NATURAL ANALOGUE
Working Group

Natural analogues of cement: safety assessment implications of the unique systems in Jordan

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Cementitious NA

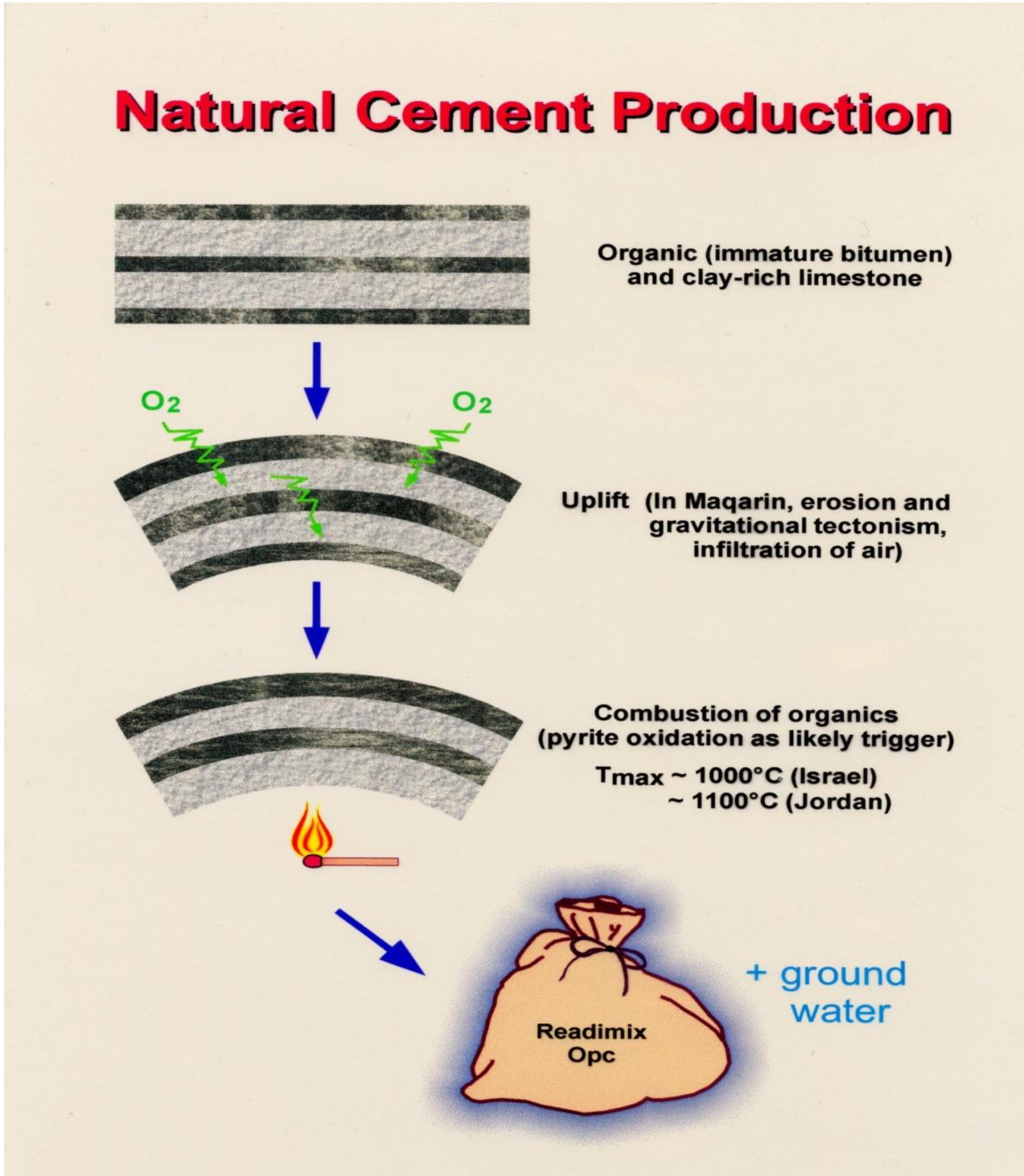
- There are very few relevant cementitious analogues and they include:

