals
C = interaction between cement leachates and rock



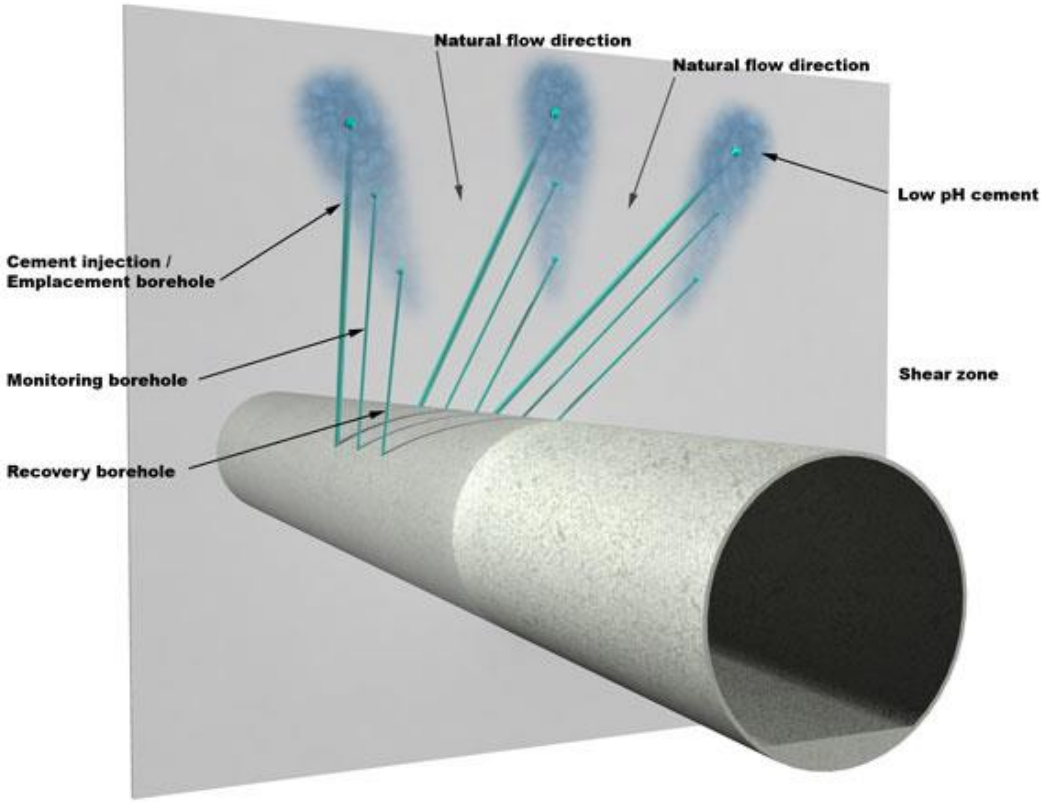
Repository

A = host formation groundwater
B = interaction of groundwater with cement minerals
C = interaction between cement leachates and rock

Linklater (1998)

Update on the work in the LCS project, GTS

- Last field work in Jordan in 2004, little done until the last few years in the LCS (Long-term Cement Studies) project in the GTS rock laboratory in Switzerland
- This also looking at impact of cement leachates on the host rock
- New results include updated secondary mineral diagenesis sequence and model tests (see Martin et al., 2016)



But how can Jordan help us today?

- **In 2009, SSM (Swedish regulator) noted that it would like to see the long-term degradation of cementitious materials (waste, barriers, backfill, tunnel liners) treated in a more realistic manner**

- **Current treatment is highly simplistic in most national programmes, utilising simple mixing tank approaches with emphasis on over-prediction of consequences (i.e. relatively rapid degradation of the cement leading to release of radionuclides to the surrounding host rock)**

