Iodine and chlorine mobility in the biomicrite of the Bituminous Marl Formation at Maqarin

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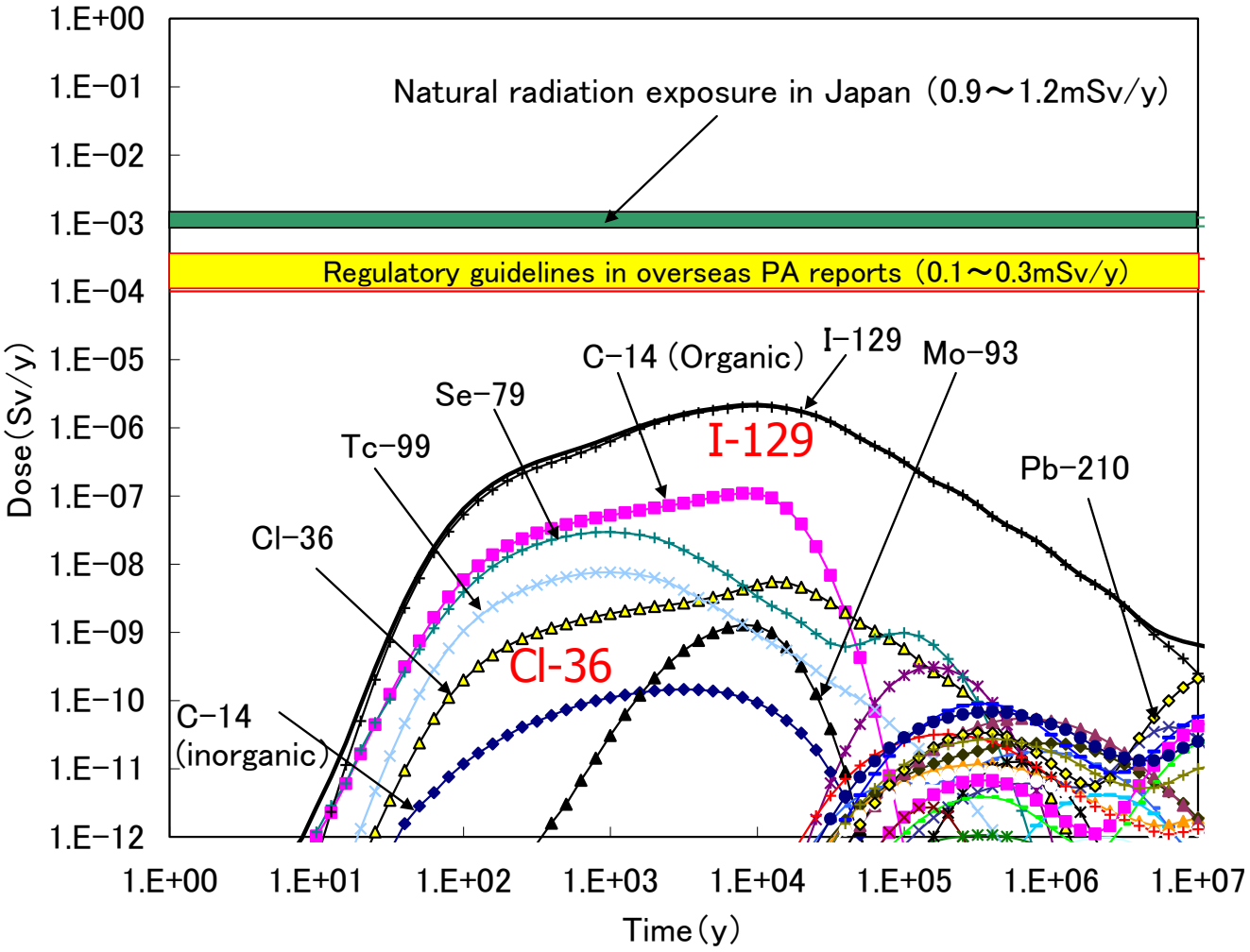
Japan Atomic Energy Agency (JAEA)
☆ Bedrock Geosciences

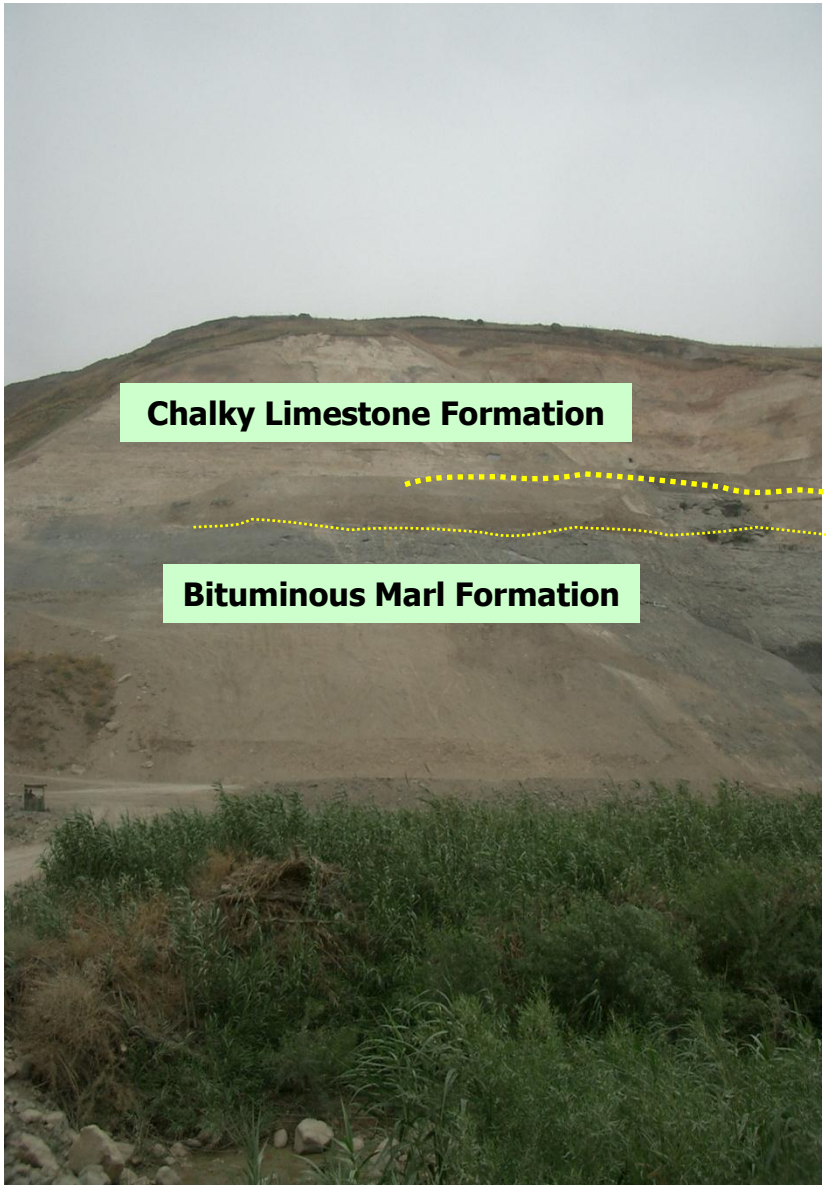
A Calculation Result of Dose Rate for TRU waste

○ Key radionuclide:

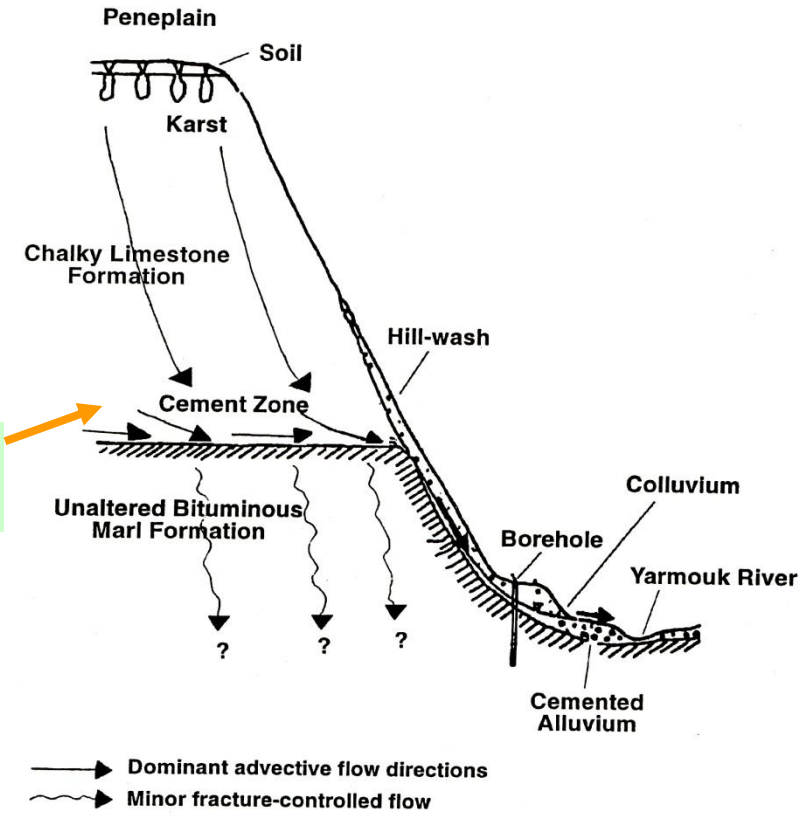
I-129



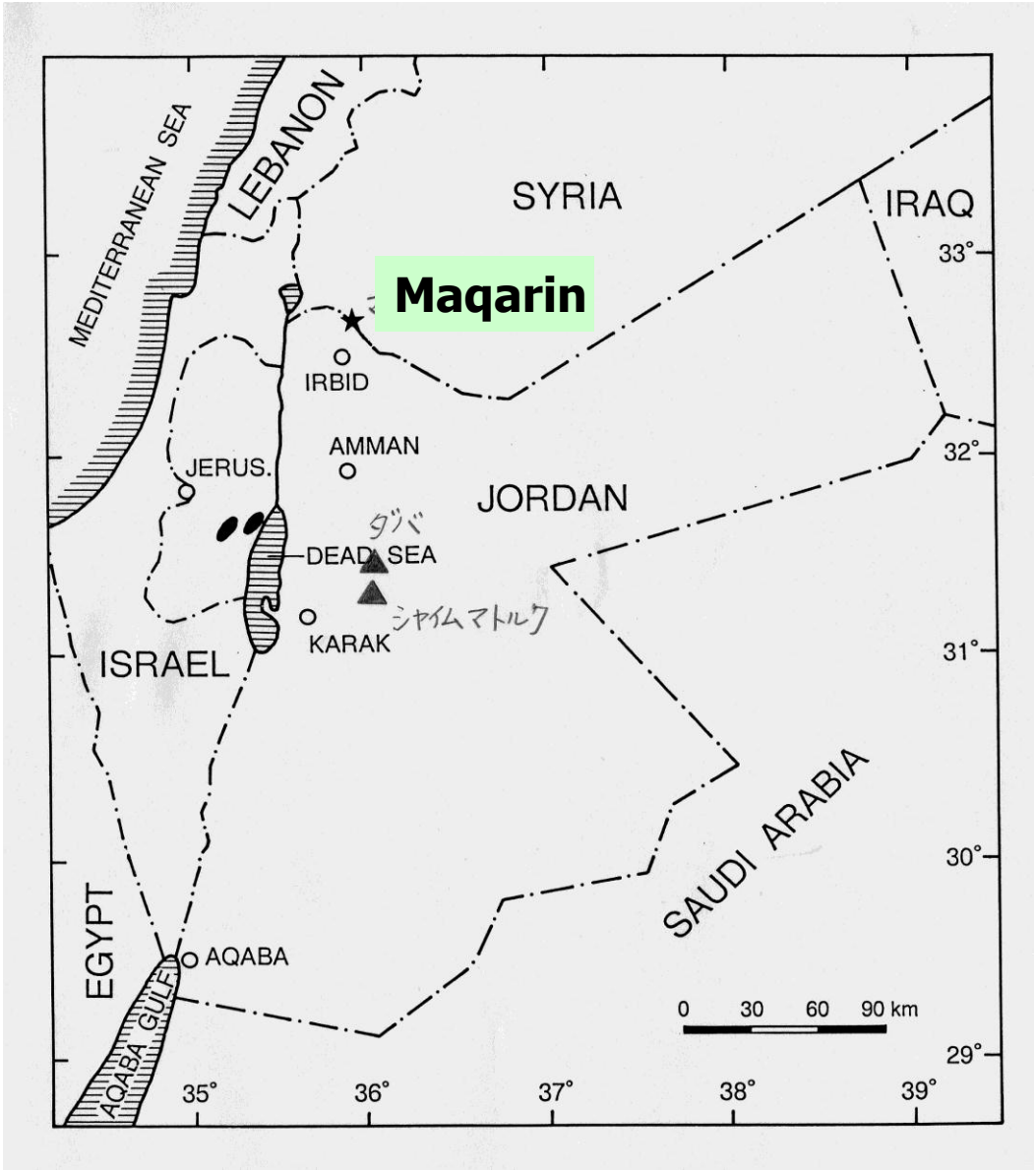
Maqarin Site

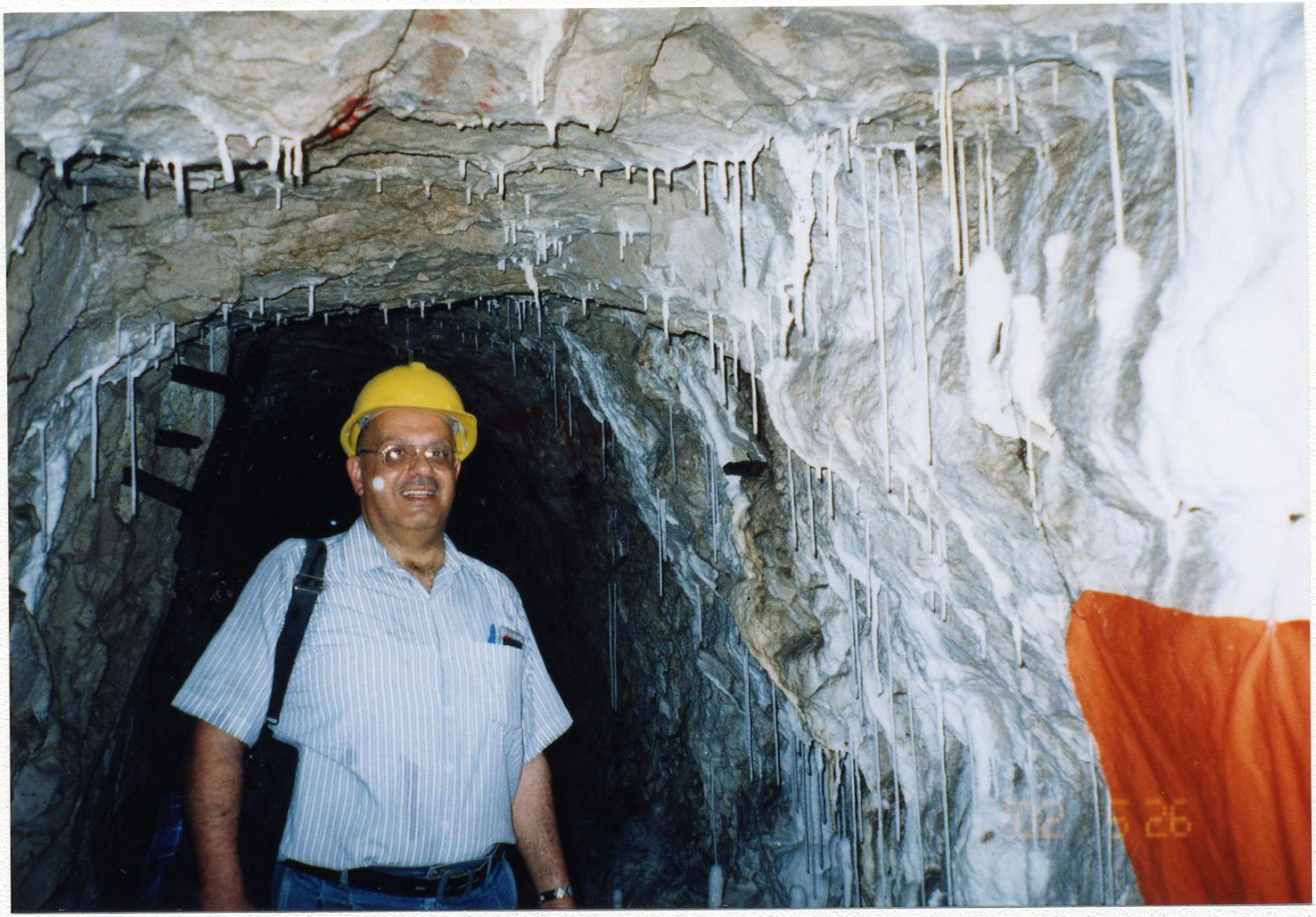


Natural cement

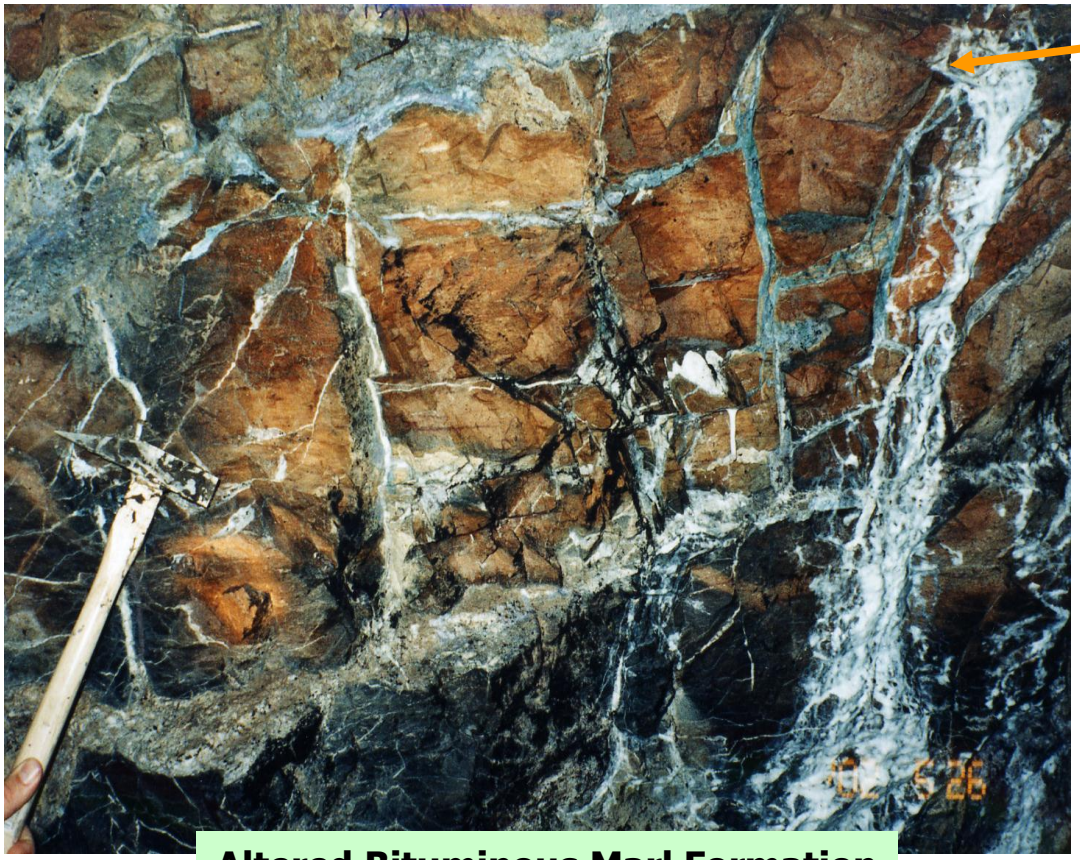


Khoury et al.(1998)


Maqarin
MEDITERRANEAN SEA
LEBANON
SYRIA
IRAQ
IRBID
AMMAN
JERUS.
JORDAN
DEAD SEA
KARAK
ISRAEL
EGYPT
AQABA
AQABA GULF
SAUDI ARABIA
0 30 60 90 km
33°
32°
31°
30°
29°
35°
36°
37°
38°
39°

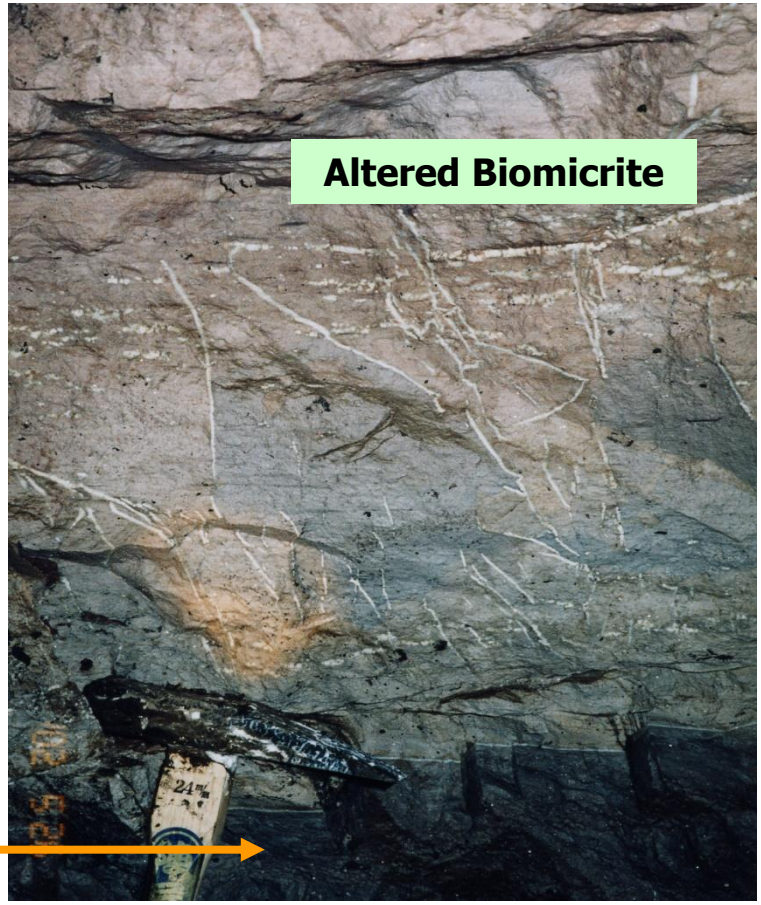


Bituminous Marl Formation



Natural cement

Altered Bituminous Marl Formation (Altered Biomicrite)



Altered Biomicrite

Secondary minerals fill in fractures

Unaltered Biomicrite

Objectives

Motivation

Alkaline solution (groundwater) flow from TRU waste repository possibly disturbs the expected matrix diffusion function in terms of Iodine (and Chlorine) behaviour in the natural barrier.