Cementitious NA: Jordan

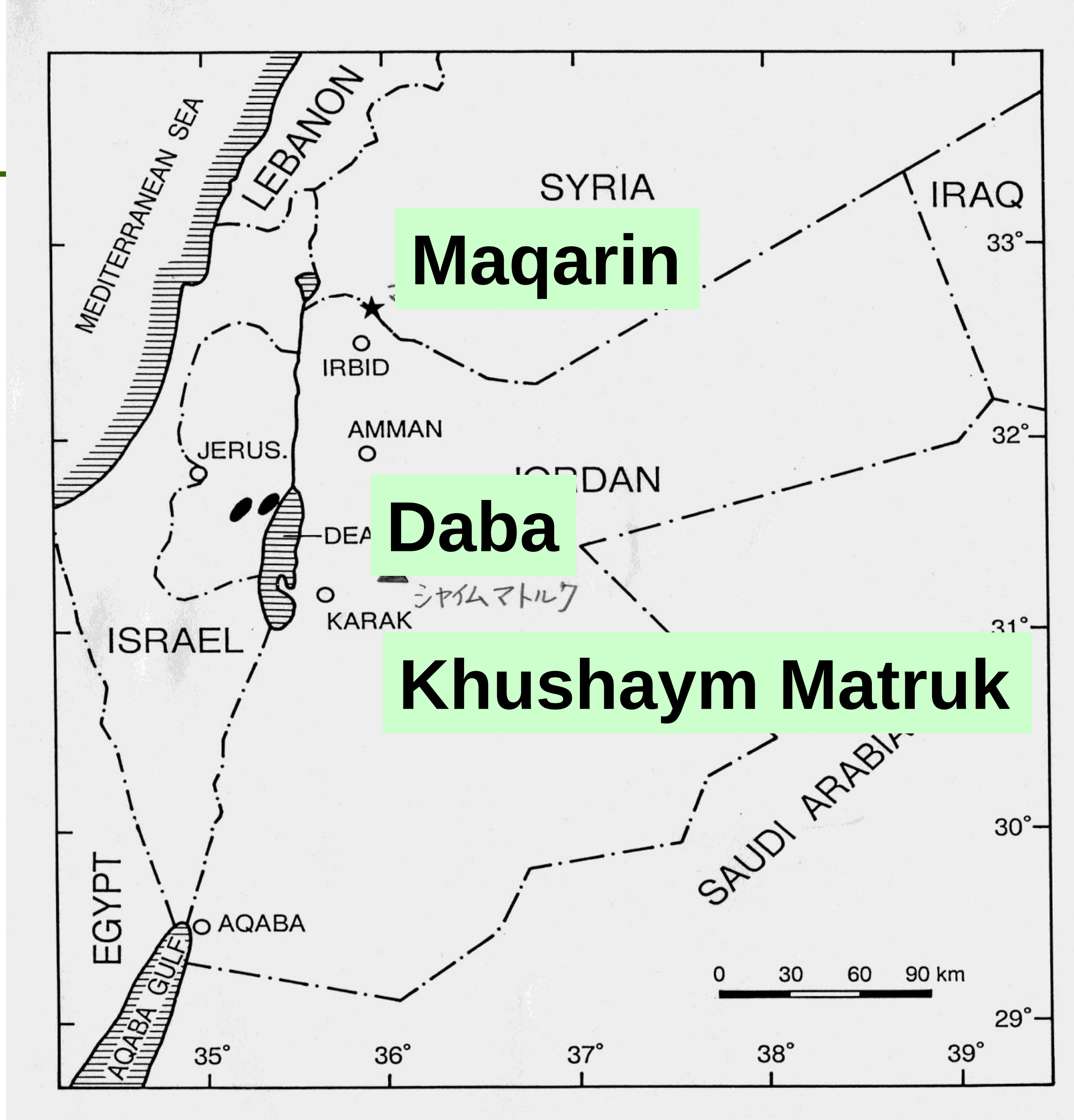
The Jordan Natural Analogue

- **Hyperalkaline groundwaters produced by leaching an assemblage of natural cement minerals produced as a result of high temperature-low pressure pyrometamorphism of marls (*i.e.* clay biomicrites) and limestones, producing a mineral assemblage which belongs to the sanidinite and pyroxene hornfels facies**
- **The natural cement is a reasonable analogy of industrial OPC (Ordinary Portland Cement)**

The Jordan Natural Analogue




Spontaneous Combustion in Maqarin


SYRIA
IRAQ
LEBANON
MEDITERRANEAN SEA
Maqarin
IRBID
AMMAN
JERUS.
JORDAN
Daba
DEA
シャイムマトルク
KARAK
ISRAEL
Khushaym Matruk
SAUDI ARABIA
EGYPT
AQABA
AQABA GULF
0 30 60 90 km
33°
32°
31°
30°
29°
35°
36°
37°
38°
39°

