Long-term durability of concrete

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Low-alkali cements

- **Bentonite is unstable under the highly alkaline conditions induced by OPC (initial porewater pH>13) and this has driven interest in using low-alkali (low-heat) cements (initial porewater pH9-11) as an alternative to OPC**

- **Currently under consideration for tunnel liners, plugs and seals and for borehole plugs and supports**

- **However, there are little data available which address the likely long-term durability of such cements and this has been an issue in recent investigations of the likely impact of low-alkali cement on the EBS and host rock**

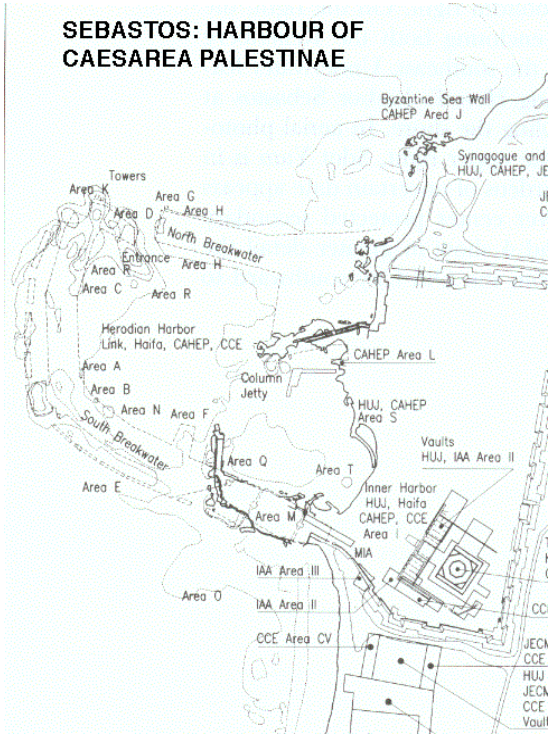
Archaeological analogues

- **Oldest known cements are from ca. 5000 BC**

- **But low-alkali cement is essentially the same as the pozzolanic cements developed by the Romans in the 3rd century BC (or Tiryns and Mycenae a millennium earlier; Middleton, 1888)**

Archaeological analogues

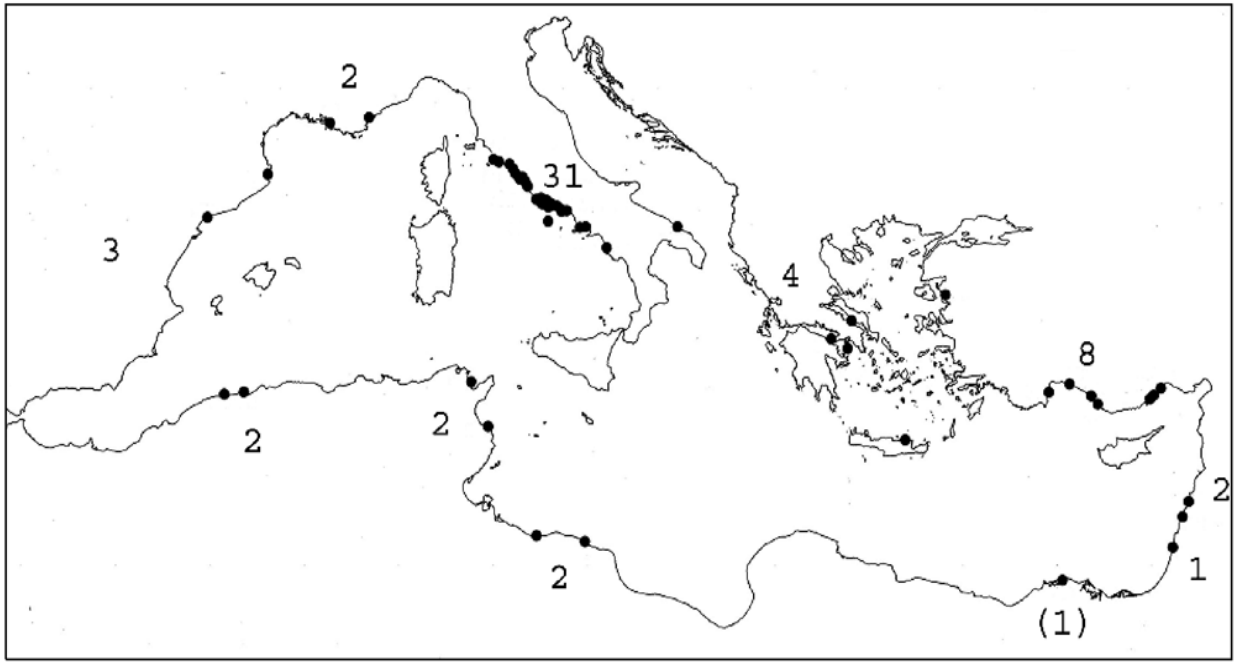
- Romans used low alkali cements where it was important to prevent the penetration of water or damp, such as lining water channels and tanks (Aqua Marcia, Rome, 144 BC)
- The cement also offers good resistance to seawater and so was used extensively for Roman harbours, breakwaters etc (Caesarea Palistinea, Israel, constructed by King Herod during the years 23 to 10 BC)



