NATURAL ANALOGUE
Working Group

The Jordan Natural Cement Analogue: Phase IV

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Cementitious NA

- There are very few relevant cementitious analogues and they include:

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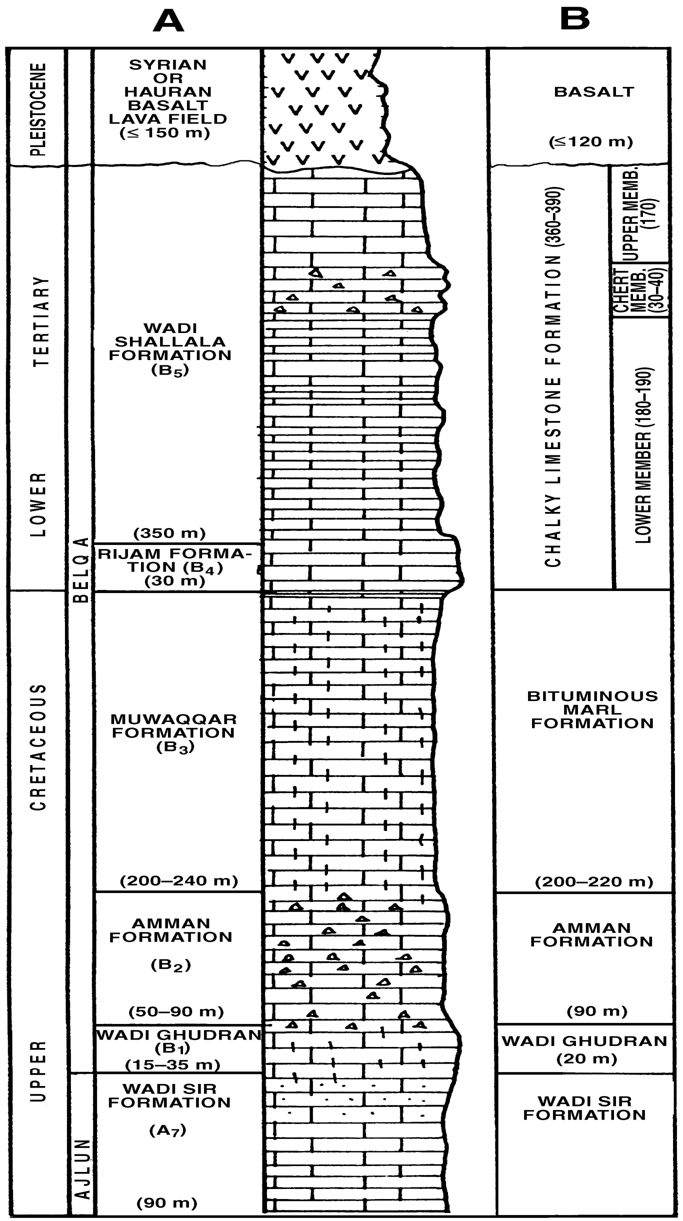
Jordan: background

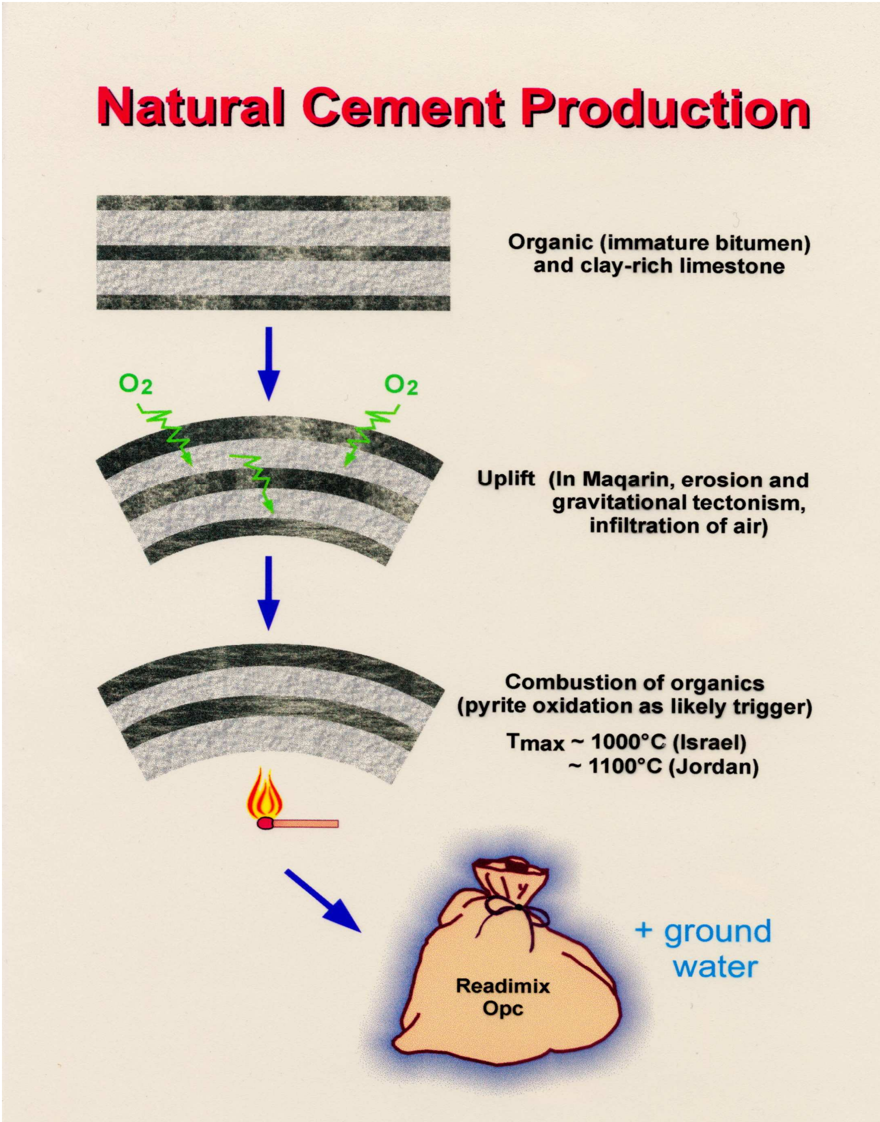
- Beginning in 1989, the work in Jordan is currently in the 4th Phase* and includes the partners:
  - Nagra
  - Nirex
  - SKB
  - ANDRA
  - CEA
  - JAEA
  - (formerly also Ontario Hydro and UK HMIP)