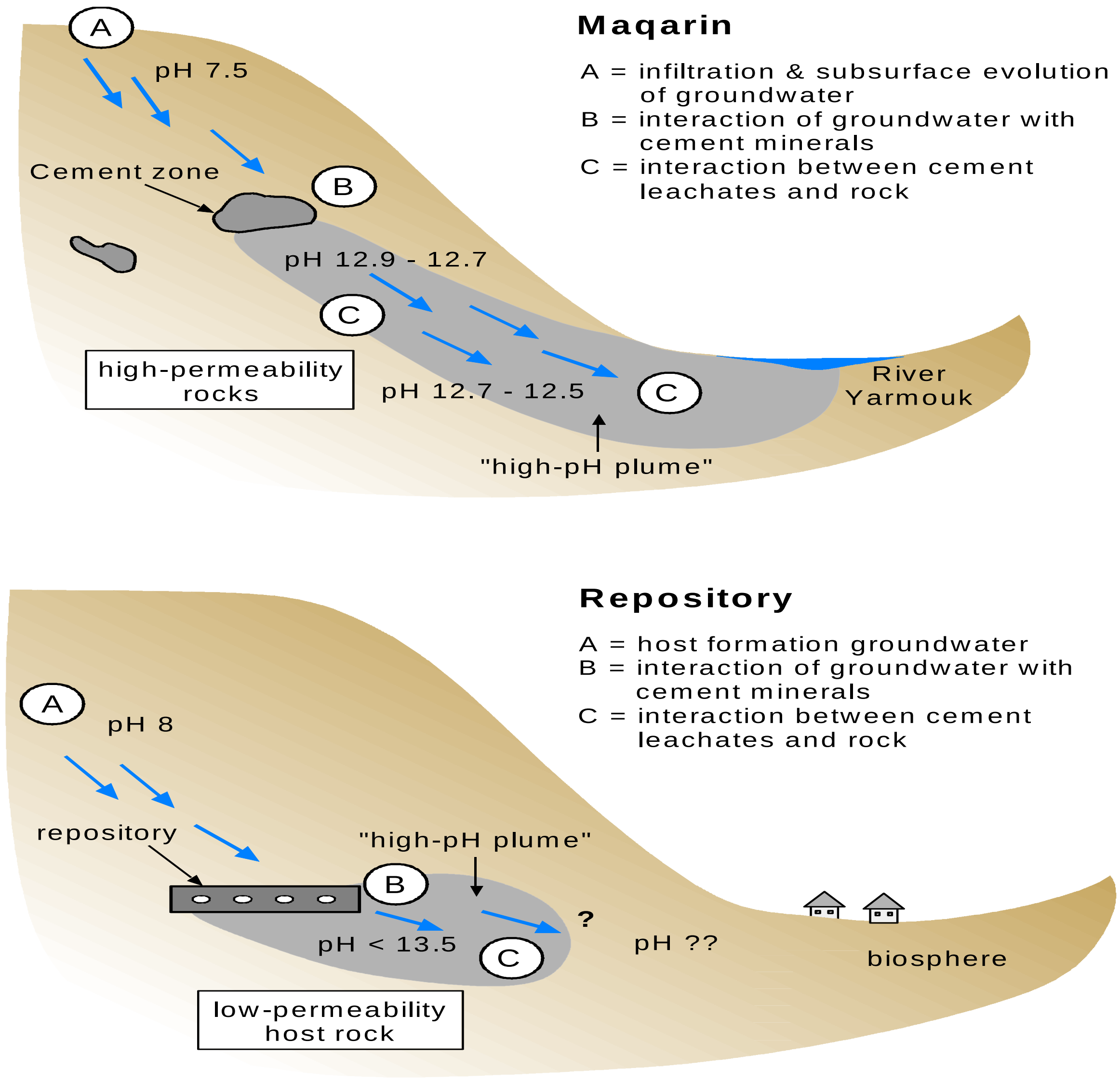
Maqarin: 20 years ago

Maqarin: today

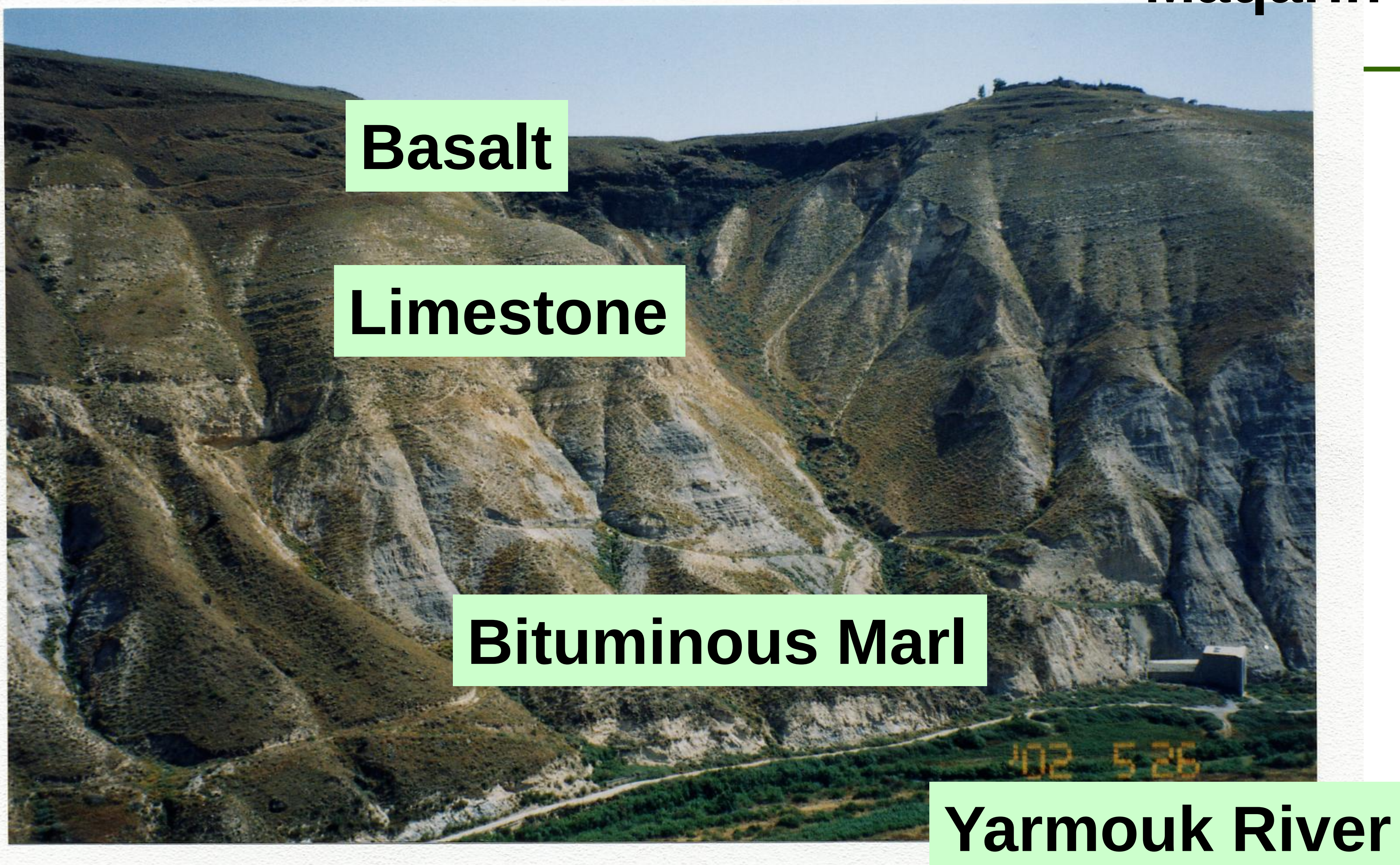
Kushaym Matruk: 10 years ago

Kushaym Matruk: today

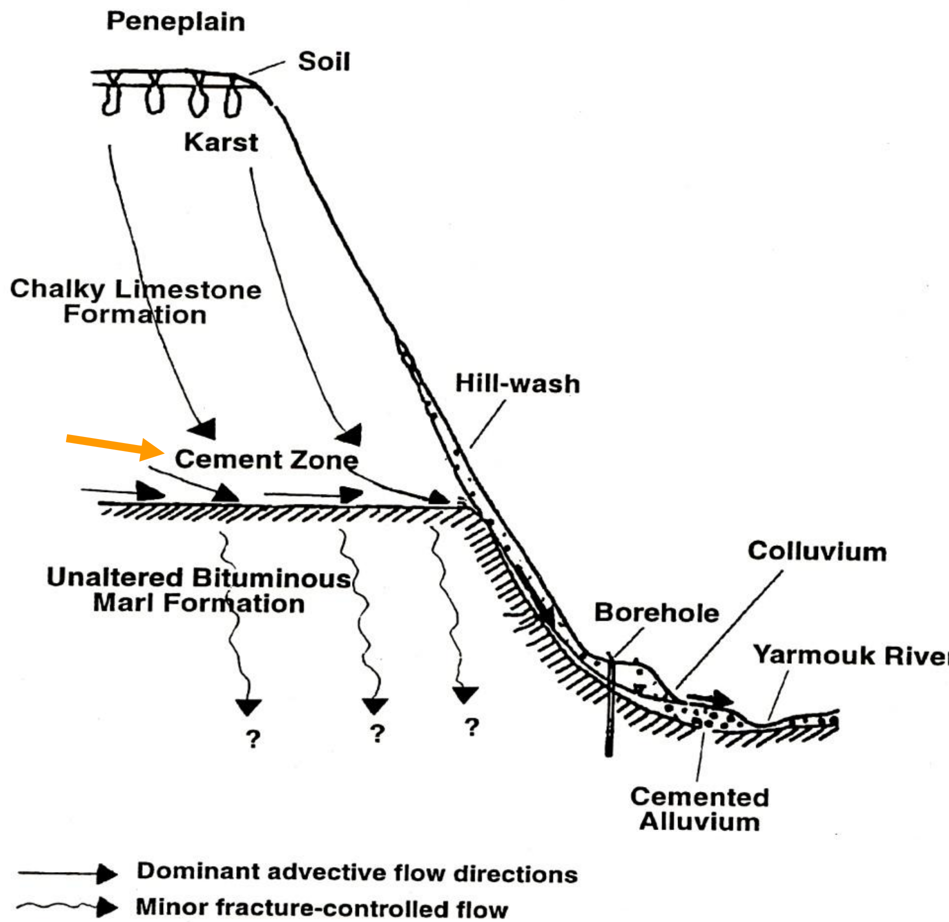
Maqarin – the analogy



Maqarin



Western Springs

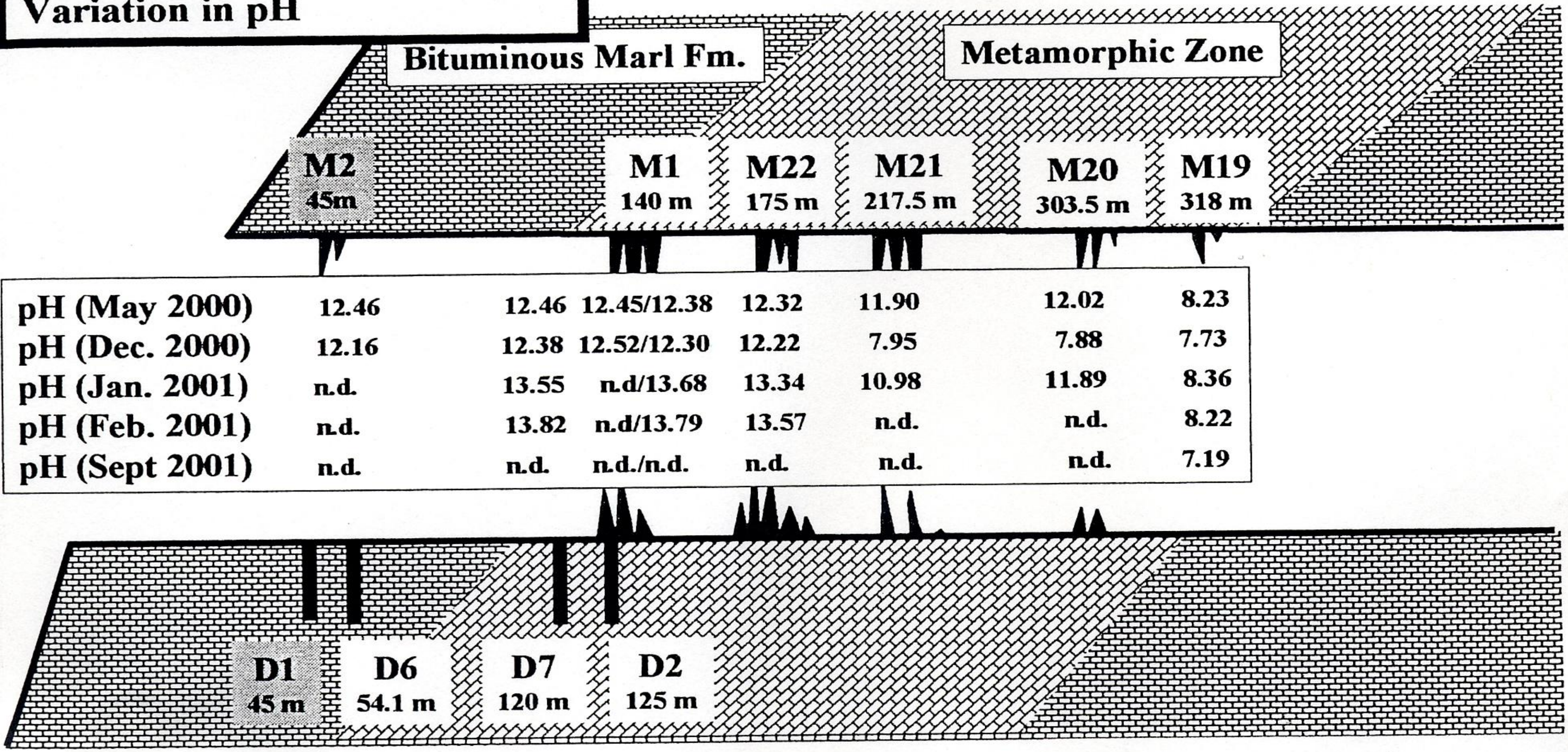