The Bituminous Marl Formation (biomicrite) at Maqarin is a good natural analogue to investigate the I and Cl migration behavior under alkaline solution environment.

Analyses for

- Concentration profiles of I and Cl along a direction lying at right angles to the fracture, where the alkaline solution flowed.

- Estimation of chemical compound of I and Cl in the non-disturbed biomicrite. → Three times extraction was done to I, Cl and Organic matter (OM).

Sample Preparation

Fracture filled with white precipitates

1. Back Ground (BG) sample (non-disturbed)

- Take a core sample at a point distant from fracture
- Clash it into small pieces
- Grind each slice to a powder (under 106μm)

'Adit 6' core (Photo 1)

2. Sample near the fractute (disturbed)

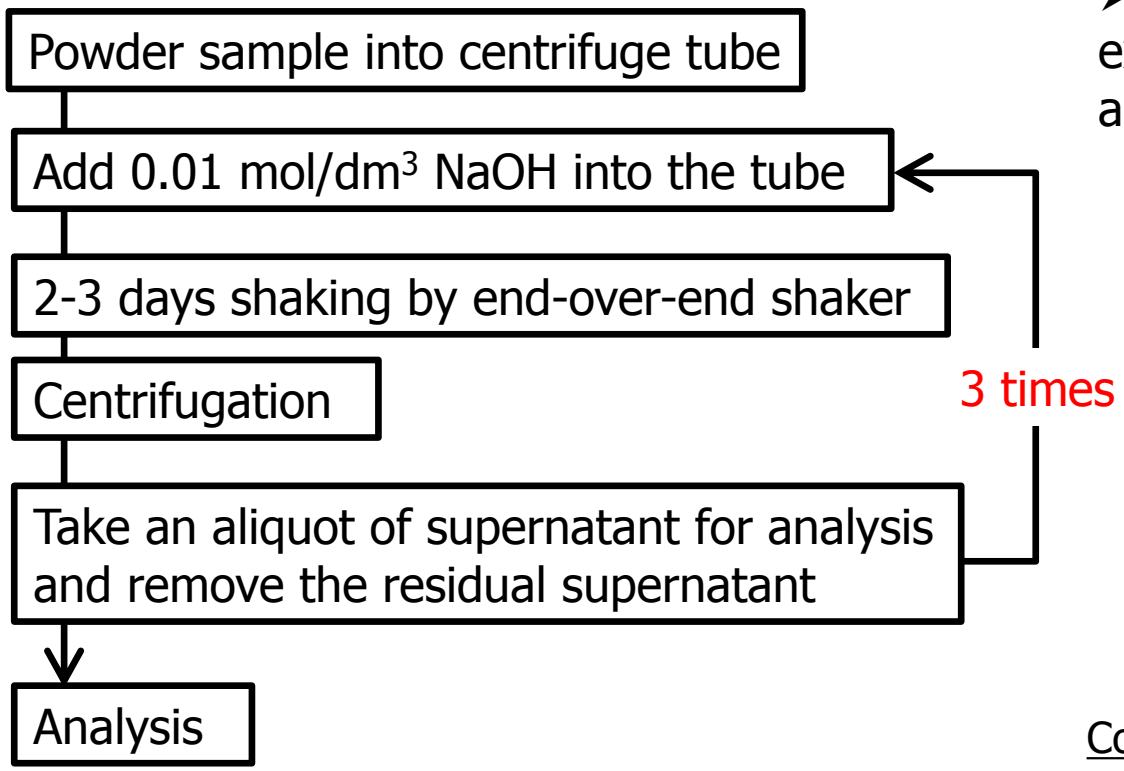
- Cut the core perpendicularly to the fracture
- Cut it into a form of square column (Photo 1 and 2)
- Cut the column at 5mm interval
- Grind each slice to a powder under 106μm

