Natural analogue study of hyperalkaline geochemistry at Oman

Could we expect a retardation of anion migration at hyperalkaline condition?

Tsutomu Sato
Laboratory of Environmental Geology,
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Project (2009-2011)

on

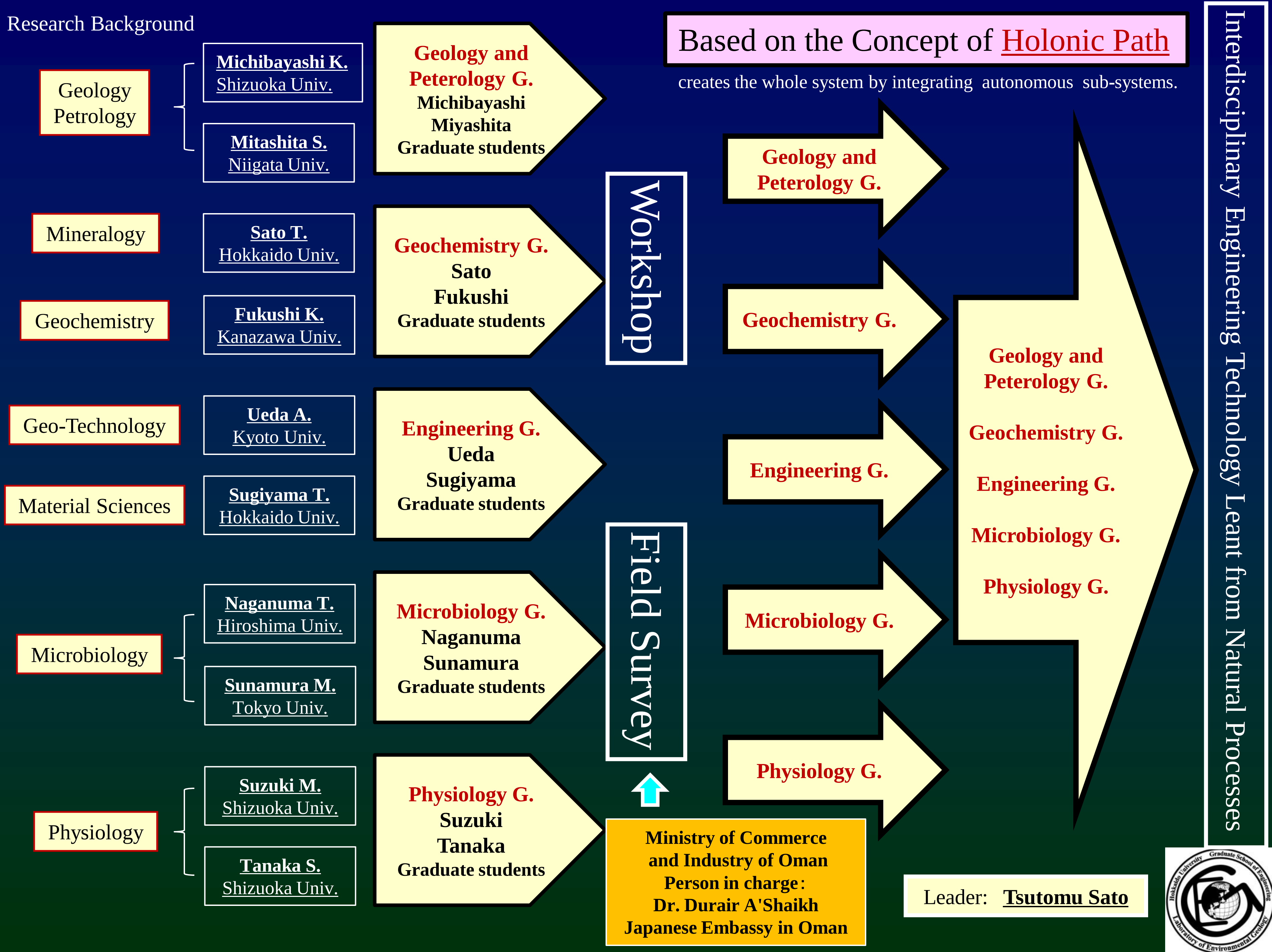
Geo- and Bio-resource Science and Technology Learnt from the Processes in Hyperalkaline Springs at Oman

Supported by Japan Society for the Promotion of Science

Hokkaido University Graduate School of Engineering
Laboratory of Environmental Geology

Based on the Concept of Holonic Path

creates the whole system by integrating autonomous sub-systems.