Maqarin: the only groundwater site

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

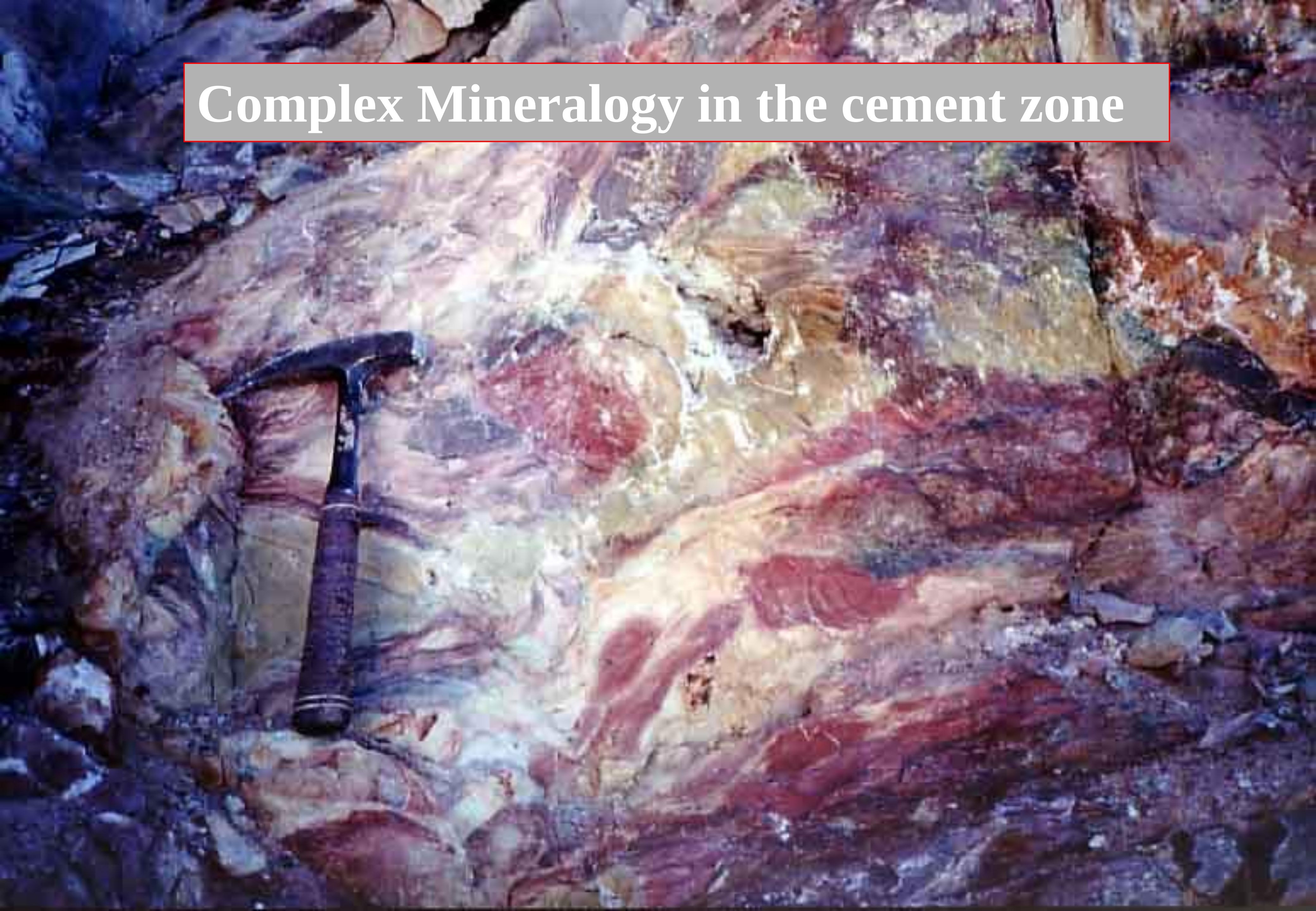
Sample	East (M1)	West (M5)
pH (field)	12.74	12.92
pH (lab.)	12.67	12.83
Eh (field)	+278 mV	+242 mV
Ca	674	1120
Na	47.2	136
K	9.88	526
Cl	52.4	46.6
SO_4	305	1580
NO_3	3.28	39.1