Archaeological analogues

- **First recorded use of Roman pozzolanic cement to build a harbour is that of the Port of Cosa, Italy in 200 BC, the pier of which "…is still usable at the end of the second millennium for its intended purpose if the need exists." (Bremner, 1993).**

Pozzolanic cement was so good that the Romans transported it for thousands of kilometres in order to ensure that they could use the same technology over and over again

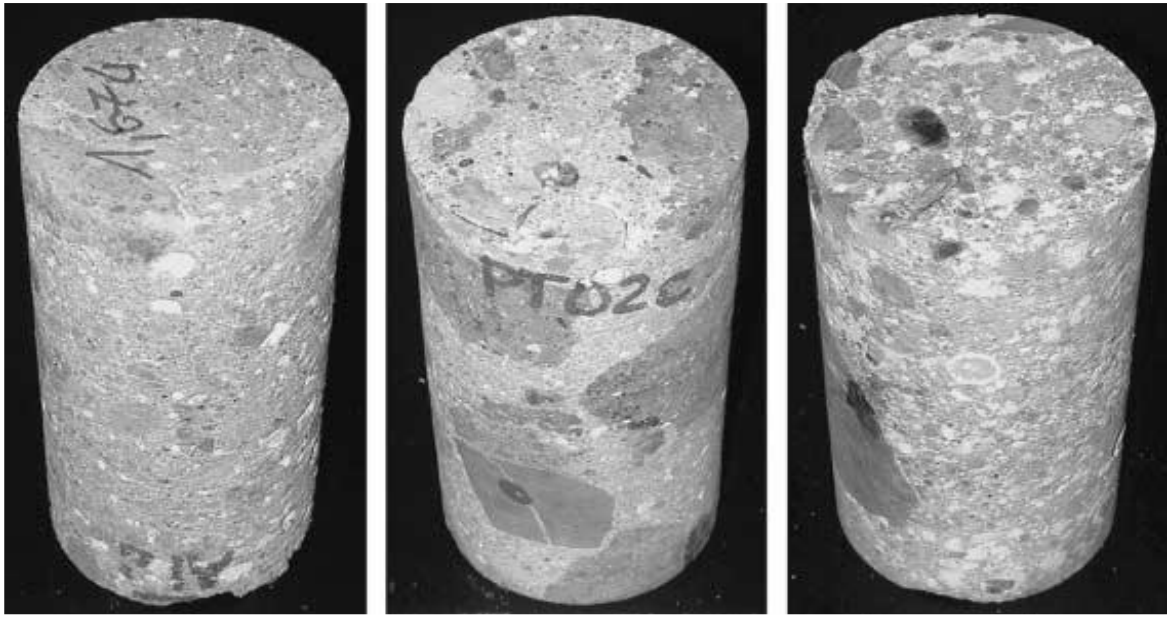


ROMANCONS

ROMANCONS (Roman Maritime Concrete Study) group consists of an international consortium of universities and CTG Italcementi Group