**now in reporting stage*

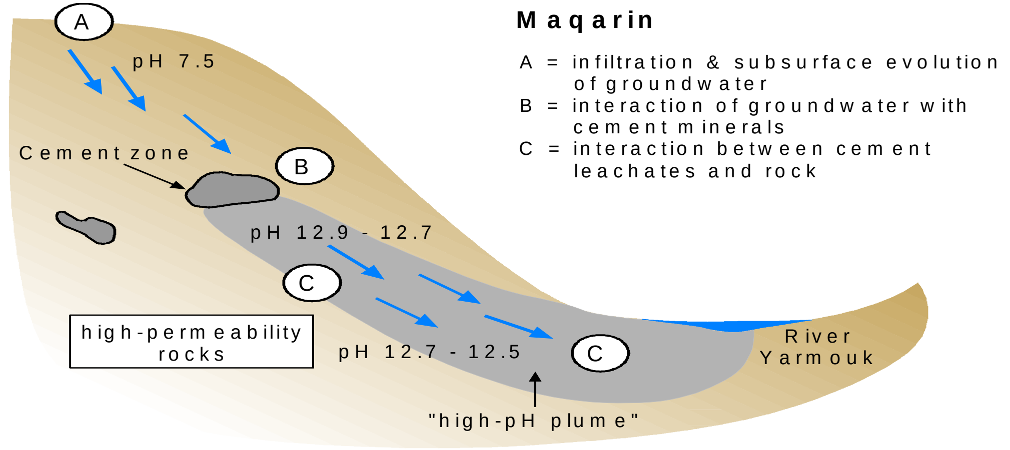
Maqarin - stratigraphy

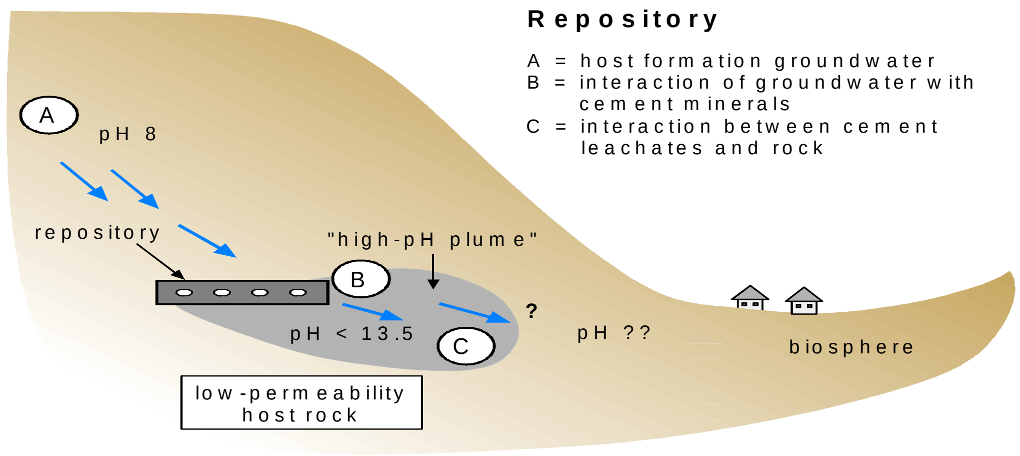


Jordan: the basis of the analogy (1)

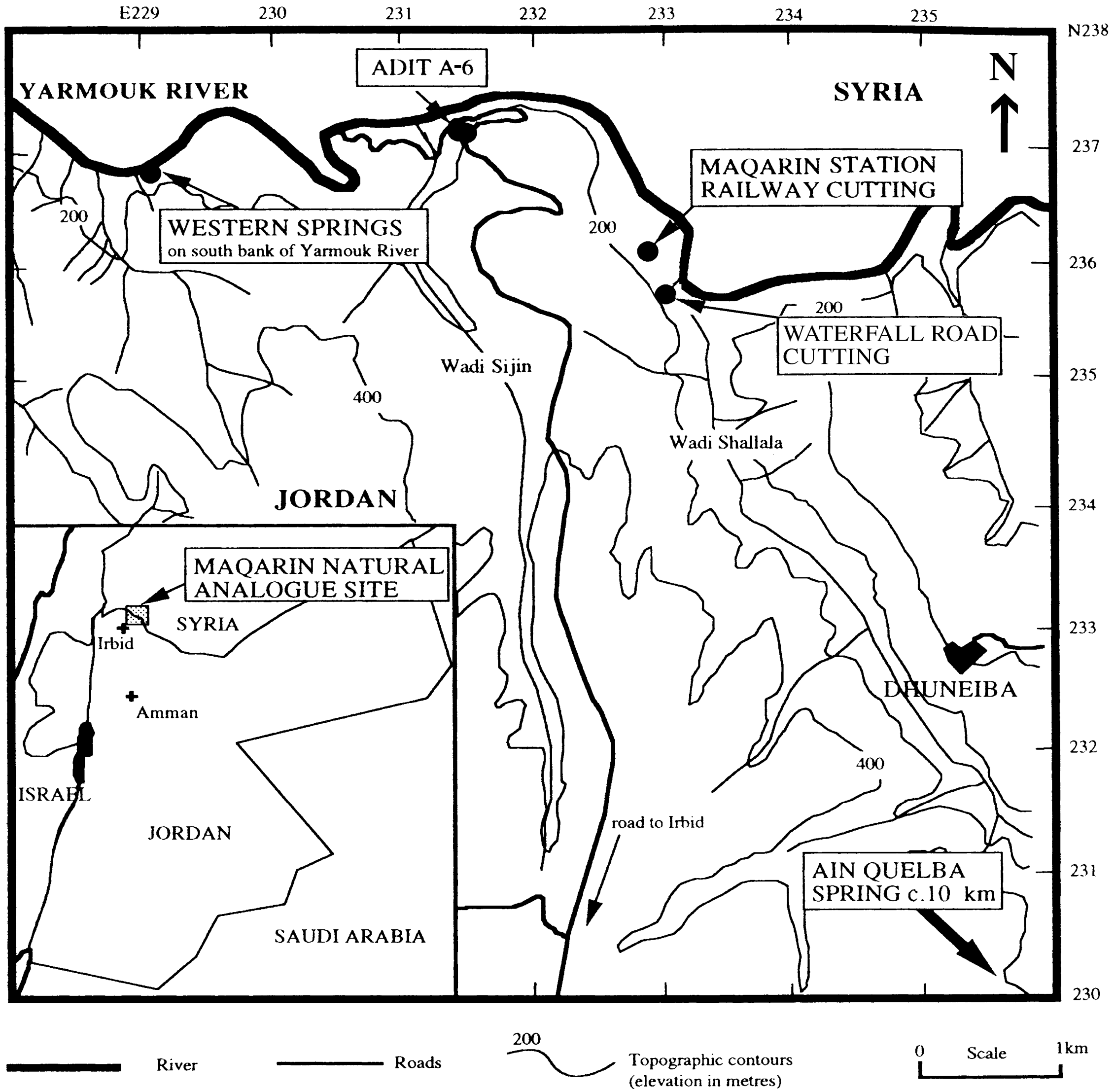


Maqarin – the the basis of the analogy (2)