Photo 2

Photo 3

Extraction of Iodine, Chlorine and Organic matter

Extraction Procedure



➢NaOH solution was used for the extraction to avoid loss of Iodine and Chlorine by evaporation

Iodine: ICP-MS

Chlorine: Ion Chromatograph

Organic Matters: Total Organic Carbon (TOC)

Size Exclusion Chromatography (SEC)

Condition of SEC analysis

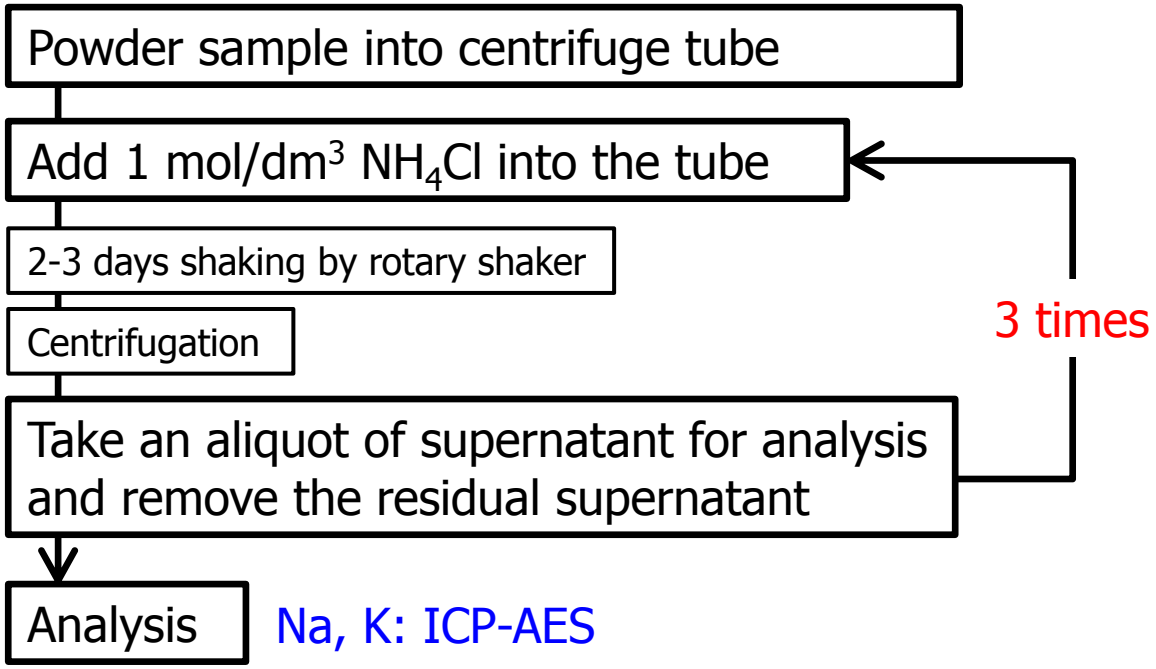
Column: TSKgel SuperSW2000 (Toso)

Eluent: 3×10^{-3} M phosphate buffer in 0.3M NaCl

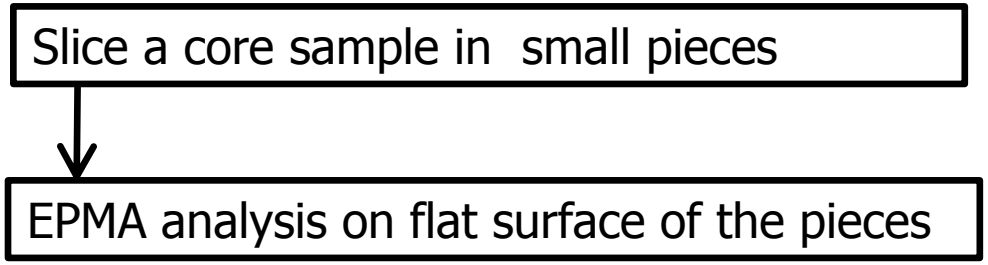
Detector: UV-Vis at 300nm

Leaching cation and EPMA analysis

Ammonium Extraction for Na and K (Leaching Cation , LC)



Sample preparation for EPMA analysis



➢Samples were processed in a dry state to avoid dissolution of Iodine and Chlorine into water

Results - Extraction of I and Cl from BG sample

Result of **Iodine** Extraction

	Extracted I (ppm)			Total (ppm)
	1 st	2 nd	3 rd	
BG Sample **1**	0.026±0.002	0.009±0.002	n.d.	**0.035±0.005**
BG Sample **2**	0.022±0.002	0.006±0.002	n.d.	**0.028±0.005**
BG Sample **3**	0.018±0.002	0.005±0.002	n.d.	**0.023±0.005**

Result of **Chlorine** Extraction

	Extracted Cl (ppm)			Total (ppm)
	1 st	2 nd	3 rd	
BG Sample **1**	14.3±0.12	n.d.	n.d.	**14.3±0.12**
BG Sample **2**	19.3±0.12	n.d.	n.d.	**19.3±0.12**
BG Sample **3**	14.8±0.12	n.d.	n.d.	**14.8±0.12**

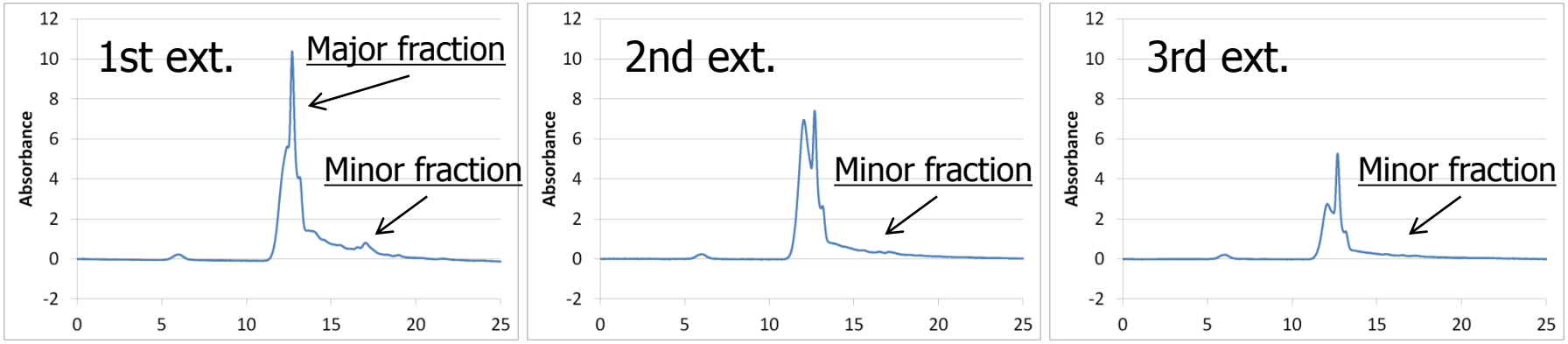
- I and Cl are retained in the non-disturbed biomicrite.
- I and Cl were completely extracted by 3 times extraction from the biomicrite.

Results - Extracted Organic Matters

Total Organic Matter (TOC) Concentration in Extracted Solutions

	Extracted TOC (ppm)			Total (ppm)
	1 st	2 nd	3 rd	
BG Sample **1**	872±30	447±3	370±3	1670±36
BG Sample **2**	662±24	372±3	269±3	1303±30
BG Sample **3**	770±26	335±3	287±3	1322±31

Spectra of Size Exclusion Chromatography, BG Sample 2

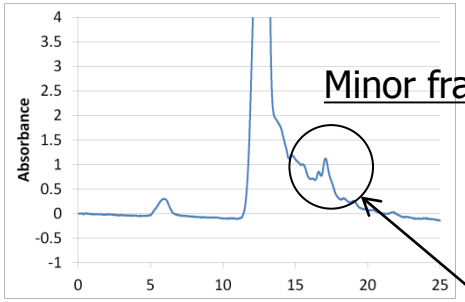


- Major fraction of organic matter (OM) remained even after the 3 time extractions.
- A Minor fraction, corresponding to smaller molecular weight OM, was mostly extracted.

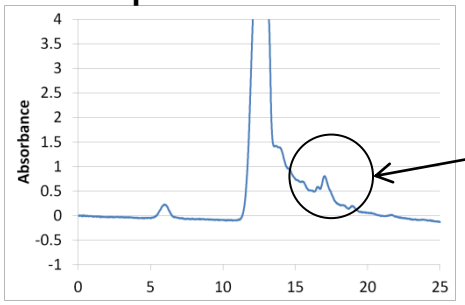
Results – OM and Iodine

SEC Spectra of 1st extraction (OM)

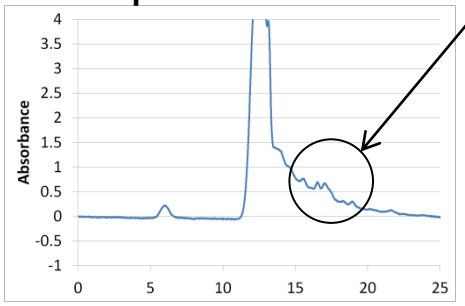
■BG Sample **1**



■BG Sample **2**



■BG Sample **3**



Result of **Iodine** Extraction

	Extracted Iodine (ppm)
	1 st Ext.
BG Sample **1**	0.026±0.002
BG Sample **2**	0.022±0.002
BG Sample **3**	0.018±0.002

□Iodine concentration: **Sample 1> 2> 3**

■ OM conc.: **Sample 1> 2> 3**

➢Good consistency between extracted Iodine and smaller molecular weight (minor fraction) OM.