ROMANCONS' aims include

- analysis of the concrete matrix to determine size, material, and proportions of micro and macro-aggregate
- identification of the sources of pozzolana, tuff, and other aggregate used in the concrete structures
- comparison of the relative compressive strength and density of various concrete mixes



ROMANCONS' results

- **Overall degree of preservation is "remarkably high"**
- **Young's modulus and compressive strengths of pozzulans are generally quite low, but a few samples have Young's modulus values approaching low-alkali cement**
- **Mortar:aggregate ratios are generally a little high (1.3-3.4)**

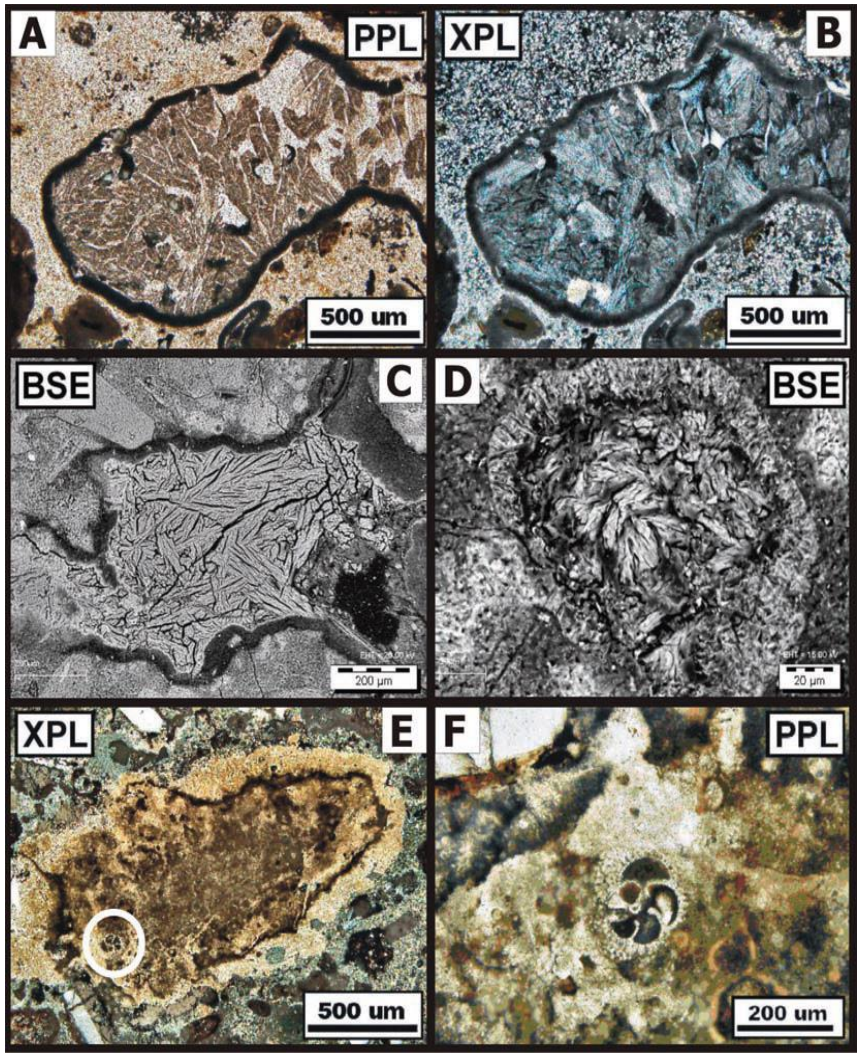
Subcores	Height (mm)	Density (kg/m^3)	Youngs Modulus (MPa)	Compressive Strength (MPa)
PO2	171.0	1583	5560	7.8
A1D	184.0	1549	6440	6.3
PTO2C	176.5	1665	7570	4.9
PCO1B	211.2	1624	7200	7.4
PCO2B	216.6	2163	18,800	9.4
PCO3B-a	214.6	1652	7050	8.0
PCO3B-b	217.2	1587	8750	7.9
PCO4B-a	206.4	1589	6500	5.5
PCO4B-b	215.7	1557	5750	6.4
PCO4B-c	205.2	1635	4850	5.1
PCO4B-d	214.7	1542	6900	5.5
Typical modern portland cement concrete	NA	2325	24,820	27.6