Groundwater chemistry
Variation in pH



pH (May 2000)	12.46	12.46	12.45/12.38	12.32	11.90	12.02	8.23
pH (Dec. 2000)	12.16	12.38	12.52/12.30	12.22	7.95	7.88	7.73
pH (Jan. 2001)	n.d.	13.55	n.d/13.68	13.34	10.98	11.89	8.36
pH (Feb. 2001)	n.d.	13.82	n.d/13.79	13.57	n.d.	n.d.	8.22
pH (Sept 2001)	n.d.	n.d.	n.d./n.d.	n.d.	n.d.	n.d.	7.19

Complex Mineralogy in the cement zone



Primary minerals in the natural cement

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

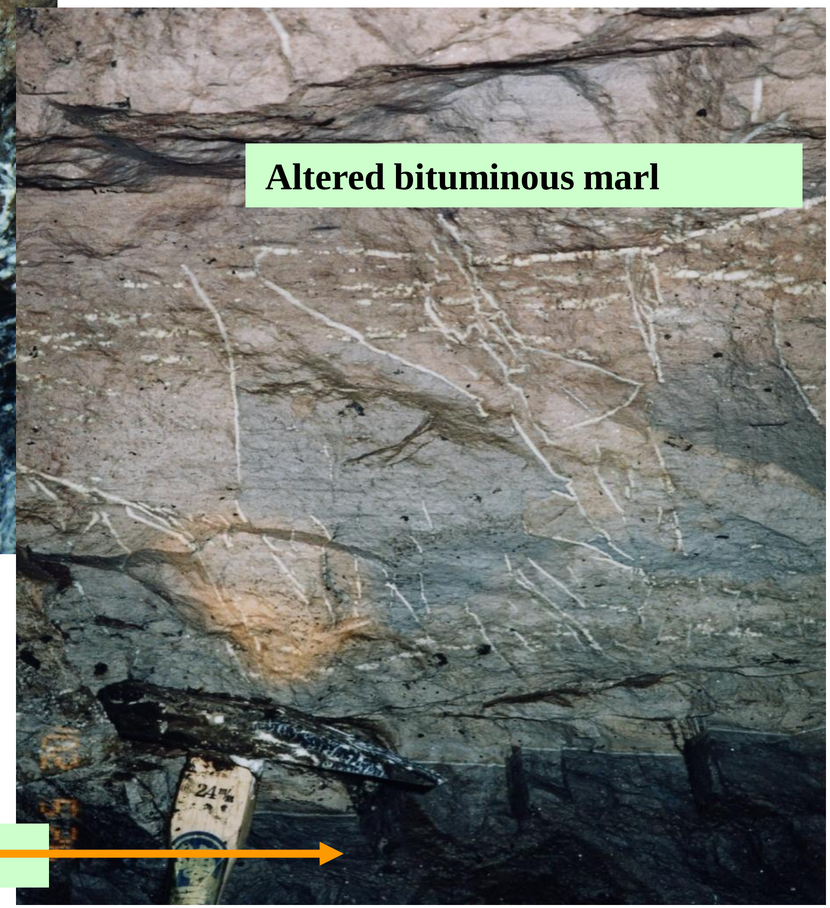
A: Khoury and Nassir (1982)
B: Milodowski et al. (1992)

Natural cement

Example of fractures and joints in the ACZ (brown, top of photo) and the protolith (black, bottom) in Adit A-6, sealed by secondary CSH (and locally zeolite) phases.