Jordan



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ADIT A-6
YARMOUK RIVER
SYRIA
N
MAQARIN STATION
RAILWAY CUTTING
WESTERN SPRINGS
on south bank of Yarmouk River
200
WATERFALL ROAD
CUTTING
Wadi Sijin
400
Wadi Shallala
JORDAN
MAQARIN NATURAL
ANALOGUE SITE
SYRIA
Irbid
Amman
ISRAEL
JORDAN
SAUDI ARABIA
DHUNEIBA
road to Irbid
AIN QUELBA
SPRING c.10 km
River
Roads
Topographic contours
(elevation in metres)
0
Scale
1km

Jordan

Maqarin

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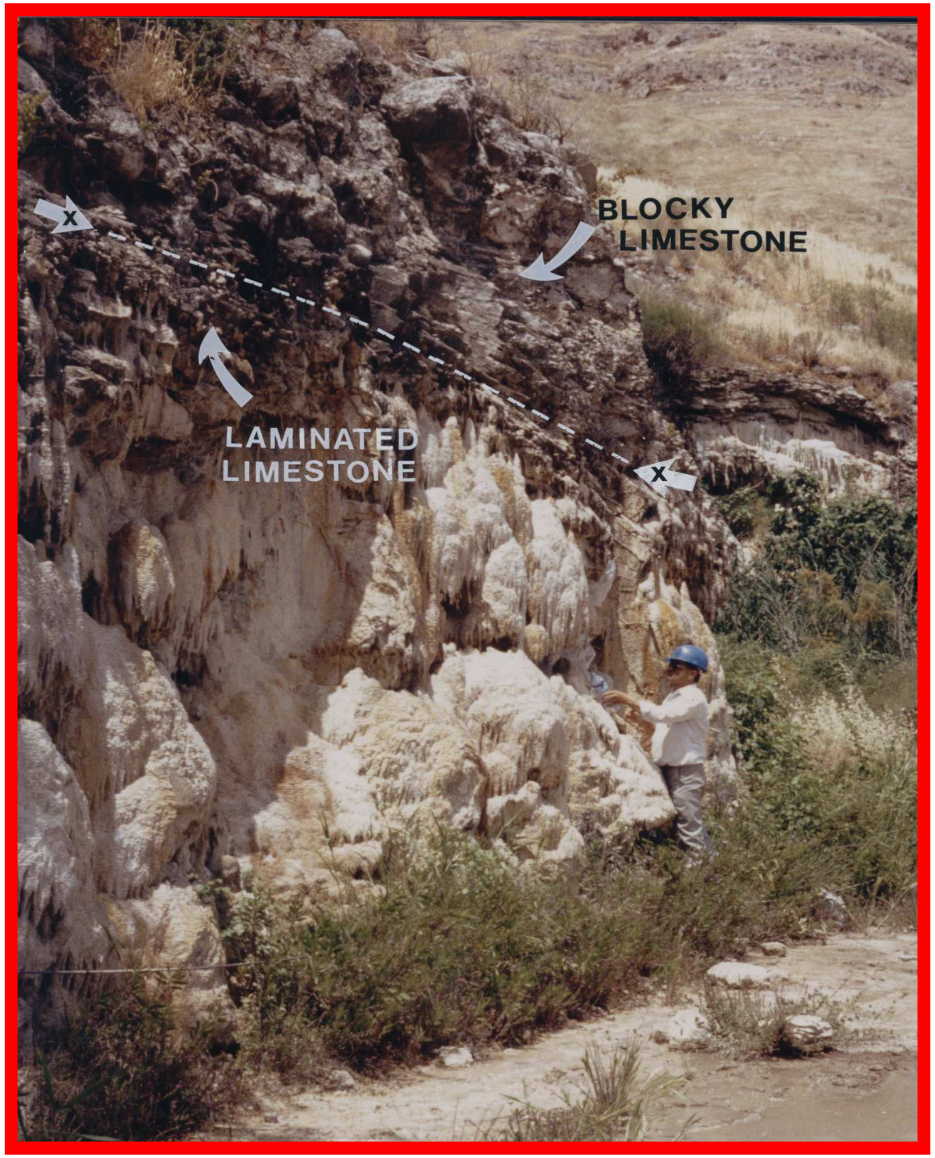
The Yarmouk Valley

Jordan: areas of study

- **Phase I:**

  - **focussed on the source term definition at Maqarin (ie was the site really a good cementitious analogy?) but also studied:**
  - **Groundwater chemistry**
  - **BPM (blind predictive modelling) of TDB (thermodynamic databases) under hyperalkaline conditions (4 codes, 4 databases)**
  - **study of the viabilty of microbes**