Property	SHPC	LHHPC
Unconfined Compressive Strength (28 days and 23°C)	122 MPa	75 MPa
Unconfined Compressive Strength (28 days and 50°C)	87 MPa	68 MPa
Unconfined Compressive Strength (28 days and 90°C)	77 MPa	67 MPa
Direct Tensile Strength (28 days and 23°C)	4.5 MPa	3.3 MPa
90-day drying shrinkage (μ) (after 7 days curing)	440	330
Tangent Elastic Young's Modulus (28 days at 40% of unconfined strength)	40 GPa	36 GPa
Young's Modulus in Tension (at 40% of direct tensile strength)	43 GPa	31 GPa
Poisson's Ratio	0.2	0.16
Hoek-Brown Failure Parameter m (at 23◦ C with s=1)	14.9 MPa	8.2 MPa

Man & Martino (2009)

ROMANCONS' results

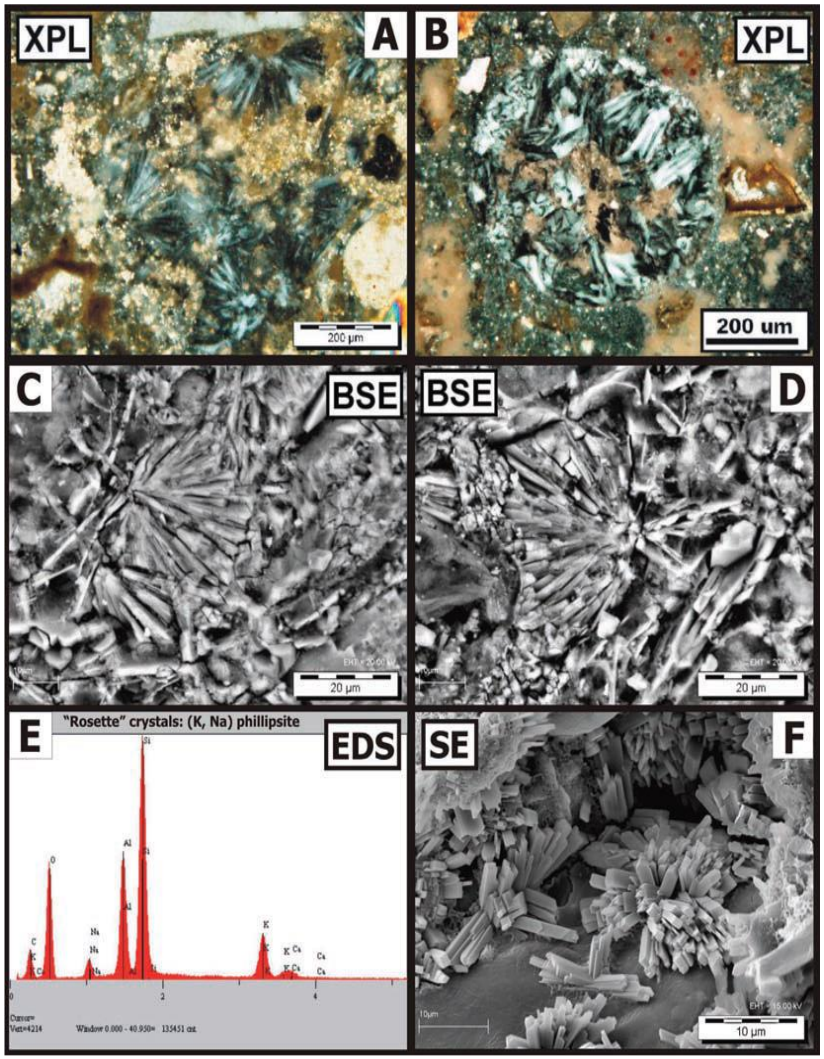
- Recent work focussed on temporal changes
- Little aggregate reaction
- Cementitious matrix includes gel-like, silica-rich C-A-S-H, with subordinated "sparry" calcite cement and grains of calcite, tobermorite, and ettringite (i.e. seawater slaked lime)