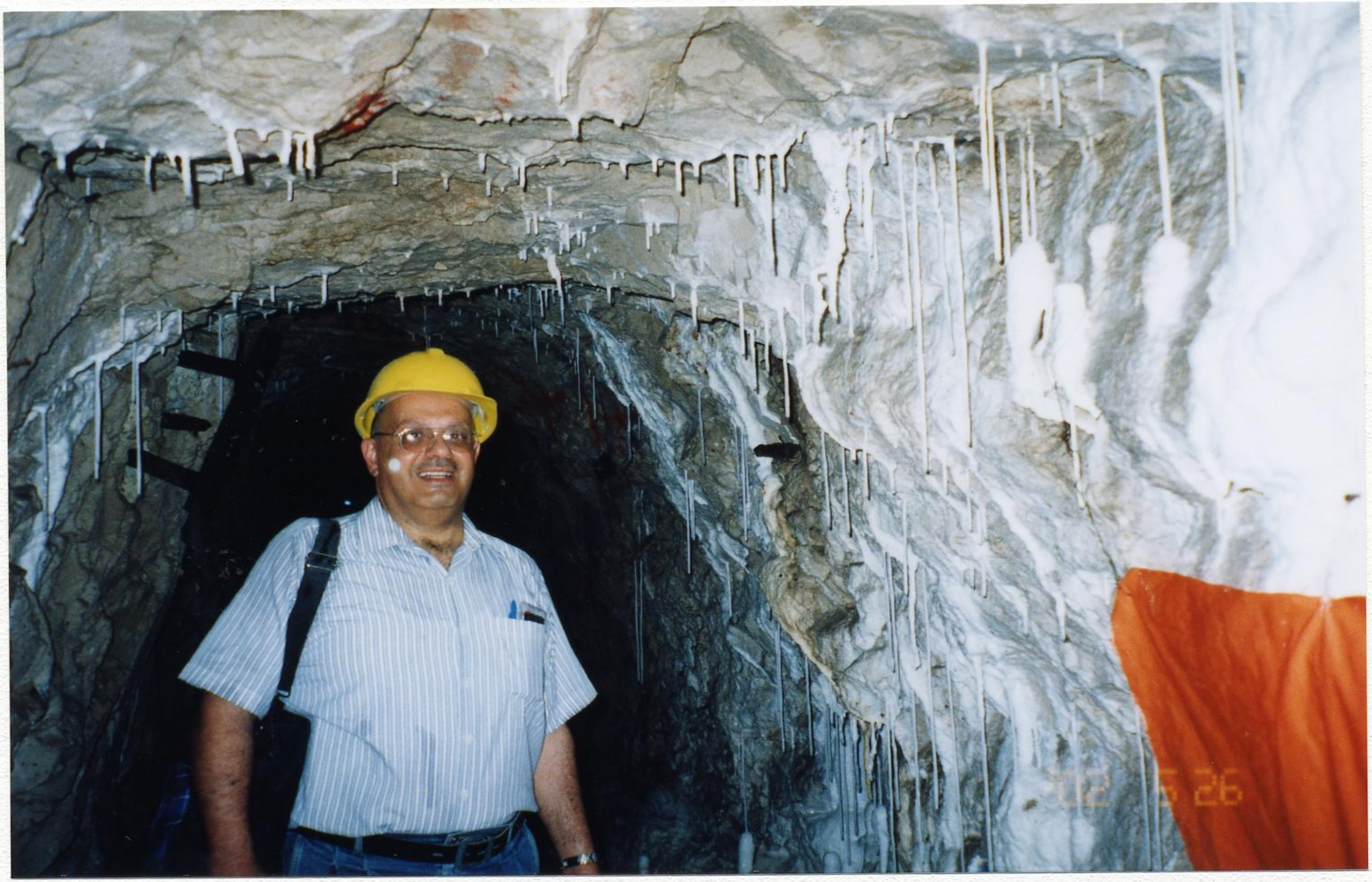
Bituminous marl

Secondary minerals fill in fractures.



Altered bituminous marl

Unaltered bituminous marl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Secondary minerals precipitated from the hyperalkaline waters

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	KCaSiO0(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)

^{230}Th dating

Secondary calcite (fracture)
500 ka-2 Ma

Tobermorite, Jennite-ettringite (fracture)
80-90 ka

Zeolite in rock matrix
160 ka

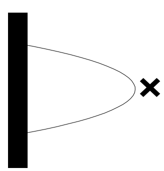
Maqarin: mineralogy main points

- 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

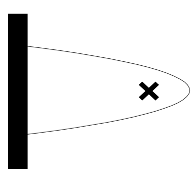
Maqarin: conceptual model

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

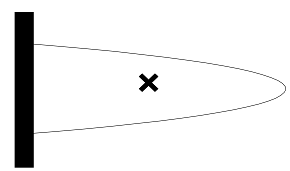
b) resaturation, plume evolution begins



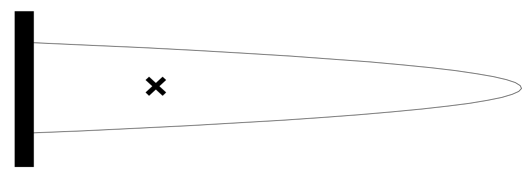
c) distal edge of plume reaches the observation point, initiation of zeolite formation



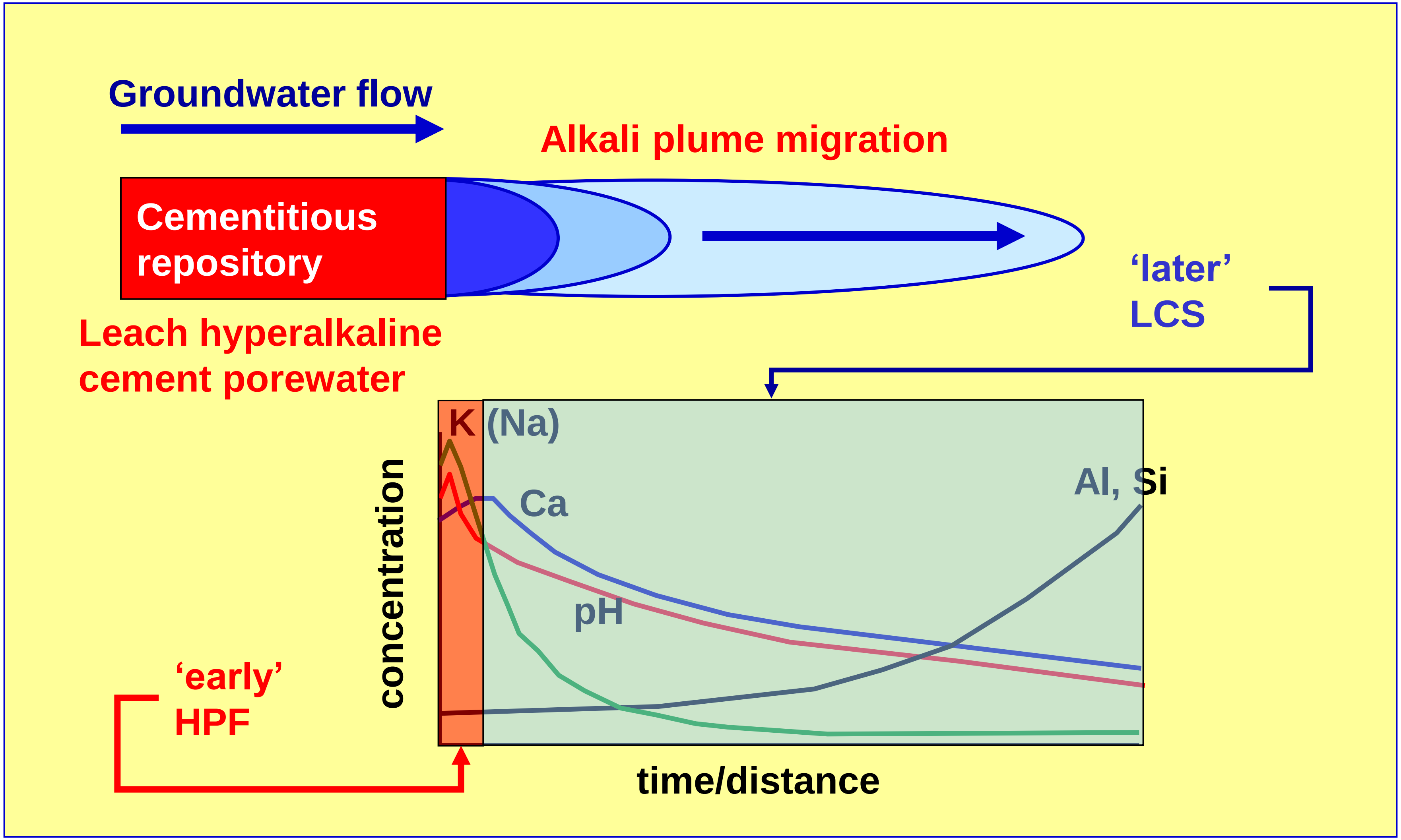
d) middle of plume reaches observation point (as the rock buffer capacity is being consumed) CASH formation initiated