Maqarin: the only active site known

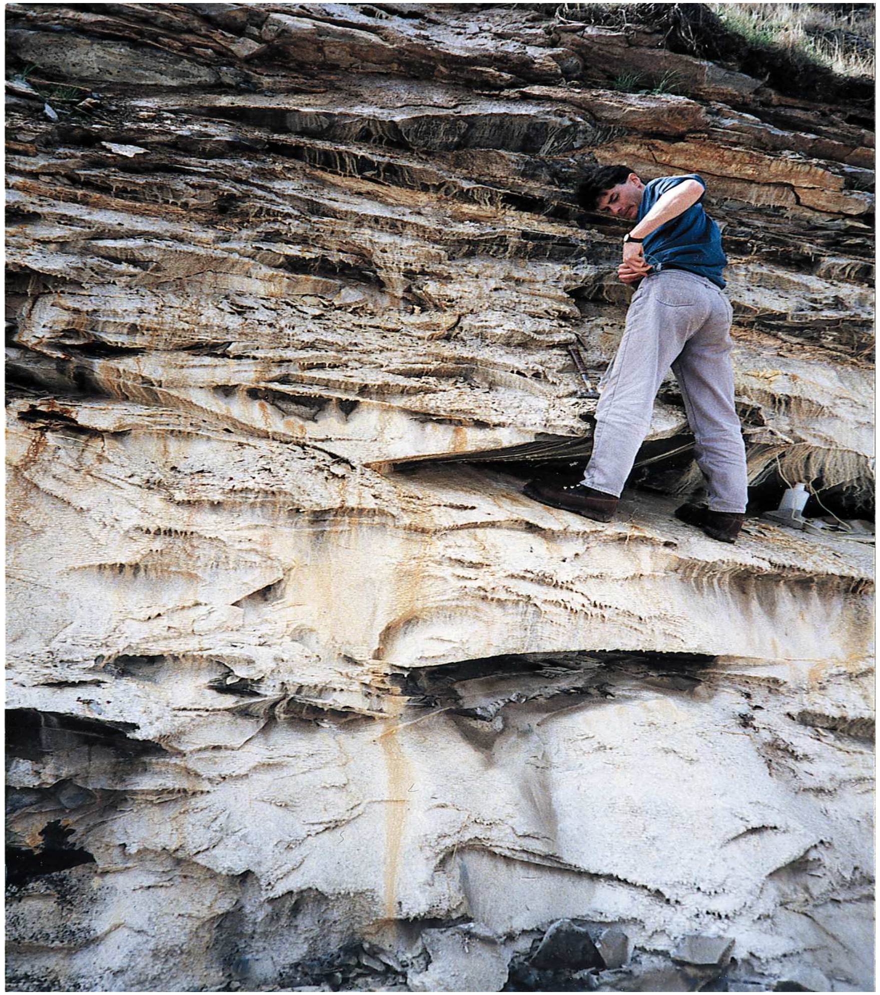


Maqarin Station railway cutting.

The station was built in 1905 (destroyed, 1916 by Lawrence of Arabia.....) so this represents >100 years of deposition

With the help of German engineers, the Turkish Army in WWI used the Bituminous Marl to directly fuel the trains which ran on this line

Maqarin: the only active site known



Jordan: areas of study

- **Phase II:**
  - **hyperalkaline leachate-host rock interaction**
  - **BPM modelling of TDB under hyperalkaline conditions (incl. *in situ* trace element speciation)**
  - **further study of microbes, including testing a SA microbiology code**
  - **coupled code (transport-geochemistry) intercomparison**

Jordan: areas of study

- **Phase III:**
  - **detailed study of very high pH (12.9) site at Maqarin (West)**
  - **additional coupled code testing**
  - **geomorphological studies**
  - **study of cement colloids at the cement/host rock interface**
  - **literature review of zeolite mineralogy of relevance to the hyperalkaline conditions at the site**
  - **organics in the rock-water system**
  - **stability of clays in the hyperalkaline system**
  - **matrix diffusion**
  - **study of new sites in central Jordan (Sweilah and Daba) - fossil systems (*ie* no groundwater)**

Jordan: areas of study

- **Phase IV: has seen a more detailed study of specific mechanisms at Maqarin and more exploratory work in central Jordan at Daba and a new site at Khushaym Matruk**

  Maqarin *(advective)*

  - **detailed mapping of flowpaths**
  - **attempt to better constrain site hydrogeology**
  - **constraining ages of the systems**
  - **source term of the high pH site**
  - **study of Re as analogue of Tc**
  - **(matrix diffusion, coupled codes)**

  Khushaym Matruk *(diffusive)*

  - **hyperalkaline leachate-clay reaction**
  - **matrix diffusion**

Maqarin: the only active site known

Average chemistry of the Maqarin groundwater (mgl^{-1})

Sample	East (M1)	West (M5)
pH (field)	12.74	12.92
pH (lab.)	12.67	12.83
Eh (field)	+278 mV	+242 mV
Ca	674	1120
Na	47.2	136
K	9.88	526
Cl	52.4	46.6
SO_4	305	1580
NO_3	3.28	39.1

Maqarin: primary mineralogy

Mineral species	Ideal formula	Identified
fluorapatite	$Ca_{10}(PO_4)_6F_2$	A + B
francolite	$Ca_{10-x-y}(Na,K)_xMg_x(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$	A
ellestadite	$Ca_{10}(SiO_4)_3(SO_4)_3O_{24}(Cl,OH,F)_2$	B
spurrite	$Ca_5(SiO_4)_2(CO_3)$	A + B
wollastonite	$CaSiO_3$	A
larnite	Ca_2SiO_4	B
diopside-hedenbergite	$Ca(Al,Fe)Si_2O_6$	A
anorthite	$CaAl_2Si2O_8$	A
brownmillerite	$Ca_2(Al,Fe)_2O_5$	A + B
Ca-ferrite	$CaFe_2O_3$	B
(?)ferrites	undefined Ba,Cr,Al,Ti,Mg,Zn,Mn-bearing	B
hematite or ferric oxide	Fe_2O_3	B
Ca-aluminate	undefined	B
calcite	$CaCO_3$	A + B
graphite	C	A
lime	CaO	B
Ba,Ca,S-silicate	undefined	B
Ba,Ca,Zr,Mo,silicate	undefined	B
oldhamite	CaS to $CaS_{0.9}Se_{0.1}$	B
Cu,K,Na-selenide	$Cu_{10.2}K_3Na_{0.2}Se_{7.7}S_{2.3}$(approx)	B
UCa-oxycarbonate (?)	Ca : U = 2	B

Maqarin: secondary mineralogy

Mineral species	Ideal formula	Identified
calcite	$CaCO_3$	A + B
aragonite	$CaCO_3$	B
vaterite	$CaCO_3$	A + B
kutnahorite	$Ca_{0.75}(Mn,Mg)_{0.26}CO_3$	A
strontianite	$SrCO_3$	B
hematite	α-Fe_2O_3	A + B
maghemite	β-Fe_2O_3	A
gibbsite	α-$Al(OH)_3$	A + B
brucite	$Mg(OH)_2$	A
portlandite	$Ca(OH)_2$	A + B
quartz	SiO_2	A + B
opal-CT	SiO_2	A
opal-A	$SiO_{2.n}H_2O$	A
baryte	$BaSO_4$	A + B
barytocelestite	$(SrBa)SO_4$	B
calcian barytocelestite	$(SrBaCa)SO_4$	B
hashemite	$BaCrO_4$ to $BaSO_4$ complete solid solution	B
Cd-sulphate	undefined	B
Pb-sulphate	undefined	B
gypsum	$CaSO_4$	A + B
bassanite	$CaSO_4.0.5H_2O$	A
ettrinigte	$Ca_6Al_2(SO_4)_3(OH)_{12}.25H_2O$	A + B
thaumasite	$Ca_6Si_2(SO_4)_2(CO_3)_2(OH)_{12}.24H_2O$	A + B
Cu,Zn-sulphate	undefined	B
hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	A
fluorapatite	$Ca_{10}(PO_4)_6F_2$	A + B
francolite	$Ca_{10-x-y}(Na,K)_xMg_x(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2$	A
ellestadite	$Ca_{10}(SiO_4)_3(SO_4)_3O_{24}(Cl,OH,F)_2$	A + B
afwillite	$Ca_3Si_2O_4(OH)_6$	A + B
tobermorites	$Ca_5Si_6O_{16}(OH)_2.2-8H_2O$	A + B
jennite	$Ca_9H_2Si_6O_{18}(OH)_8.6H_2O$	A + B
apophyllite	KCaSiO 0(OH,F) HO	A + B
birunite	$Ca_{15}(CO)_{5.5}(SiO_3)_{8.5}SO_4.15H_2O$	B
CSH gel	amorphous, undefined	B
U,Ca-silicate	undefined	B