Vola et al. (2011)

ROMANCONS' results

- longer-term changes include production of dendritic gypsum, fibrous ettringite and halite crusts
- hydrocalumite, hydrotalcite and brucite also present
- late-stage phillipsite rosettes replacement of tuff-ash fragments



Vola et al. (2011)

ROMANCONS interpretation

Preliminary results using existing material indicate:

- **QMS has played a significant role on survivability**
  - ***Early (ca. 250 BC) construction utilised weakly durable, soft or vitric tuffs such as Tufo del Palatino or Tufo Giallo della Via Tiberina that are susceptible to decay***
  - ***Later (ca. 100 BC) construction utilised durable, vitric–lithic tuffs like Tufo Lionato reinforced with travertine***
- **Different methods too – hand compacted vs modern vibrator**
- **Comparison with freshwater reaction not yet available, but sites exist (central Italy, 200 BC)**

ROMANCONS interpretation

Preliminary results using existing material indicate:

- **Remarkable degree of preservation of the cements ("…still usable…" according to Bremner, 1993)**
- **Cement reaction much as would be expected from current modelling studies (lack of aggregate reaction may simply reflect the high mortar:aggregate ratio)**
- **BUT cement is still not fully reacted after 2 millenia**

Low alkali cement NAs

- **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

Conclusions

- **Preliminary results using existing material (ROMANCONS - and more is in the pipeline) are promising, if still qualitative to some extent**

- **Data already used to constrain some overly pessimistic concrete degradation assumptions**

- **QMS is clearly an issue and this has been approached differently to date**
  - **SKB initial conditions report for SR-PSU**
  - **NUMO 2015SC concrete scenarios**

Outlook

- Would be good to access the Tiryns and Mycenaen material from the 1888 study as this could push back the archaeological analogue timeline by another 1 ka
- More focused re-analysis of existing material is possible (in theory), but further sampling (both freshwater and marine archaeological sites) for radwaste studies is unlikely to gain permission
- To understand handling/QMS differences
  - make modern cements using the Roman handling methods as laid down in De Architectura (Marcus Vitruvius Pollio, 27 AD)
  - make Roman cements using today's handling methods (e.g. those used in Chandler et al., 2002)
  - and then compare the physical and mechanical properties as would allow a rapid assessment of any handling-related differences which could be subtracted from the properties

OPC cement

- **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**

OPC - driving force

- **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**

- **Current treatment is highly simplistic in most national programmes, utilising simple mixing tank approaches with emphasis on over-prediction of consequences**