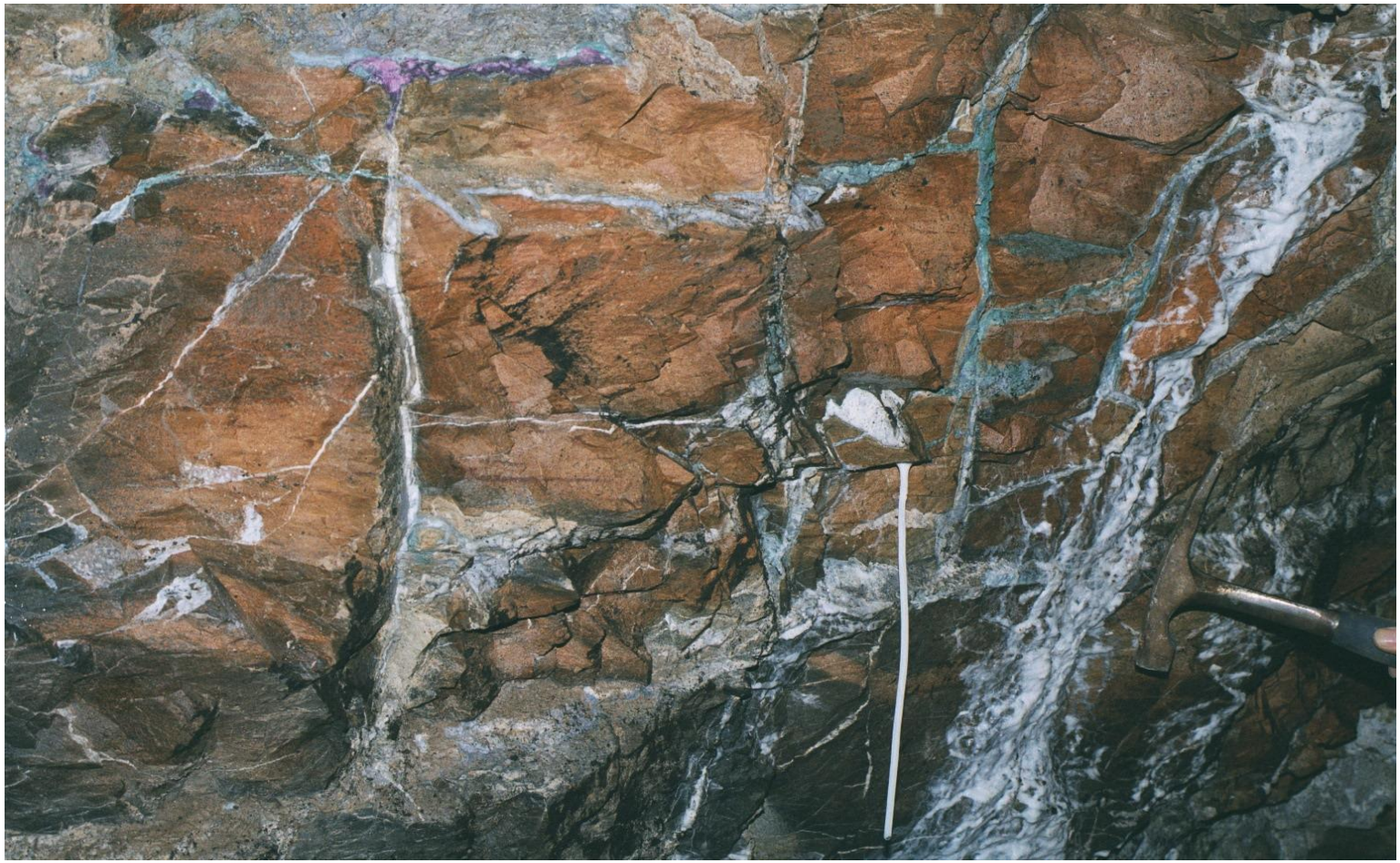
- **The reactive transport codes used for these assessments are supported by short-term laboratory experiments, so require additional support from long-term natural systems**

- **NB current approach ignores/minimises positive processes such as carbonation or self-healing that will minimise the overall degradation**

But how can Jordan help us today?