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

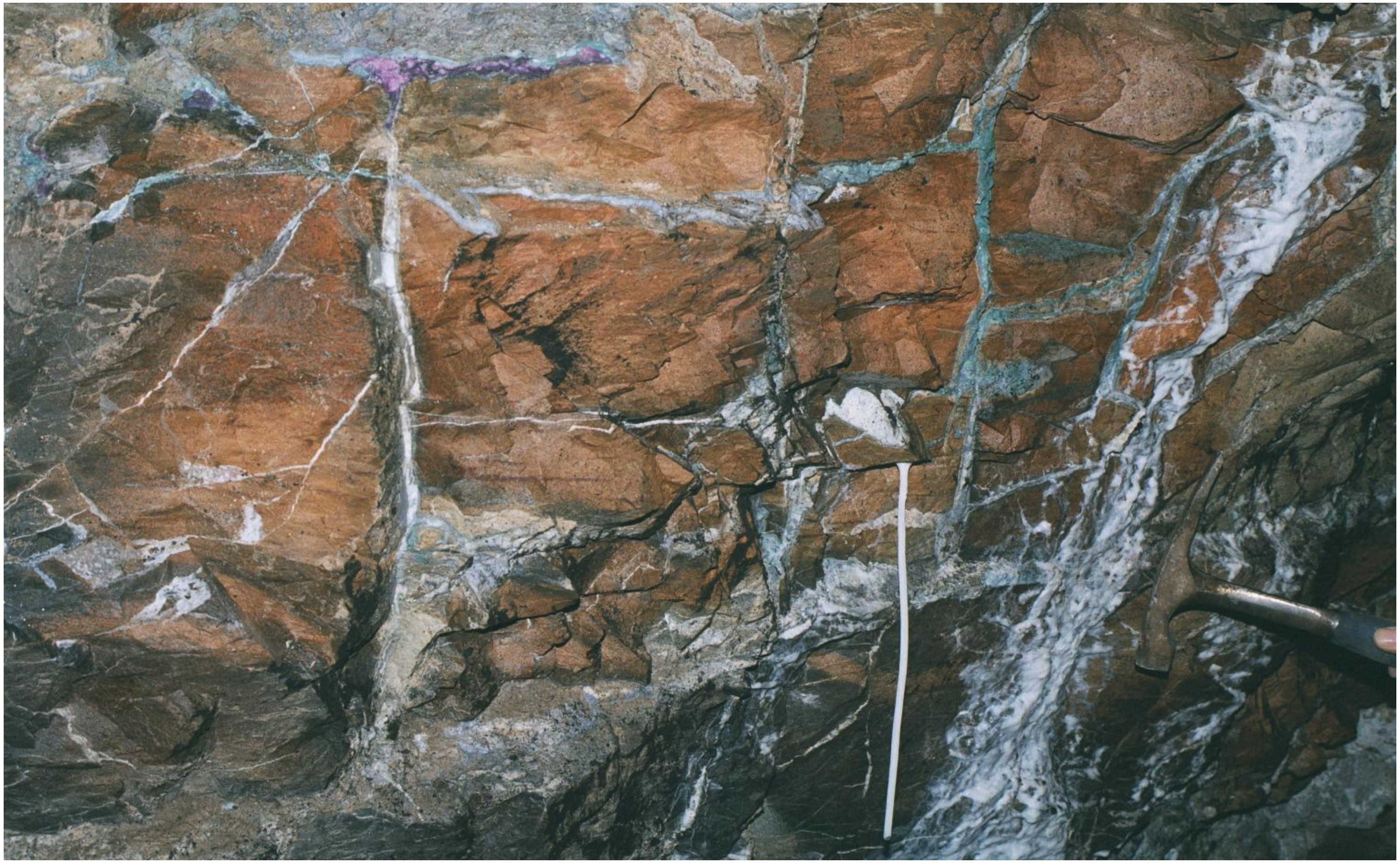
- Hyperakaline pore fluid conditions generated by minerals analogous to those in cements are long-lived (in excess of tens of thousands of years) under the Maqarin flow conditions

- 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
- Interaction between hyperalkaline waters and the host rock occur extensively and (small to medium aperature) 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 cm

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**
- **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**

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**
- **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**

Maqarin: qualitative conclusions (2)

- **Once a fracture is sealed, no further alteration can take place unless new pore-space is created by fracture reactivation**

- **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 (3)

- 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, or the site is tectonically active or near-surface…..