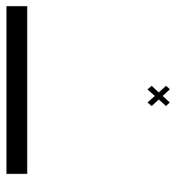
A: Khoury and Nassir (1982)
B: Milodowski et al. (1992, 1998a,b)

Maqarin: mineralogy main points

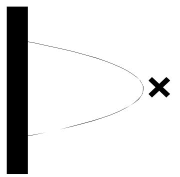
- **primary cement slag mineralogy has been confirmed as analogous to industrial cement slag (ie is a marble)**
  - **several novel minerals identified (one only found in meteorites, another only in industrial cement slag....)**
- **hydrated slag mineralogy is similar to OPC, but without the very high T phases**
  - **source term is fully relevant to an OPC-dominated repository**
- **dissolution of `OPC` minerals produces the hyperalkaline (cement) leachates**
  - **source of alkalis (Na, K) has also been identified**
- **secondary minerals produced following interaction with the host rock confirm conceptual models of leachate/host rock interaction**
  - **CSH, CASH, zeolites etc**

Maqarin: conceptual model

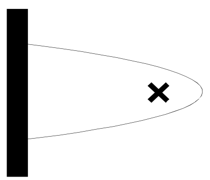
a) immediately following repository closure (x represents an observation point in a fracture)



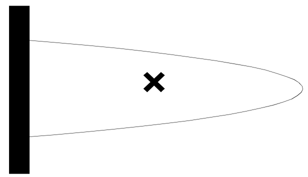
b) resaturation, plume evolution begins



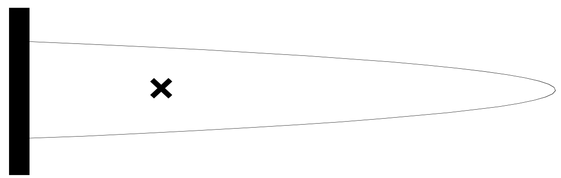
c) distal edge of plume reaches the observation point, initiation of zeolite formation



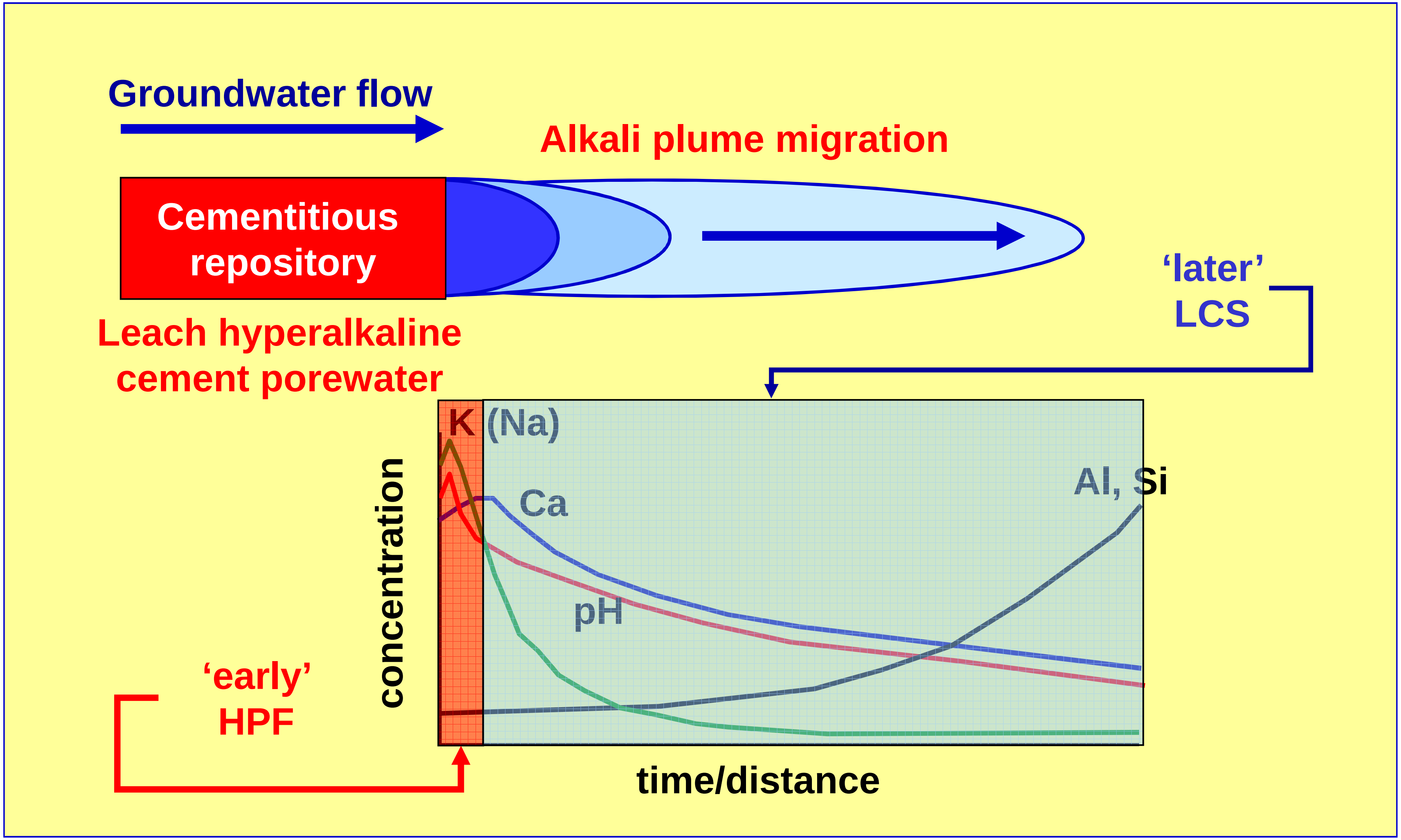
d) middle of plume reaches observation point (as the rock buffer capacity is being consumed) CASH formation initiated



e) proximal part of the plume reaches the observation point (as the rock buffer capacity is exhausted) C-S-H formation initiated



Conceptual model of ADZ evolution



Maqarin: quantitative conclusions (1)

- The conceptual model for the evolution of a hyperalkaline plume in a generic host rock is largely consistent with observations at the site

- Hyperakaline pore fluid conditions generated by minerals analogous to those in cements are long-lived (in excess of tens of thousands of years) under the Maqarin flow conditions