Iodine possibly forms organic compound in the biomicrite.

Results - Leaching Cations and EPMA Observation

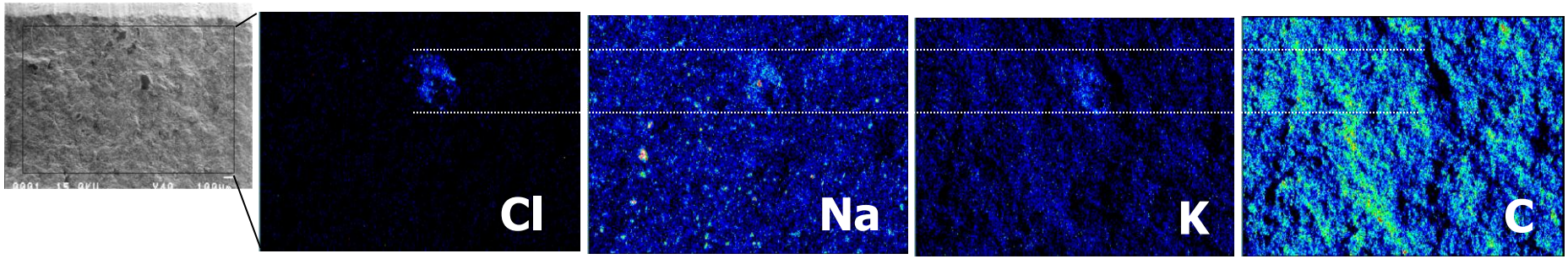
Result of LC , Cl and I measurement

	Na ($x10^6$ mol/g)	K ($x10^6$ mol/g)	Extracted Cl (ppm)	Extracted I (ppm)
BG Sample **1**	**3.57±0.12**	**10.7±0.8**	**14.3±0.12**	**0.035±0.005**
BG Sample **2**	**9.19±0.15**	**22.4±1.6**	**19.3±0.12**	**0.028±0.005**
BG Sample **3**	**7.32±0.14**	**20.8±1.6**	**14.8±0.12**	**0.023±0.005**

Na, K : Sample 2> 3>1 **Cl : Sample 2> 3> 1** **I : Sample 1> 2> 3**

- **Trend of Cl agrees with those of Na and K**

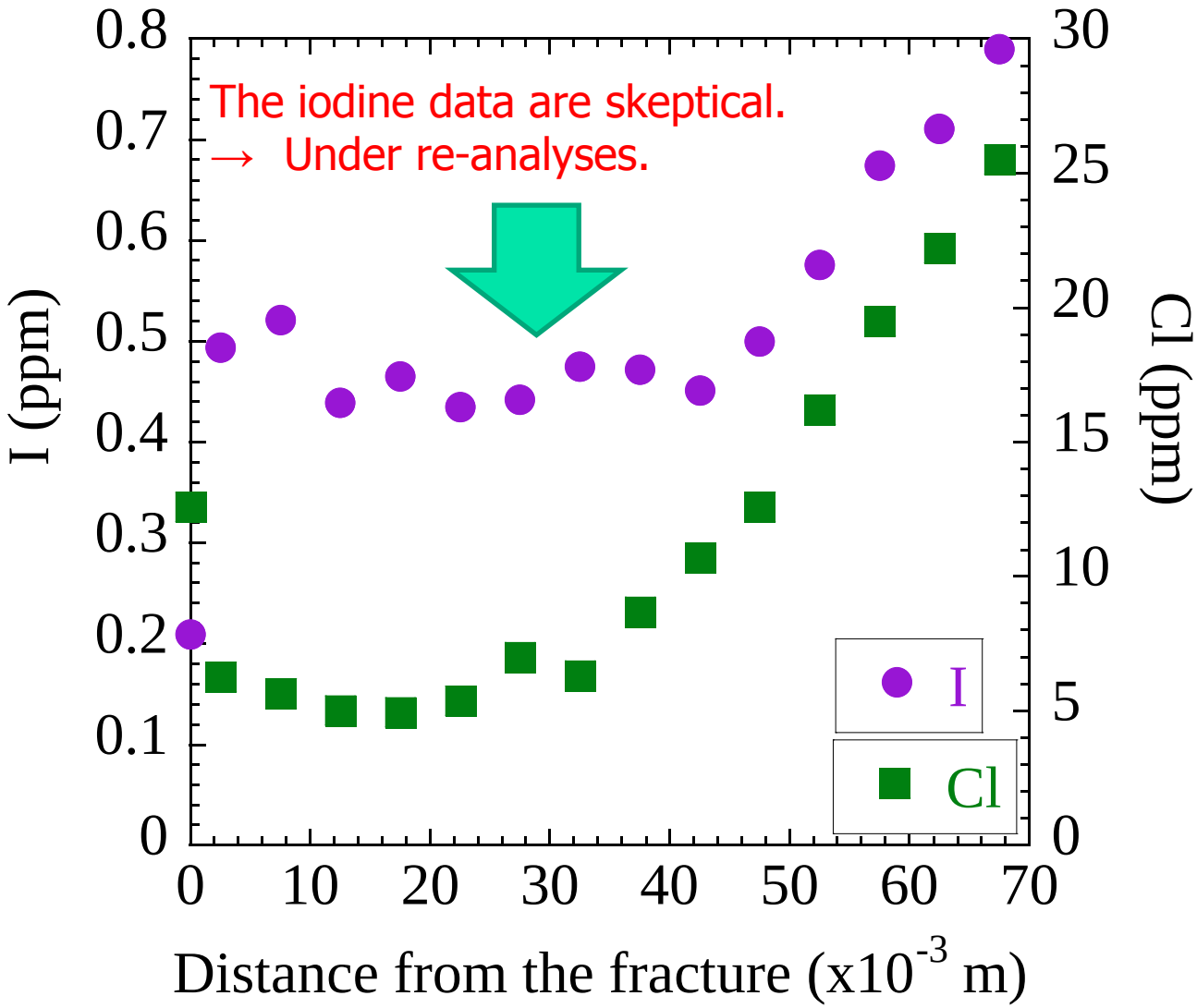
EPMA Mapping



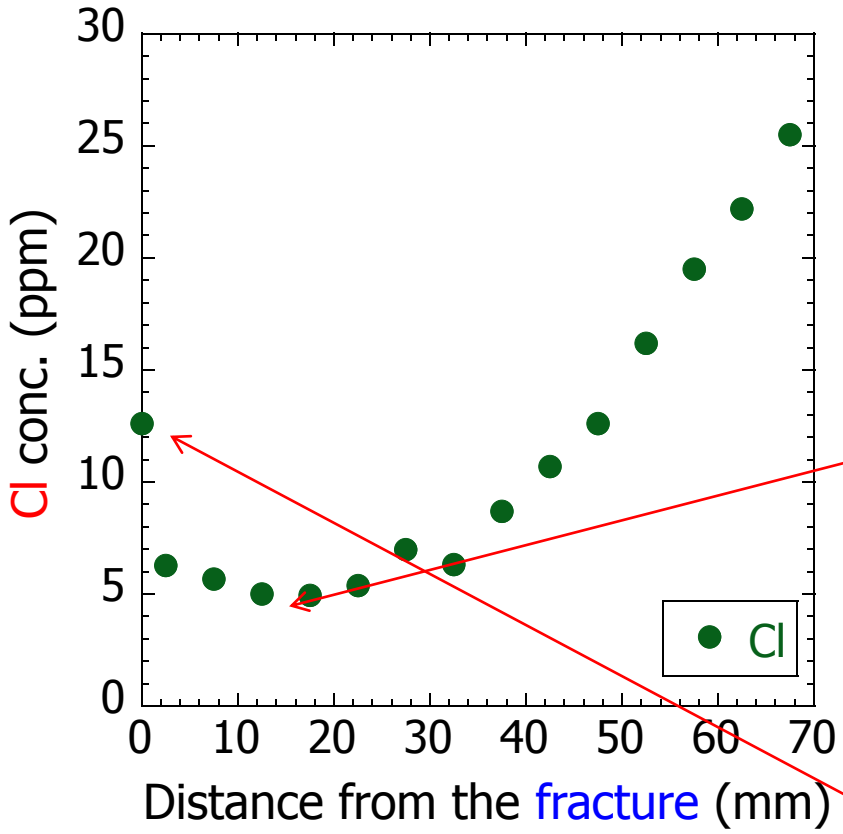
- **Cl** distributes as spots containing high concentrations of **Na** and **K**.