Interdisciplinary Engineering Technology Leant from Natural Processes

Research Background

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Workshop

Field Survey

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Person in charge :
Dr. Durair A'Shaikh
Japanese Embassy in Oman

Geology and Peterology G.

Geochemistry G.

Engineering G.

Microbiology G.

Physiology G.

Geology and Peterology G.
Geochemistry G.
Engineering G.
Microbiology G.
Physiology G.

Leader: **Tsutomu Sato**

Research Team at Oman

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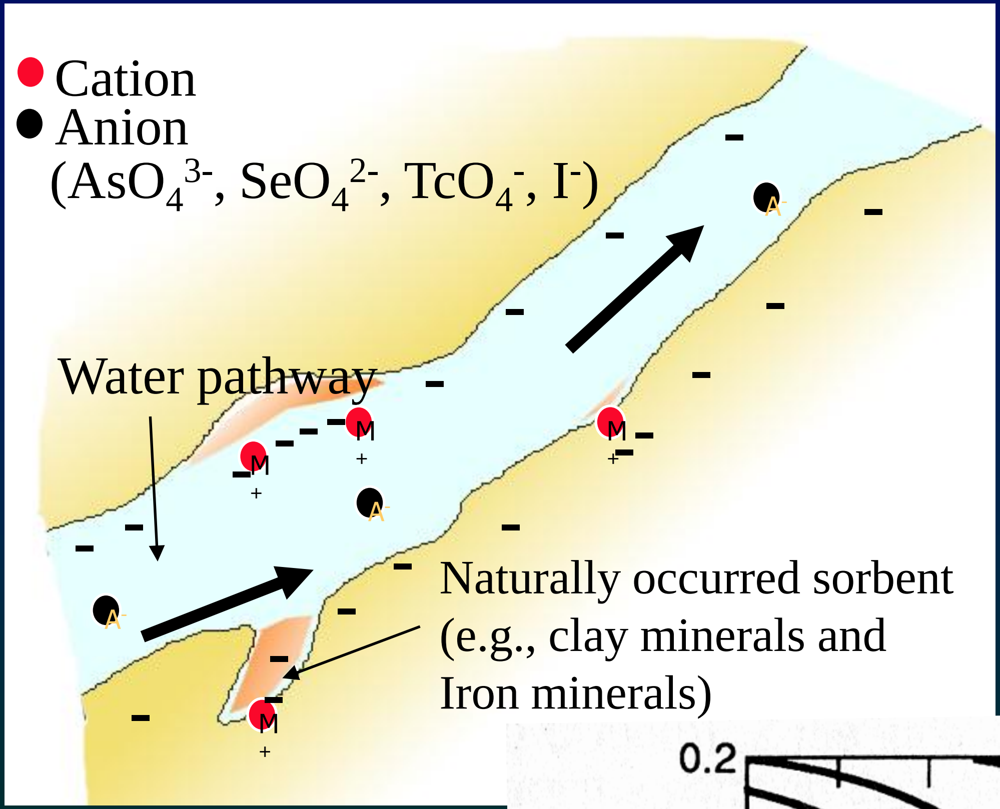
Migration of anion species in geomedia