- The effects of the site hydrology (and tectonic/erosional processes) upon fracture sealing need to be considered on a repository site-specific basis

Maqarin: quantitative conclusions (2)

- **Reactions between hyperalkaline waters and the host rock mostly have positive reaction volumes and thus fractures are sealed by the precipitation of secondary phases (NB for small aperture fractures, at least)**

- **Interaction between hyperalkaline waters and the host rock occur extensively and (small to medium aperture) fracture sealing occurs within short timescales (years to hundreds of years)**

- **The altered rock matrix appears to be accessible to diffusion of aqueous species to a depth of several centimetres**

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Maqarin: fracture sealing

Maqarin: quantitative conclusions (3)

- **Sequences of minerals predicted by coupled codes are very close to those observed in the hyperalkaline alteration zones at Maqarin, even if the specific phases cannot be represented due to a paucity of relevant thermodynamic and kinetic data**

- **Thermodynamic databases of elements of interest to radioactive waste disposal provide conservative (*ie* solubilities are overestimated) estimates of solubility, despite the fact that the representation of the solubility controlling solid phases is too simplistic (crystalline, simple chemistry etc)**

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Maqarin: quantitative conclusions (4)

- The amounts of colloidal material generated at the cement zone/host rock interface appears to be low, although any future analogue and laboratory work would benefit from a common approach to minimise method inherent differences

- Microbes are present in the hyperalkaline groundwaters, although their precise activity is currently difficult to define

Maqarin: qualitative conclusions (1)

- The cement zone at Maqarin may be considered a good analogy to an industrial cement

- To date, the majority of fractures examined within the plume at Maqarin (other than those currently water conducting) are sealed. However, as the aperatures of the fractures examined to date are generally small (mm to cm), it is currently possible to state only that thin fractures will be probably self-healing (NB Phase IV)

Maqarin: qualitative conclusions (2)

- **As a consequence of the fast rate of interaction between hyperalkaline waters and the wallrocks, it seems likely that radionuclides released from a cementitious repository will migrate through rock that has already been altered by the high-pH plume (although it must be emphasised that the radionuclide release scenarios for most repositories are still somewhat unclear here).**

Maqarin: qualitative conclusions (3)

- **Once a fracture is sealed, no further alteration can take place unless new pore-space is created by fracture reactivation (NB significant for tectonically active areas)**

- **The numerous phases of fracture precipitation (and dissolution) identified at Maqarin bear witness to recurrent events of alteration/precipitation, sealing and reactivation as does the range of ages so far reported for infill mineralogy**

Maqarin: qualitative conclusions (4)

- **In a highly porous rock (or flow system), it is possible that reaction will not rapidly seal the flow porosity. In this case, the distal part of the plume may be over-run by the middle part which may, in turn, be over-run by the proximal part of the plume. Partial to complete replacement of previous secondary phases is to be expected, with the potential implications this has for radionuclide retardation**

- **Such flow systems are probably of little relevance to deep repository host rocks – BUT if wide fractures are present………**

Maqarin: qualitative conclusions (5)

- **Due to the high permeability in the Maqarin surficial environment, the length of the plumes downstream of the cement zones appear to be on the order of hundreds of metres. In the lower advection rate systems of relevance to deep repository host rocks, plume lengths will probably be much smaller (*cf* Khushaym Matruk, below)**

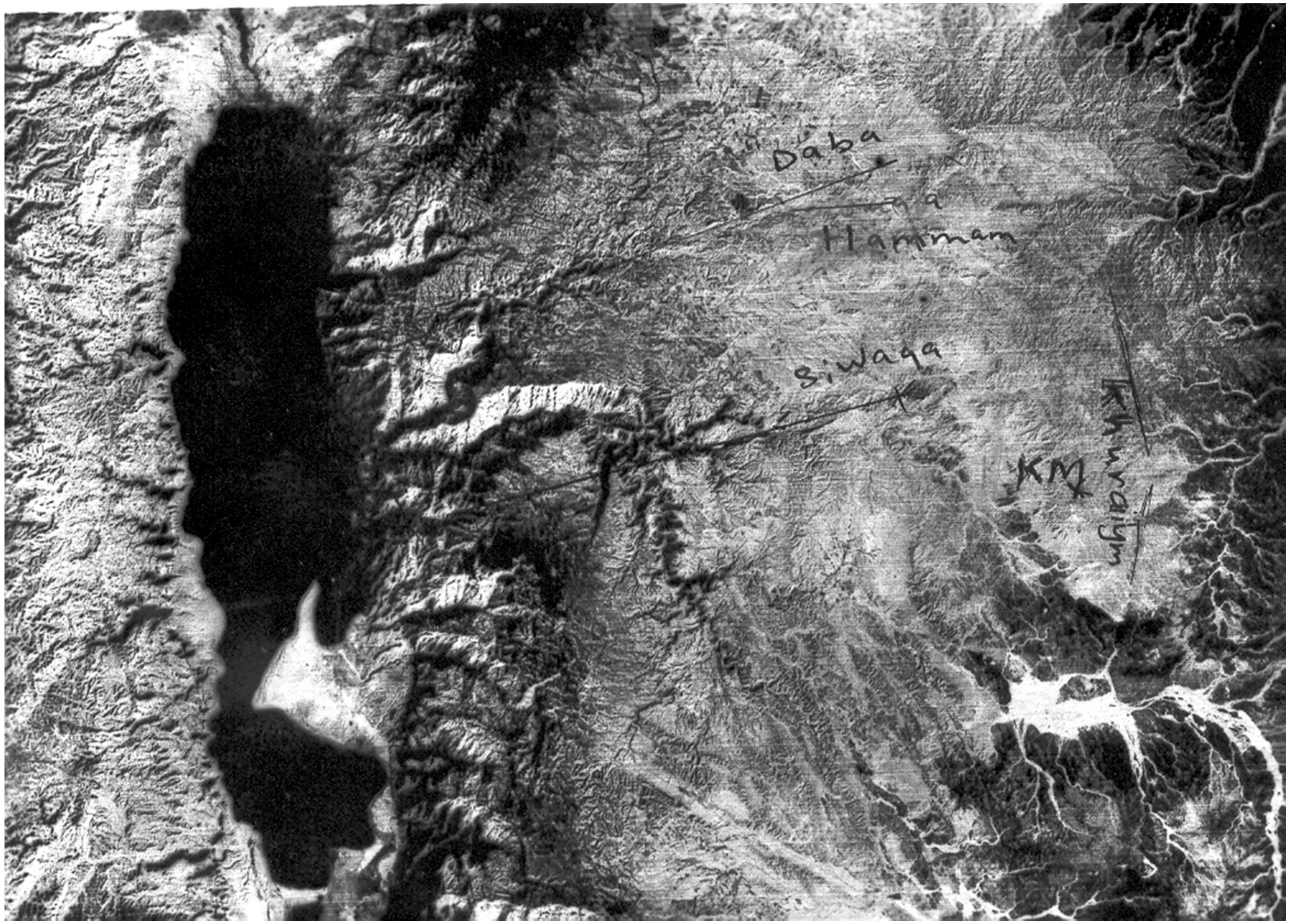
- **Despite major differences between the rock types at the Eastern and Western Springs, the mineralogical composition of the secondary minerals at both sites is very similar, implying that similar reactions could be expected to occur at a repository host rock, *ie* the mineralogical information from Maqarin appears to be directly transferable to repository condition**