Cl may precipitate as Na and/or K salt in the biomicrite

Results – Concentration Profiles from the Fracture



Results – Conc. Profiles of Cl from the Fracture (precipitates from the alkaline solution)



➢Cl conc. increases linearly from 30 mm from the fracture

Cl could be exuded into the alkaline solution (ground water) which flowed in the fracture

➢Cl conc. is almost constant (approx.5 ppm) at the extent of 2 to 30mm.

→ Cl retains in dead pores and/or re-precipitates from the alkaline solution.

➢Approx. 12ppm of Cl was detected in the precipitates filled in the fracture.

Summary

Expected migration process of Iodine and Chlorine from the biomicrite of the Bituminous Marl Formation

Iodine could be retained as organic compound in non-disturbed biomicrite.

Chlorine precipitated as sodium and/or potassium salt in non-disturbed biomicrite.

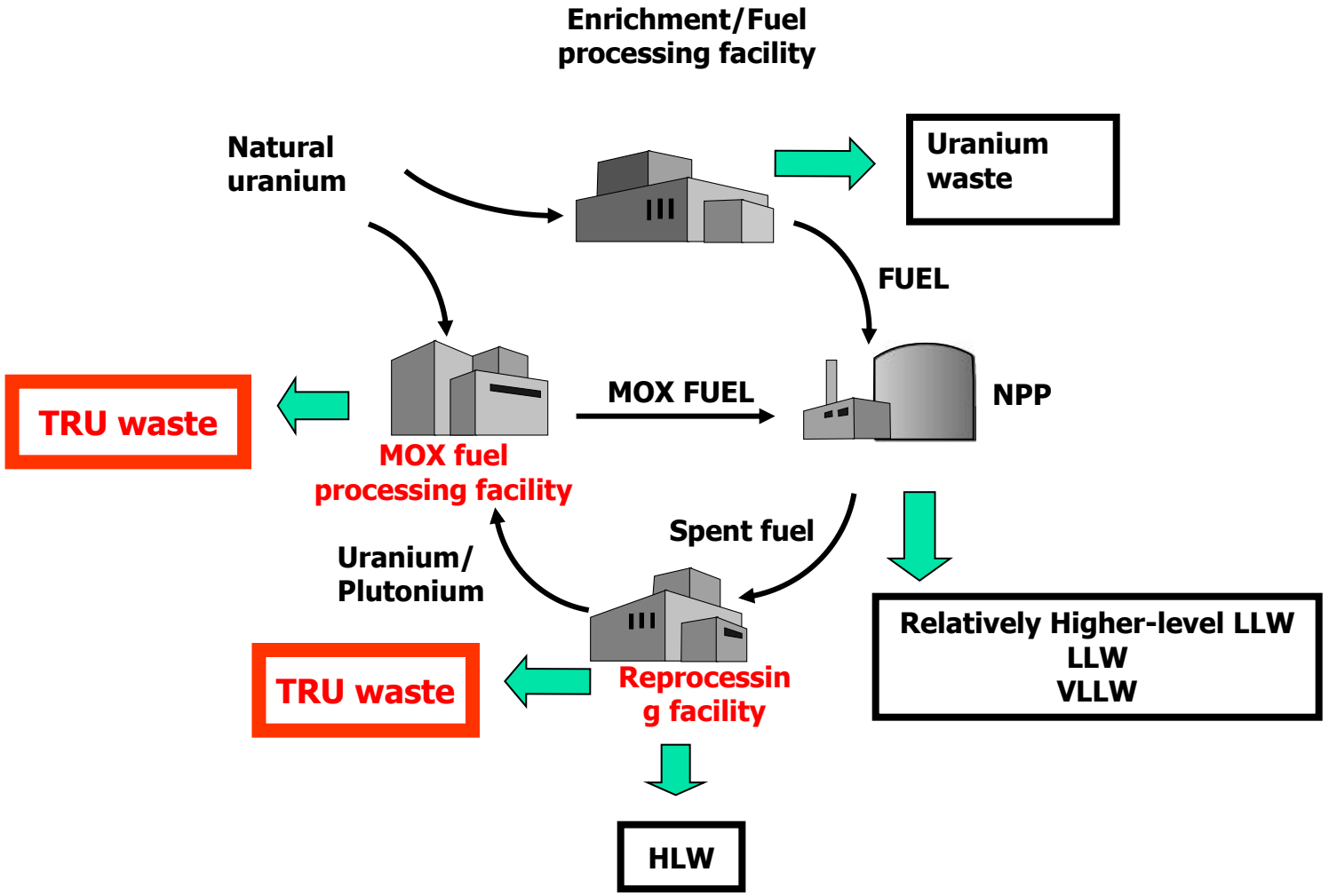
Chlorine (and Iodine?) could be exuded into the alkaline groundwater flowing in the fracture, resulting from the concentration profile.

Chlorine (and Iodine?) partly retained in the alkali-disturbed zone.
→ in dead pores and/or re-precipitate from the alkali solution.

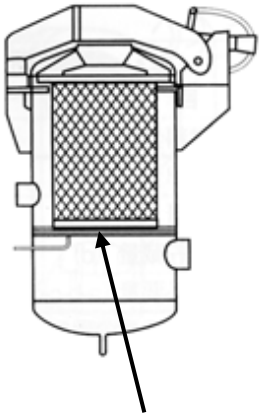
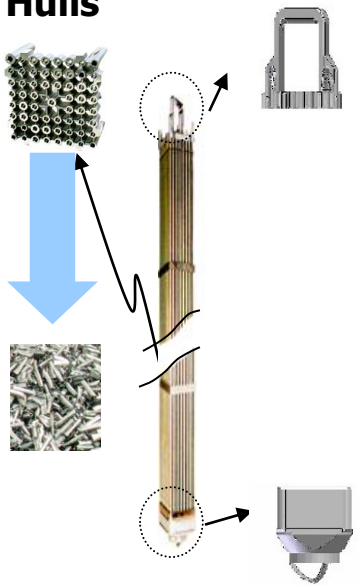
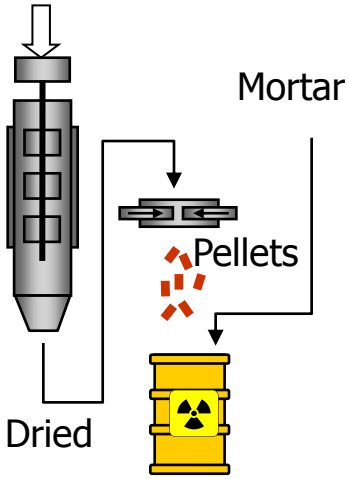
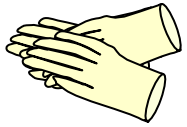
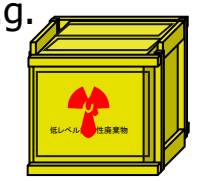
(Reanalysis of Iodine in the disturbed zone will be completed soon.)

Appendix

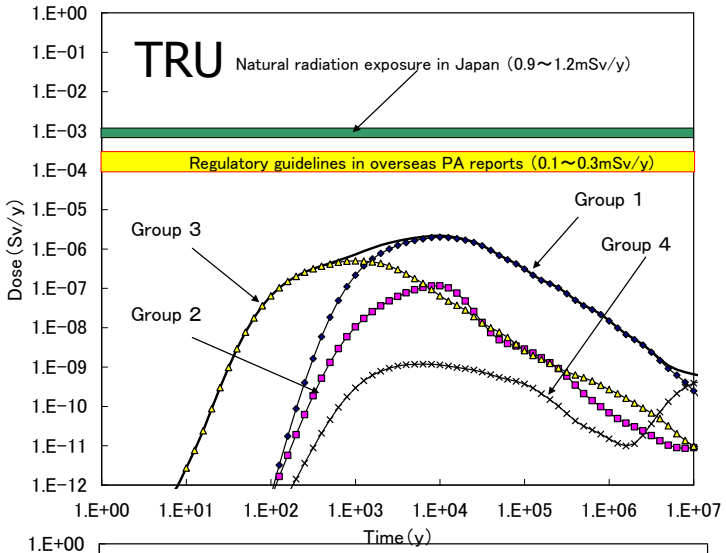
Radioactive waste in Japan (excluding medical, research, industrial wastes)