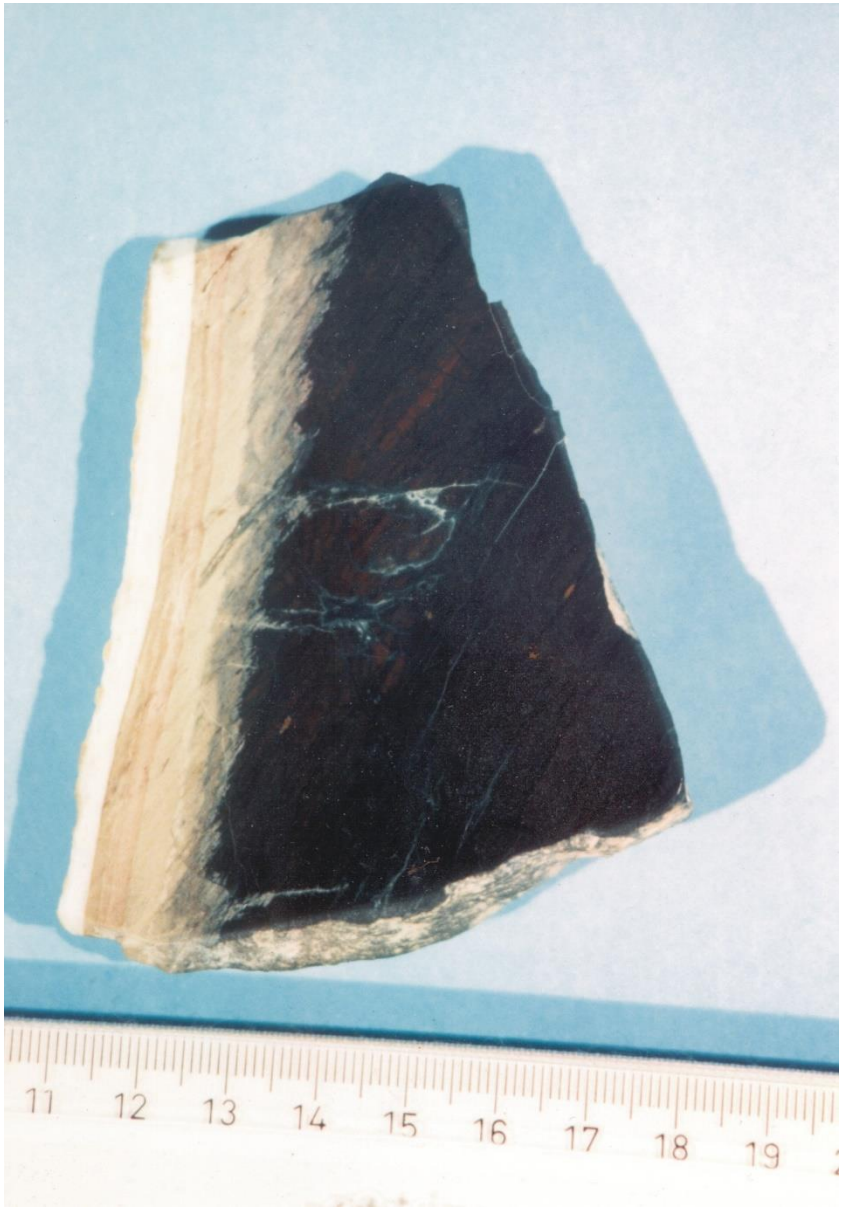
- **Questions to be addressed in Jordan today include:**
  - **What are the rates of sealing of fractures and the matrix in the cement?**
  - **What fracture apertures can be assumed to seal?**
  - **How much cement matrix (both behind the fracture walls and the bulk matrix) will be involved?**
  - **How long can these ‘sealed cements’ be assumed to last?**
  - **Could there be negative aspects of sealing (e.g. gas overpressure)?**

Maqarin: cement sealing is observed



Alexander (2012)

Daba: cement sealing is observed



Khoury et al. (2011); Alexander (2012)

Carbonation (as an example of self sealing)

- **Neall & Johnson (2006) noted that, although the carbonation mechanism can be viewed as mainly a favourable phenomenon in a SA, it has generally been neglected to date**