Maqarin: before and after

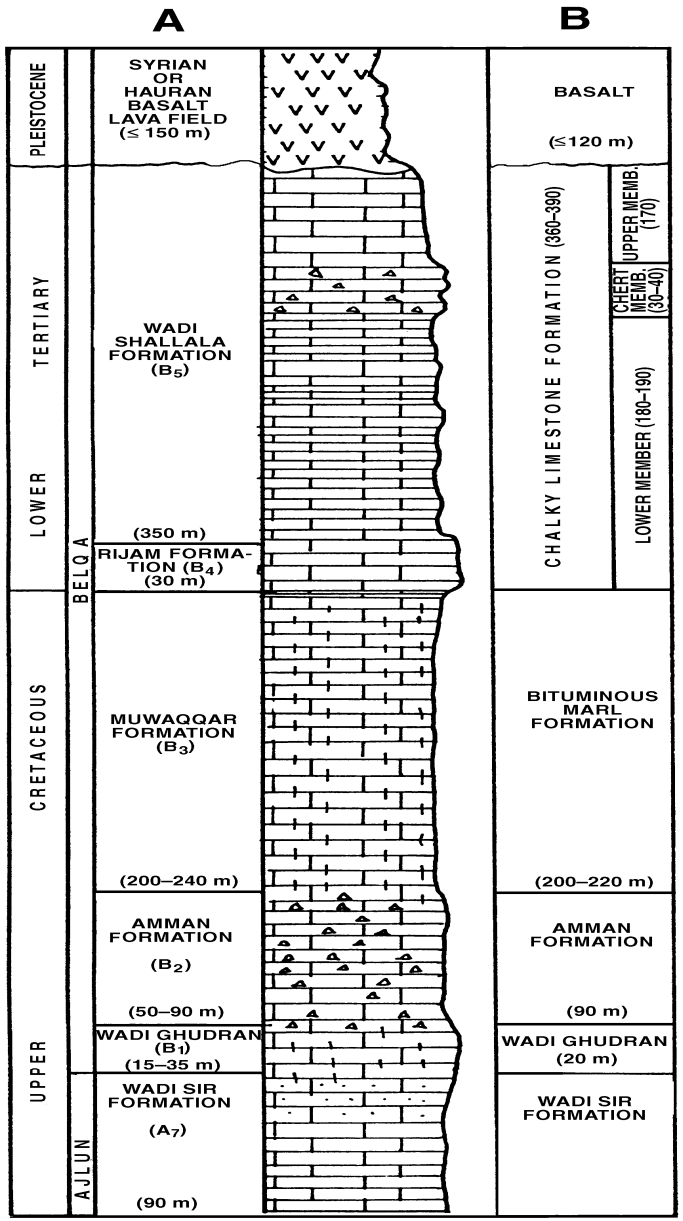
Jordan: new area of study

Khushaym Matruk

Khushaym Matruk



Khushaym Matruk - stratigraphy



Khushaym Matruk

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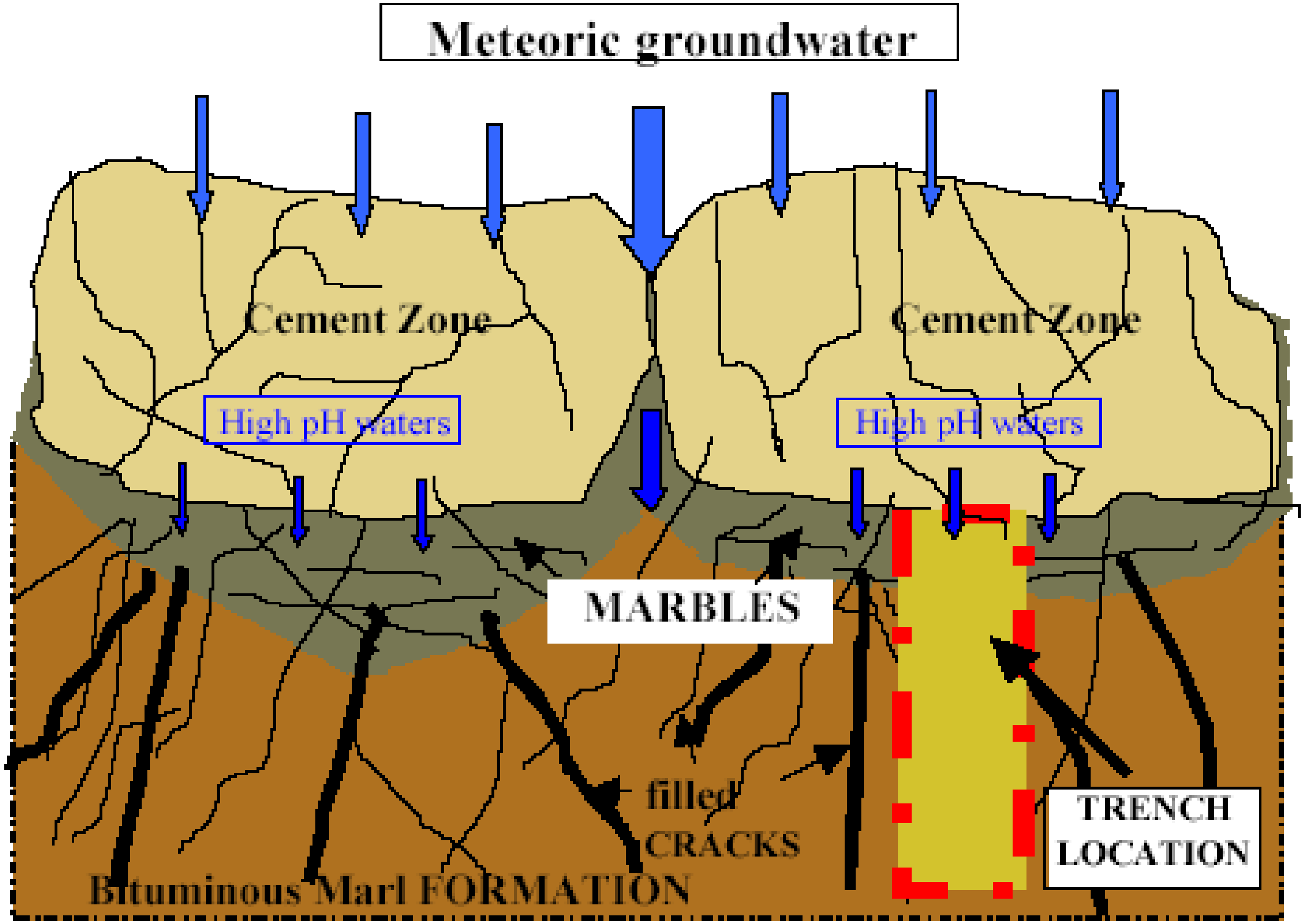
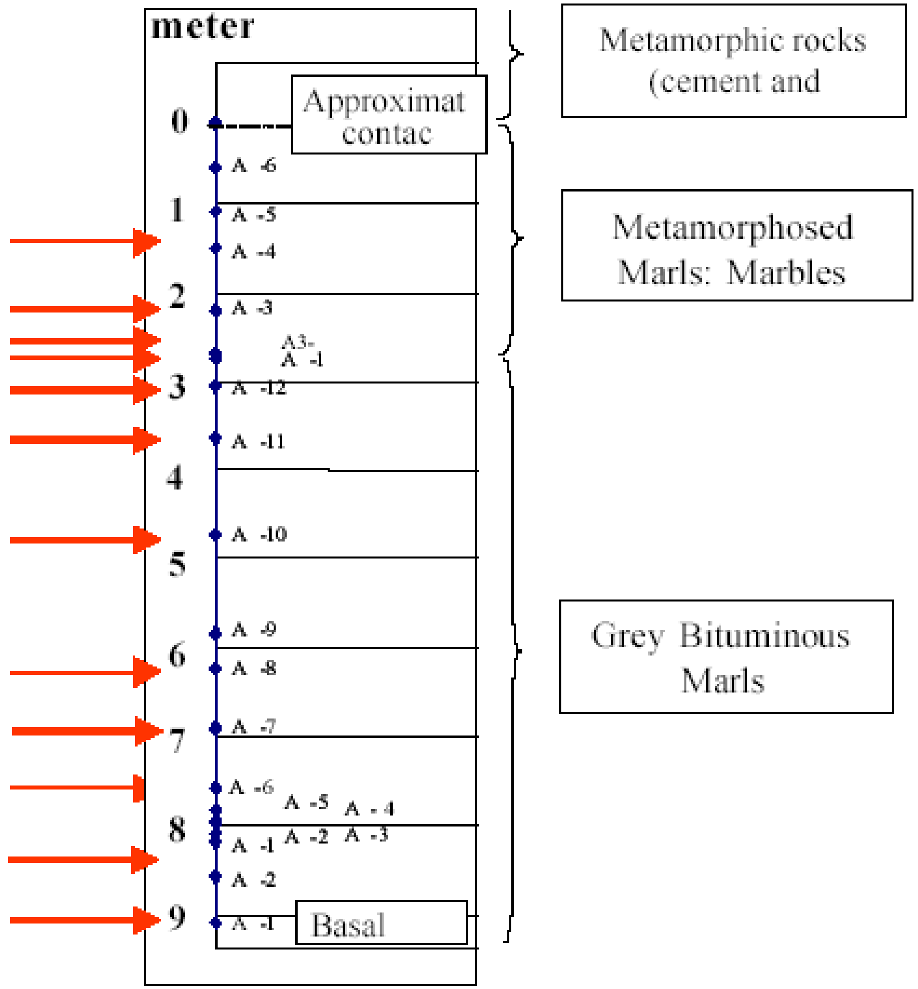


Khushaym Matruk



Khushaym Matruk – preliminary findings I

- only small number of samples studied so far
- site appears to be a diffusive system
- host rock clay content >10% (*cf*. Maqarin <5%)
- combustion event which produced the cements directly above the host rock has left a thermal `fingerprint` on the upper part of the sampled profile
- cement produced between 600 ka and 1,000 ka ago

Khushaym Matruk – preliminary findings II

- decrease in the content (80 % to 60 %) of smectite component of illite/smectite mixed layer clay minerals was observed in the host rock as approached the cement

- zeolites have been found in the joint fillings and in foram tests in the matrix

- evidence suggests that these phases have been produced by interaction with hyperalkaline fluids

Khushaym Matruk – preliminary findings III

- however, it is not yet possible to rule out if the matrix zeolites are a primary diagenetic feature of the sediments (further isotopic analyses needed)

- “Nevertheless, this should not detract from the fact that this study of a limited number of samples has clearly shown the potential of this site as a natural analogue of hyperalkaline leachate/clay interaction and emphasises the need to examine the site with enough resources to allow a wide-ranging scientific study of direct relevance to repository SA.” – Pitty (2007)

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Jordan: open questions

- What is the likely impact of microbes on such a system and how will they interact with organics and colloids?