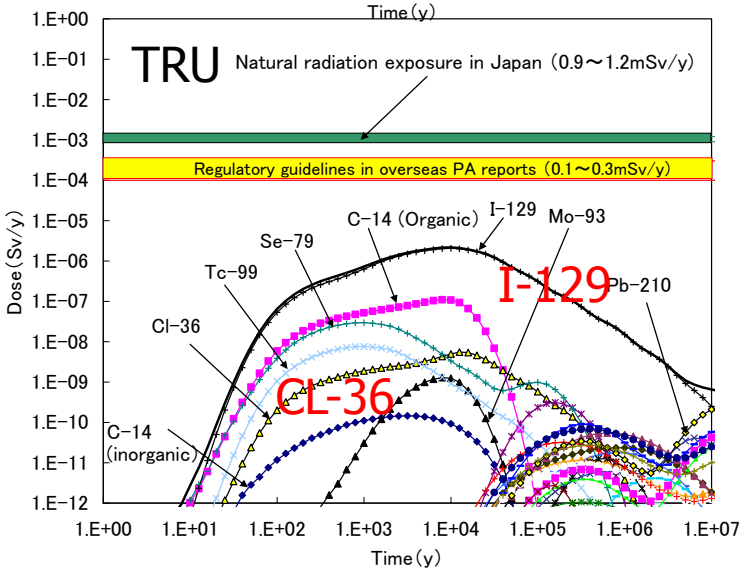


Grouping of TRU waste in Japan for deep geological disposal

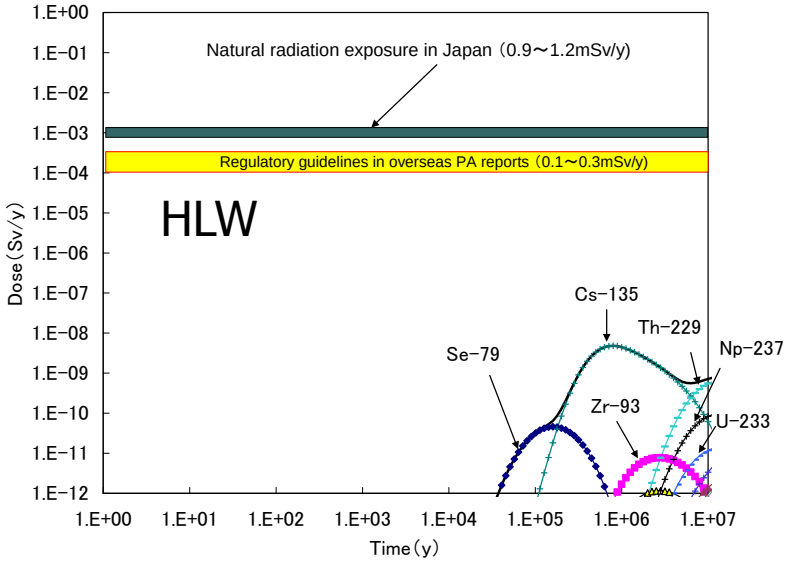
	Group 1	Group 2	Group 3	Group 4
Content	**Spent silver absorbent**  Iodine absorber	**Hulls** **End-pieces** 	**・Solidified concentrated liquid waste**  Mortar Pellets Dried **・Bituminized waste**	**Poorly combustible waste**  e.g. rubber gloves **Non-combustible waste**  E.g., tools, metal pipes
Waste package	E.g. 	E.g. 	E.g. 	E.g. 
	Includes I-129	**Heat generating; Includes C-14**	**Includes nitrates from PUREX reprocessing**	-

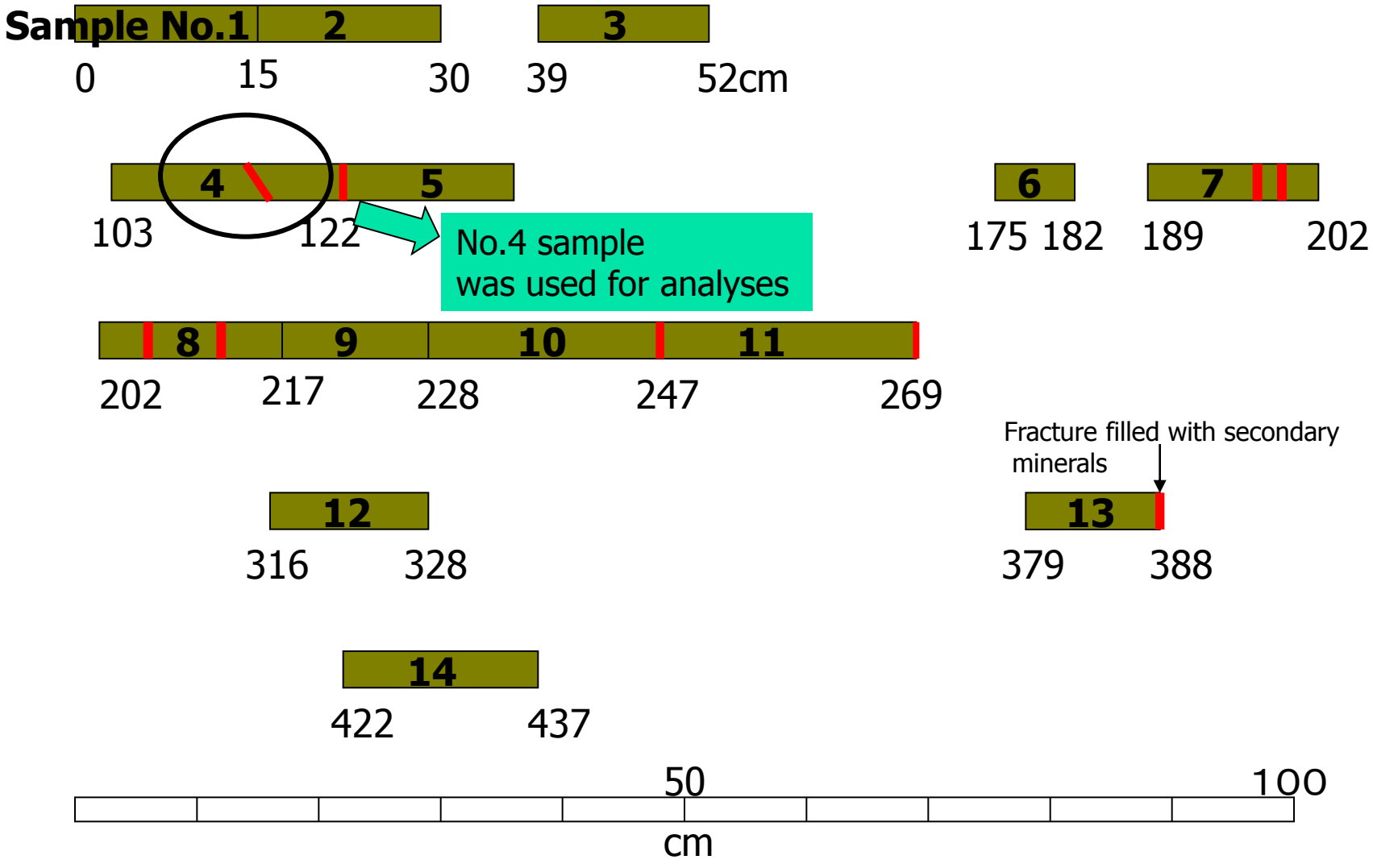
Calculations of Dose Rate for TRU and HLW (Reference Case)





- Max. approx. 2μSv/y
- Key radionuclides:
  I-129 (Group 1and 3) ,
  Organic C-14 (Group 2)