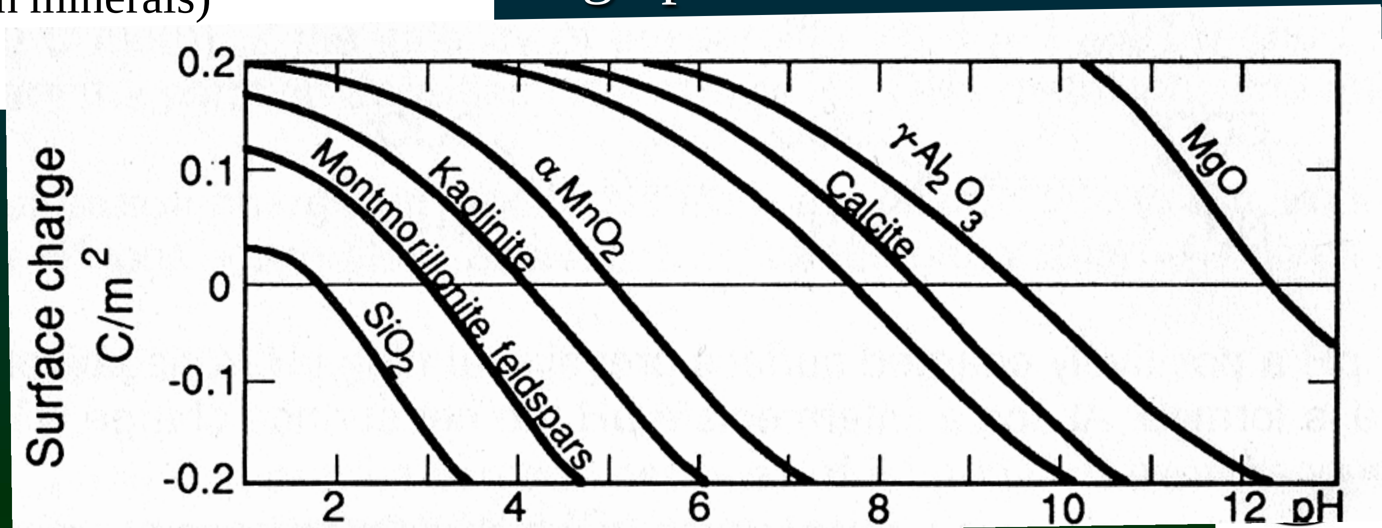
● Cation

● Anion
(AsO_4^{3-}, SeO_4^{2-}, TcO_4^{-}, I^{-})

Water pathway

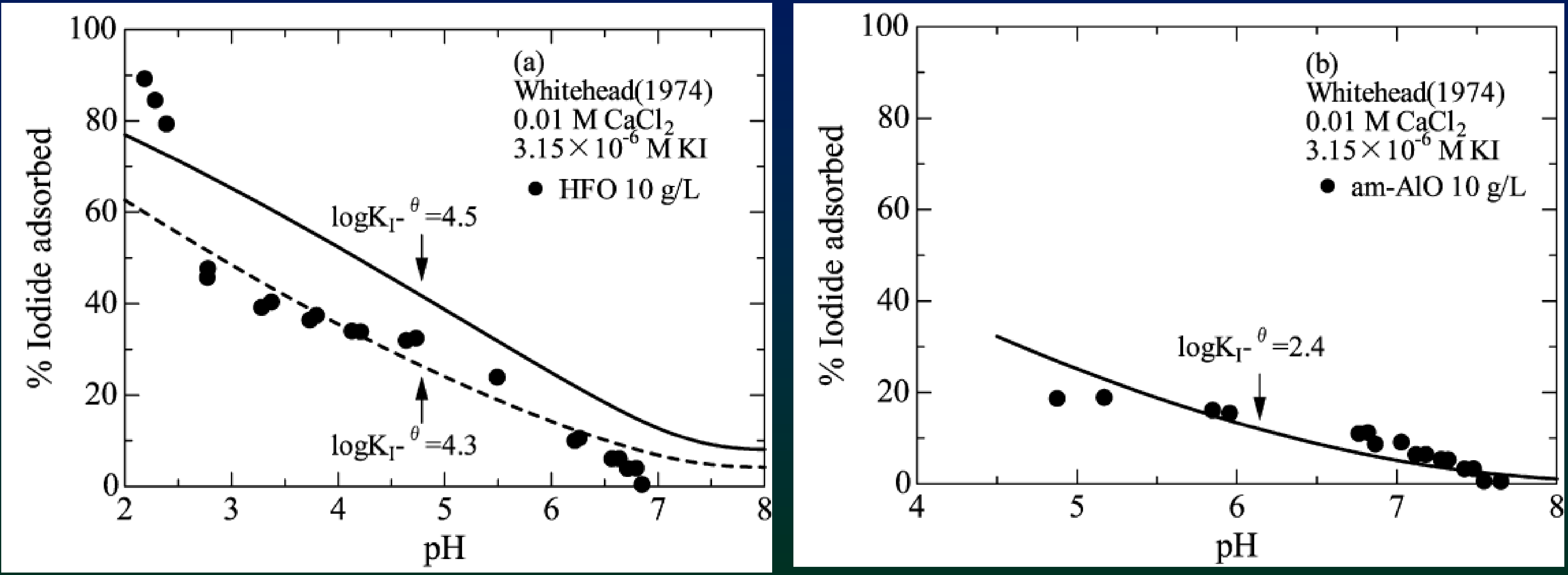
Naturally occurred sorbent
(e.g., clay minerals and
Iron minerals)

In general, retardation of anion migration has not been expected at alkaline condition because many anions are expulsed to the common rock-forming minerals of which surface charges are negative in alkaline condition , especially high pH cement water.