- Will matrix diffusion into the altered host rock be reduced (partial answer available)
- Degree of bentonite (clay) interaction over long timescales
- Likely impact of a hyperalkaline plume on a diffusive-transport controlled host rock (NB gas!!)

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Jordan: open questions

- The role of recarbonation
- The nitrate question....
- retardation of ^{129}I and ^{14}C
- and a convincing test of recent coupled codes using the existing data has still to be carried out.......

Jordan: successes and failures

- **remember! – the budget is piffling compared to a site characterisation (by end Phase III, equivalent to the cost of drilling the WLB cores – without retrieval, logging, storage, sub-sampling, examination, detailed analysis, interpretation.......)**
- **clearly verified the conceptual model of cement leachate/host rock interaction**
- **forced the implementing agencies to take the scenario seriously**

Jordan: successes and failures

- has been used directly in PA (Nagra, SKB etc)
- has been used in an analysis of likely long-term evolution of at least one site (WLB)

- the work on BMP has not been taken over by PA modellers
  - weaknesses in TDB and codes generally ignored
  - the BPM methodology not universally acknowledged, despite clear advantages to PA modellers

Jordan: successes and failures

- the work on microbiology and cement colloids has been largely ignored
- the full implications of the likely changes to a repository site hydrogeology have yet to be tackled by PA modellers. The nearest are highly simplified attempts by Vieno et al. (2003 - Posiva Report 2003-06) and Mäder (2004 – ECOCLAY II report)
- while the Maqarin dataset has been used as a case study for coupled code analyses, it has improved the codes themselves very little