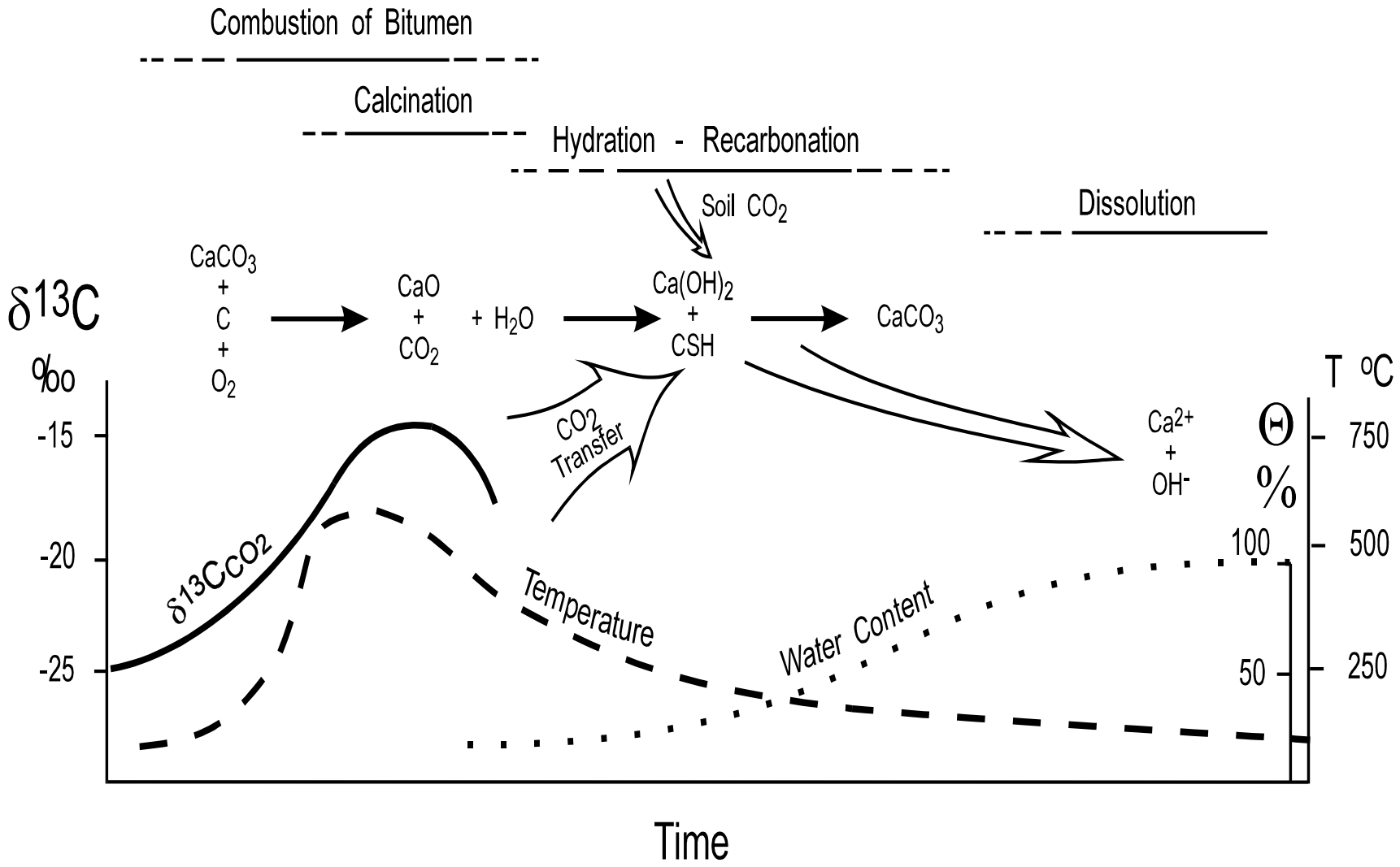
- **Most comprehensive assessment to date is that of Höglund (2014) for the SFR (Sweden) Safety Case**

- **Currently, NUMO (Japan) conducting 'more realistic' modelling within the 2015SC**

- **However, no directly relevant NA studies of carbonation exist, but there is significant potential to study the process in Jordan**

- **Based on $\delta^{13}C$ data, a period of CO_2 uptake has been identified at the site, but no more than a preliminary assessment was made originally**

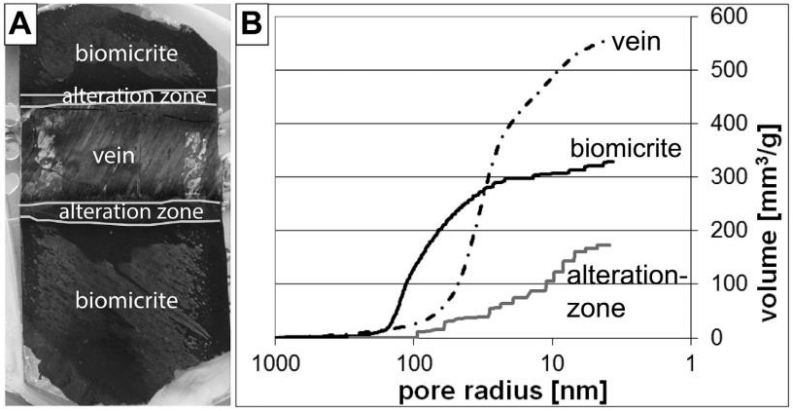
Carbonation has been studied to a degree