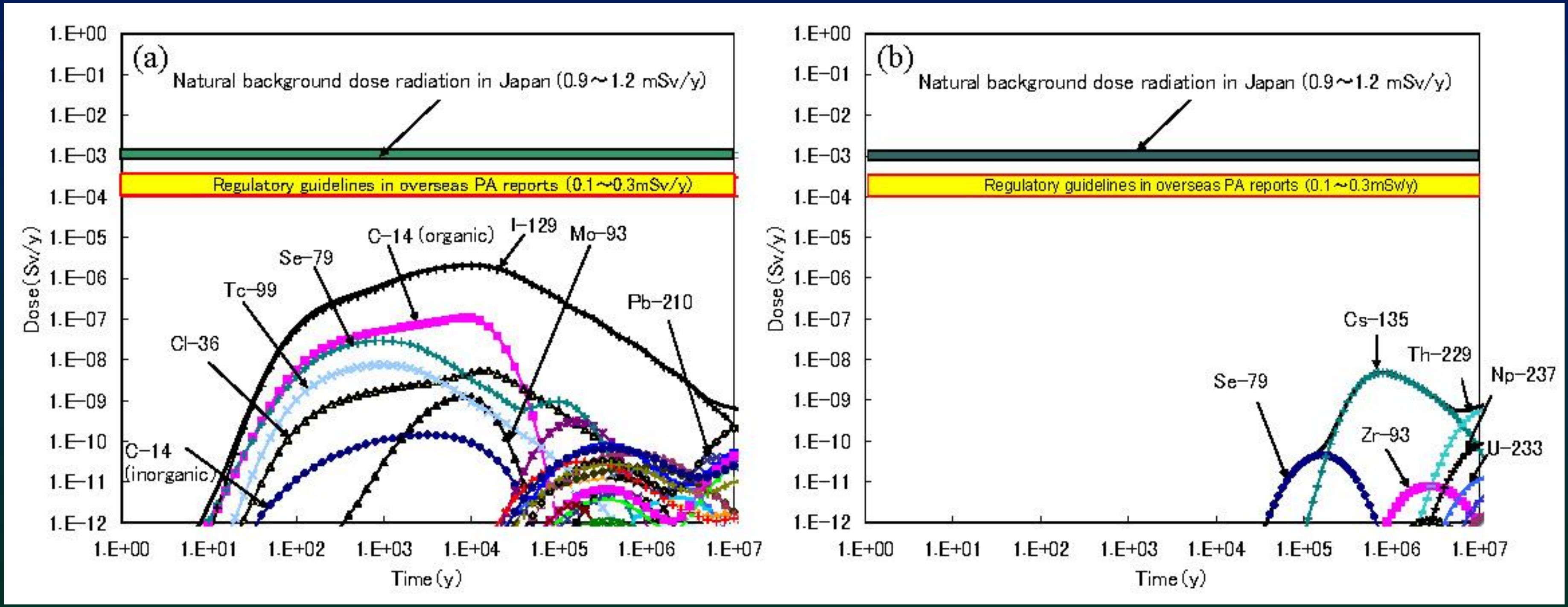
Iodide adsorption on HFO and am-AlO

(Nagata et al., 2009)



Anions

-Key Nuclides for Safety Assessment of TRU Waste-



Calculations of temporal dose rate for TRU waste (a) and HLW (b) disposal

環境地質学研究室

Laboratory of Environmental Geology

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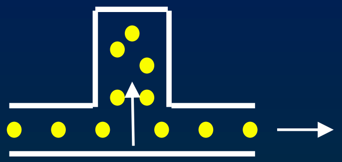
Retardation mechanism that may affect radionuclide transport in groundwater

（McKinley and Hadermann, 1984)