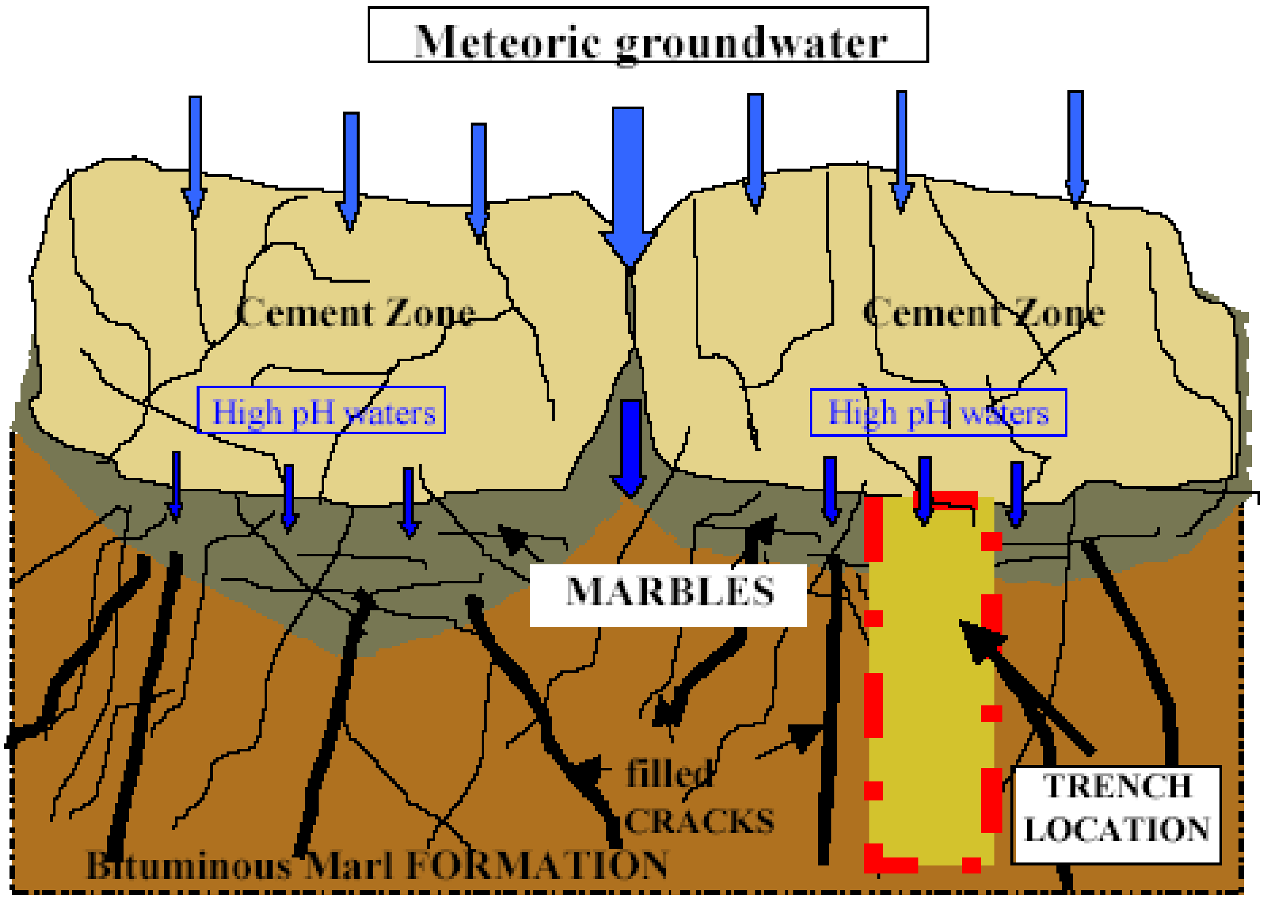
Maqarin: qualitative conclusions (5)

- **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)**

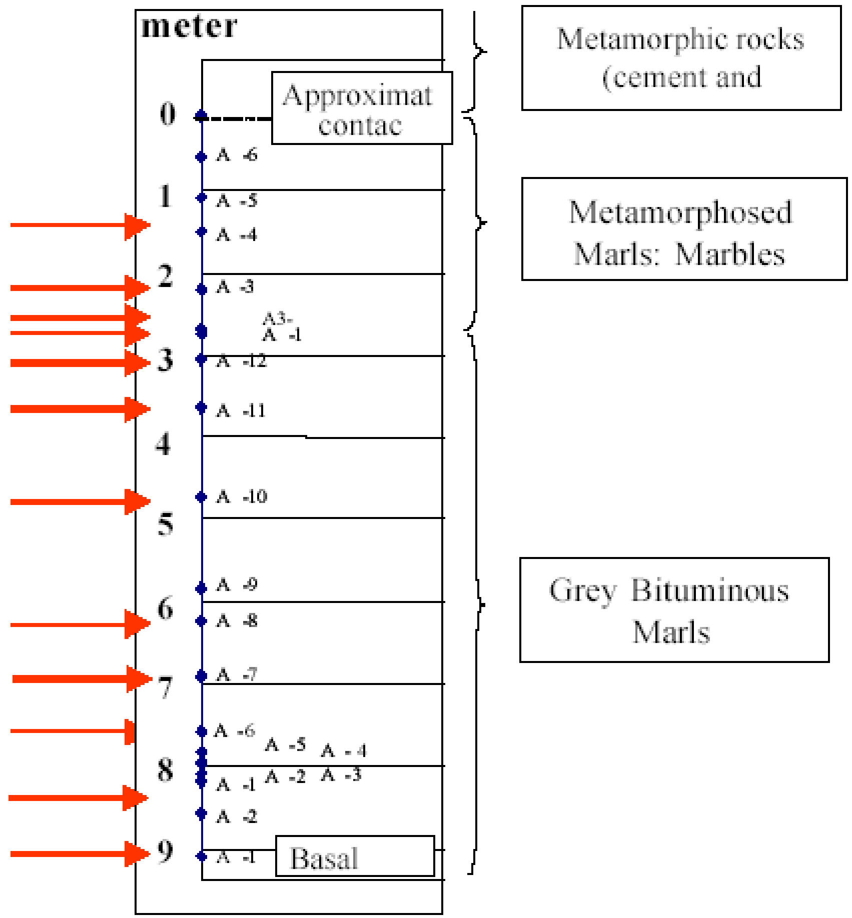
- **Despite major differences between the rock types at the Eastern and Western Springs, the mineralogical composition of the secondary minerals at both sites is very similar, implying that similar reactions could be expected to occur at a repository host rock, *ie* the mineralogical information from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

Khushaym Matruk - trenching

Khushaym Matruk



Khushaym Matruk



Khushaym Matruk

- only small number of samples studied
- 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
- decrease in the content (80 % to 60 %) of smectite component of illite/smectite mixed layer clay minerals was observed in the host rock

Khushaym Matruk

- **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**
- **however, it is not yet possible to rule out if the matrix zeolites are a primary diagenetic feature of the sediments**
- **"*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 (2011)**

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 from Gento)?
- Degree of bentonite (clay) interaction over long timescales?
- Likely impact of a hyperalkaline plume on a diffusive-transport controlled host rock (NB gas!!)?
- 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 was 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
- has been used directly in PA (Nagra)
- has been used in an analysis of likely long-term evolution of at least one site (WLB)

Jordan: successes and failures

- the work on BMP has not been taken over by PA modellers
  - weaknesses in TDB and codes ignored
  - the BPM methodology not universally acknowledged, despite clear advantages to PA modellers
- 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 a highly simplified attempt by Vieno et al. (2003) (Posiva Report 2003-06) and Alexander and Mazurek (1996) (unpubl. Nagra report)
- while the Maqarin dataset has been used as a case study for coupled code analyses, it has improved the codes themselves very little

Jordan: thank you

- **Beginning in 1989, field work in Jordan continued to 2002 and included the partners:**
  - **Nagra**
  - **Nirex (NDA-RWMD)**
  - **SKB**
  - **ANDRA**
  - **CEA**
  - **JAEA**
  - **Ontario Hydro**
  - **UK HMIP (EA)**
- **Final reporting just completed…..**