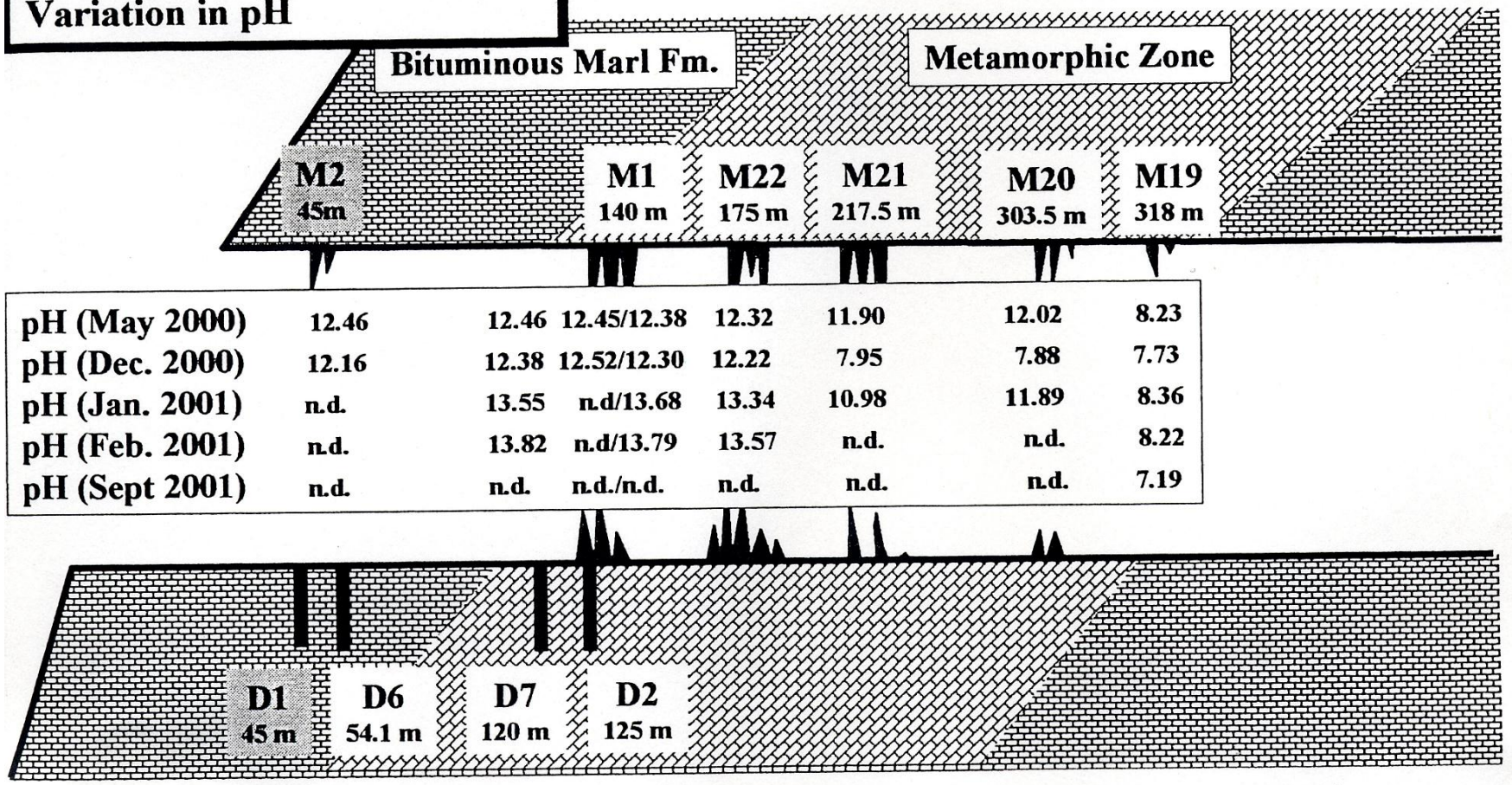


Core samples from Adit 6, Maqarin

Core samples from Adit 6 (BGS)

Jordan Natural Analogue Project Phase IV: Helsinki Workshop, November 2001
Maqarin Site - Groundwater Chemistry

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

British Geological Survey
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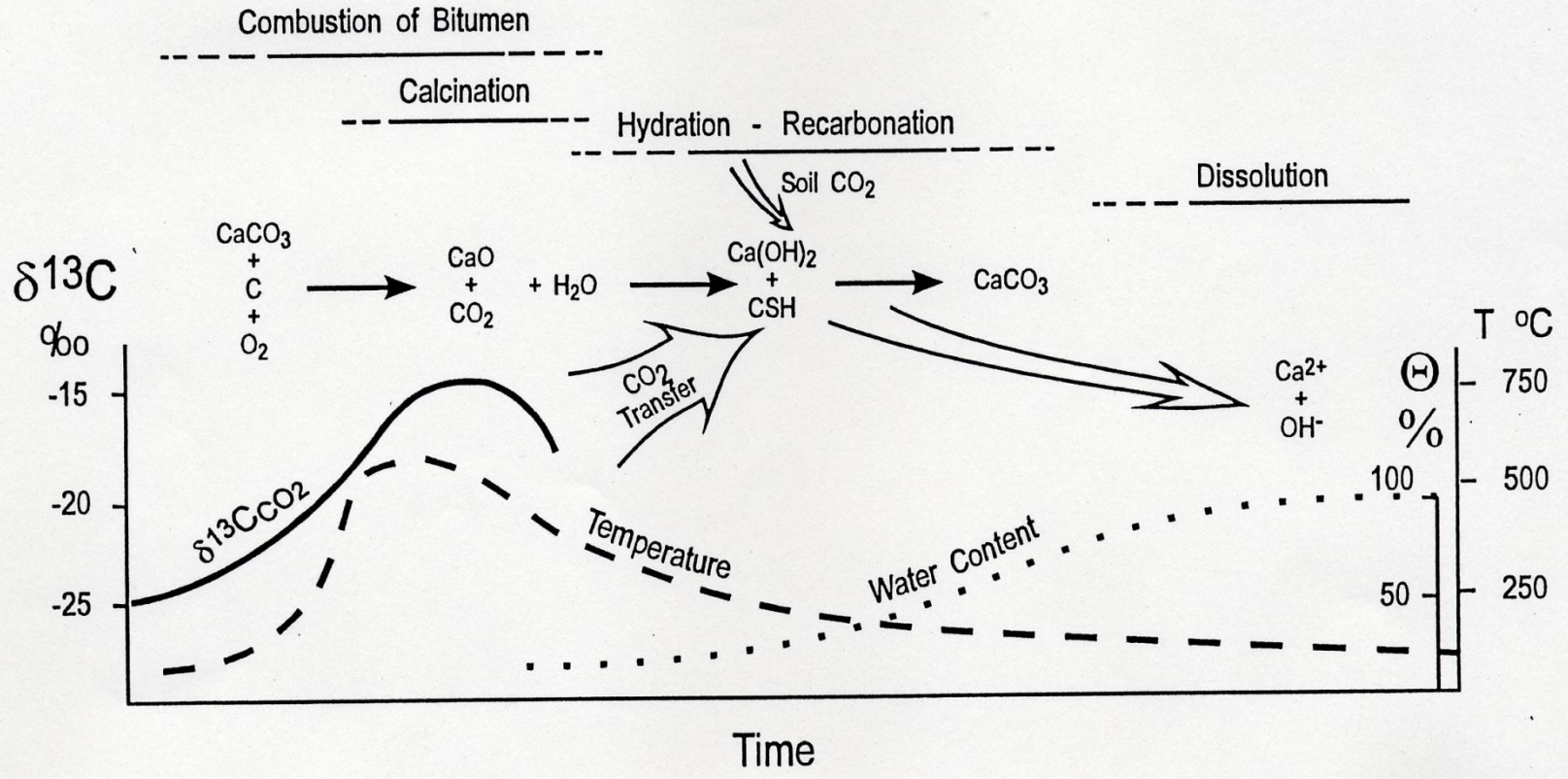

Figure 3-1: Conceptual model showing sequence of thermal metamorphic and retrograde alteration reactions with changes in temperature and humidity in the reaction zone (from Clark et al., 1994).

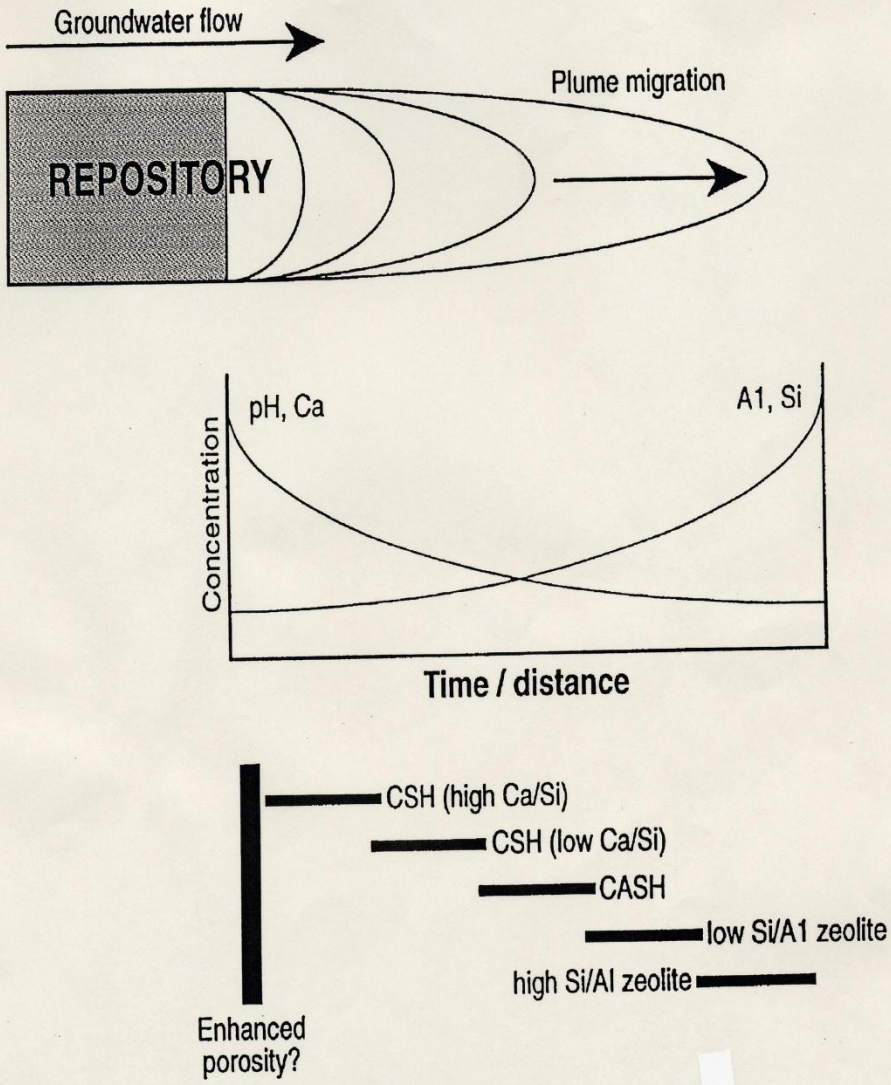

Figure 2.1: Conceptual model of the hyperalkaline plume evolution (from Savage, 1998)