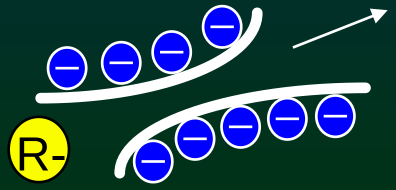
Physico-chemical retardation

Diffusion into dead-end pores



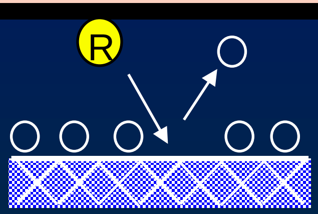
Molecular filtration

Ion exclusion

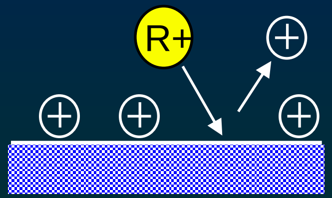


Chemical retardation

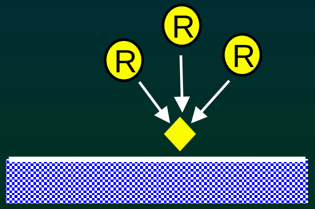
Adsorption



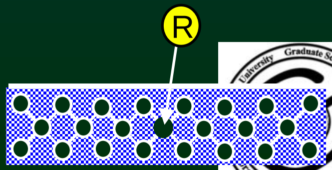
Ion exchange



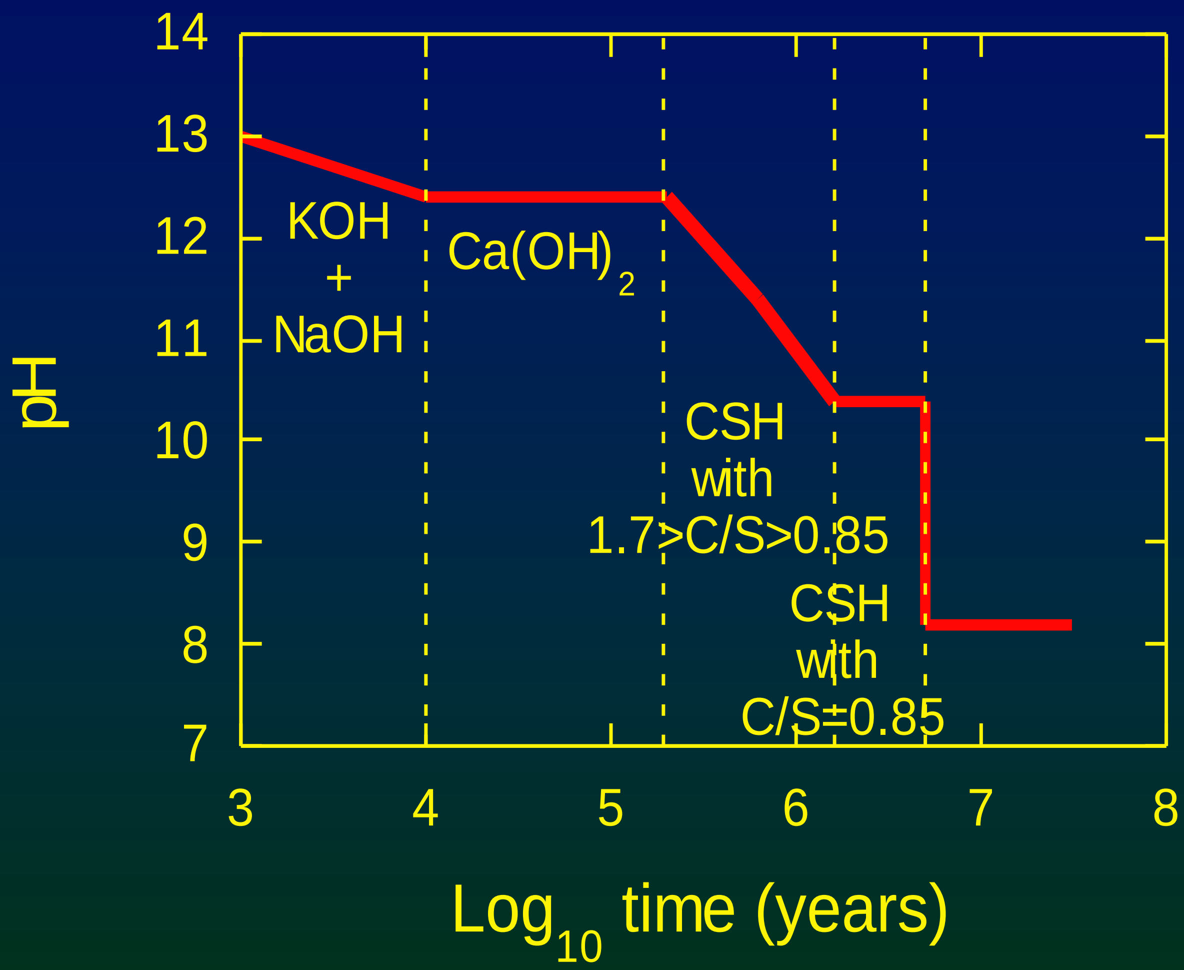
Precipitation



Mineralization



pH Evolution of Cement Pore Fluids

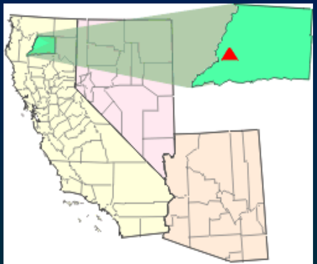


Predicted evolution of the pH within the near-field of the reference case U.K. Nirex Ltd. cementitious low and intermediate-level waste repository with an average cement content of 185 kg/m3 and a water flux density of 10-10 m/s. After 1000 years a pH of 13 will be attained which will gradually decline with time but remain above pH 10 for, at least, the first one million years （after Atkinson,1985）.

Extreme pH condition at surface of the Earth

pH −3.6

Richmond Mine, Iron Mountain, CA



PNAS, Vol. 96, Issue 7, 3455–3462, March 30, 1999

$$4FeS_{2(s)} + 15O_{2(g)} + 14H_2O_{(l)} \text{ ---> } 4Fe(OH)_{3(s)} + 8SO_4{}^{2-}{}_{(aq)} + 16H^+{}_{(aq)}$$

pH 12.9

Maqarin, North Jordan

http://www.natural-analogues.com/

Maqarin, Jordan-Marl Alteration and Production of High pH Groundwater-

- **Water-rock interaction** - Maqarin Natural Analogue Site Study Group (1991), Khoury et al. (1992), Milodowski et al. (1992), Savage (1996), and Alexander et al. (1996)
- **Groundwater chemistry** - Clark et al. (1994)
- **Colloids** - Pearce et al. (1996)
- **Microbiology** - West et al. (1995)