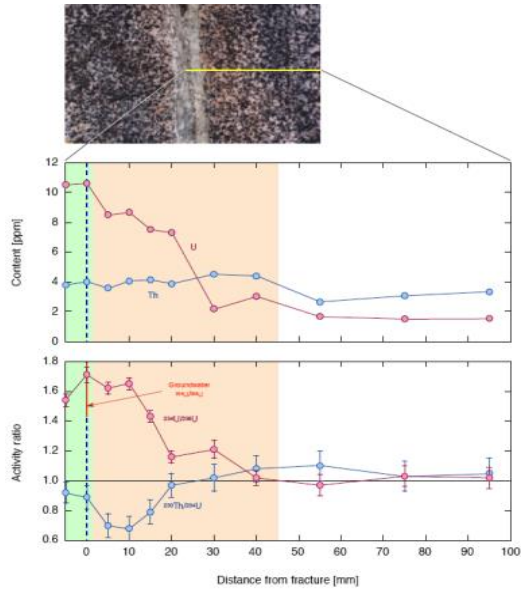


Clark et al. (1994); Khoury et al. (2011)

Cement sealing: what next?

- **What we propose doing at the sites in Jordan is to conduct something along the lines of the recent work in the LCS project which provided a good *physical* indication of sealing in the *rock matrix* (cf. Martin et al. 2016)**
- **We will do the same for the *cementitious materials* in Jordan, but with the addition of using *isotopic* means**
  - **NDS to assess depths of reaction and sealing (cf. Alexander & Mazurek, 1996)**
  - **NDS/Th ingrowth/etc to assess the initiation of reaction, ages of sealing etc.**
  - **$d^{13}C$ to identify sites of carbonation (cf. Clark et al., 1994)**
  - **$d^{34}S$ to asses sites of ettringite/thaumasite pore blocking**





Cement sealing: end product

- **Would be a dataset showing the impact of long-term sealing processes on the longevity of cementitious materials in a repository**
- **This should include samples covering:**
  - **a range of palaeo-environments in Jordan to cover a range of original cement mineralogies/densities, groundwater flow and cement degradation scenarios**
  - **a range of flow system ages and time since sealing (and/or re-sealing in tectonically active zones*) of the cementitious material may be relatively fast in some host rocks and slow in others**
  - **zones where groundwater transport has been in fractures in the cement (e.g. in the Maqarin and Daba areas) and other zones where groundwater transport appears to have been diffusive (e.g. the Khushaym Matruk area)**
  - **if possible, where gas may have occurred**
- **As both the rates of sealing and depth of matrix infiltration are important parameters for coupled transport model testing, these will be addressed with particular care**
- **Finally, a realistic dataset for long-term cement degradation!**

Cement sealing: conclusions

- **Current repository safety assessment assumptions on the longevity of cementitious wastes are highly pessimistic**

- **This is now changing (cf. SKB and NUMO ongoing work), but the new assessments still use (reactive transport) models which are largely based on short-term laboratory experiments**

- **As such, the assessments require support from observations of natural systems which have been running for comparable timescales to the those of interest for a repository**

- **The well characterised 2 Ma natural cements from Jordan offer an excellent opportunity to provide this support by building on existing information**

Low alkali cements

- **Quick last words…..**

Jordan – 2 Ma OPC – with low alkali cement?

In Syria and northern Jordan, for example, the Formation is punctured by Late Oligocene to Quaternary volcanics so sites which include pozzolanic ash mixed with the Bituminous Marl could exist and so could produce natural low-alkali cements

Indeed, they have been tentatively identified in northern Jordan (Prof H.Khoury, *pers comm.* May, 2013).

Italy - low alkali cement?

- **It has been speculated (e.g. Oleson et al., 2004) that the formation of natural concrete at sea level around Puteoli in Italy, formed when calcium carbonate saturated groundwaters seeped through pozzolana, may have suggested the formula for hydraulic mortar to Roman engineers**
- **”Just as pozzolana (*pulvis puteolanus*) becomes rock if it touches water....” (Questions about Nature 3.20.3)**
- **The long-term exposure of these natural low-alkali cements to fresh groundwater, seawater (and possibly brines, due to the presence of many lagoons in the area) suggest these may be a more appropriate long-term analogy to modern low-alkali cements**

Italy - low alkali cement?

A view from Puteoli (Bacoli) looking towards Naples and Vesuvio

Puteoli area overview

Potential study sites - steep cliff access

Further reading I

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