- **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)**

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**

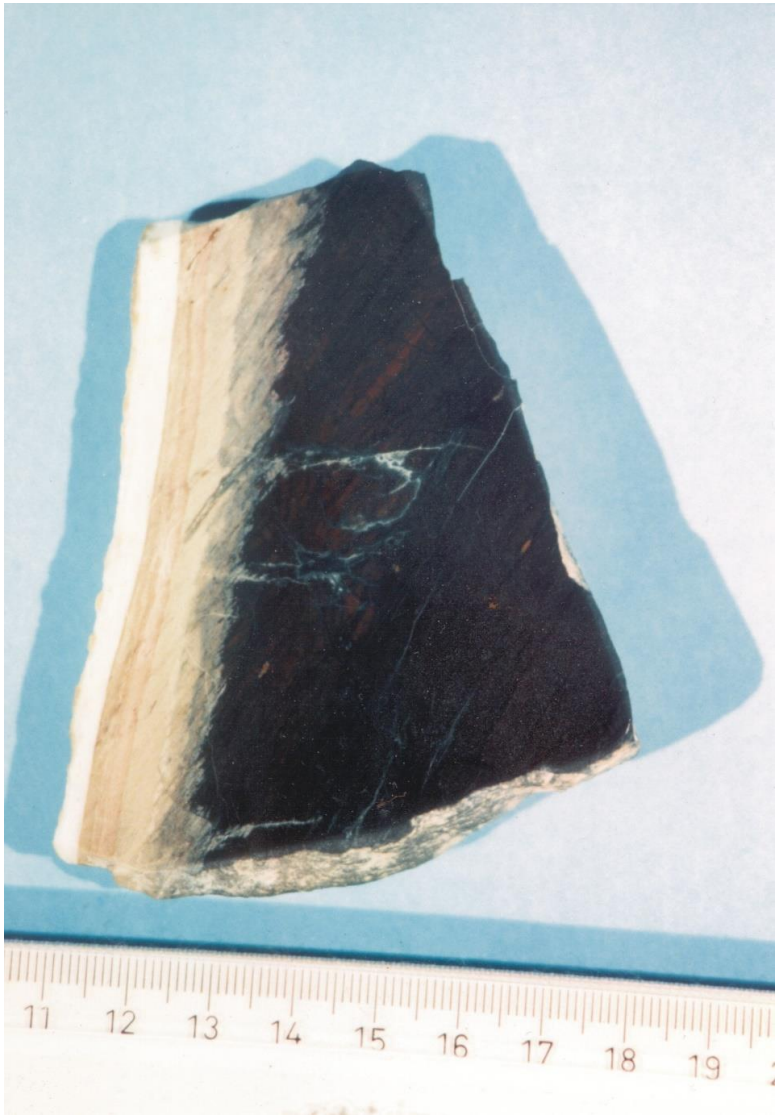
Maqarin & Khushaym Matruk

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

Maqarin: cement sealing is observed

Alexander (2012)

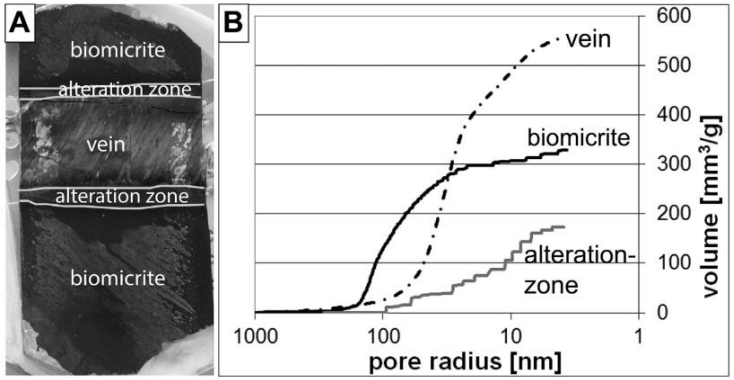
Daba: cement sealing is observed

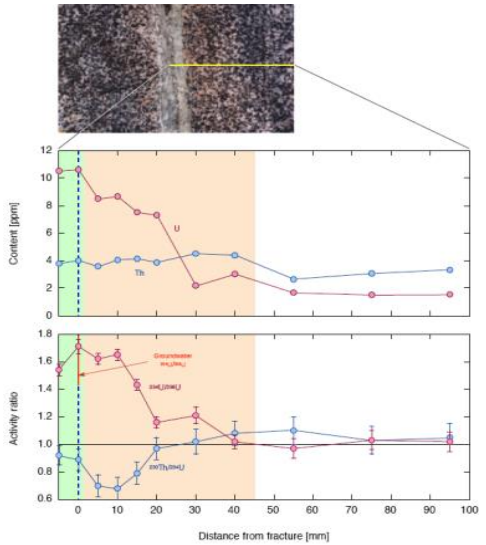


Khoury et al. (2011); Alexander (2012)

Cement sealing: what next?

- **What we propose doing at the sites in Jordan is to conduct something along the lines of the work in the LCS project in Grimsel 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**

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