- **Database testing and trace element modeling** - Alexander et al. (1992) and Linklater et al. (1994)

Semail Ophiolite, Oman
-Impact of High pH Groundwater-

Serpentinization of upper mantle rocks
(harzburgites: olivine and pyroxene)

↓

Strongly alkaline and reducing groundwater

- **Solubility and speciation** - McKinley et al. (1987), Bath et al. (1987a, b), McKinley et al. (1988)
- **Microbiology** - Bath et al. (1987a, b),
- **Test geochemical thermodynamic codes and databases** - McKinley et al. (1988)

Hazardous Anions in Alkaline Materials

Table Ranges of total content of oxyanion forming elements expressed in mg/kg in MSWI residues, FFC residues and metallurgical residues (modified from Cornelis et al., 2008)

Element	Litho-sphere	Soils	MSWI residues 都市ゴミ焼却スラグ		FFC residues 化石燃料焼却灰		Metallurgical slag 鉄鋼スラグ	
			Bottom ash	Fly ash	Coal bottom ash	Coal fly ash	Blast furnace slag	Steel slag
As	5	1-50	0.1-200	40-300	0.02-200	2-400	<0.7	5
Cr	200	1-1000	20-3000	100-1000	0.2-6000	4-900	30	8-30k
Mo	2	0.2-5	2-300	15-200	1-500	1-100	<6	20
Sb	0.2-0.5	-	10-400	300-1000	NA	NA	NA	NA
Se	0.09	0.1-2	0.05-10	0.4-30	0.1-10	0.2-100	NA	NA
V	200	20-500	20-100	30-200	10-500	10-1000	400	1-10k
W	-	-	30	NA	NA	NA	<13	400

MSWI : municipal solid waste incineration
FFC : Fossil fuel combustion
NA : not available

Fluorine and Boron contaminations are also big issue.

Objectives

- This study focused on
  - the sorption behavior of anions such as CO_3^{2-}, $H_3SiO_4^-$, I^- and formation of their host minerals at naturally-occurring hyperalkaline springs in the Oman ophiolite
  - to learn how to retard migration of anions from natural processes.

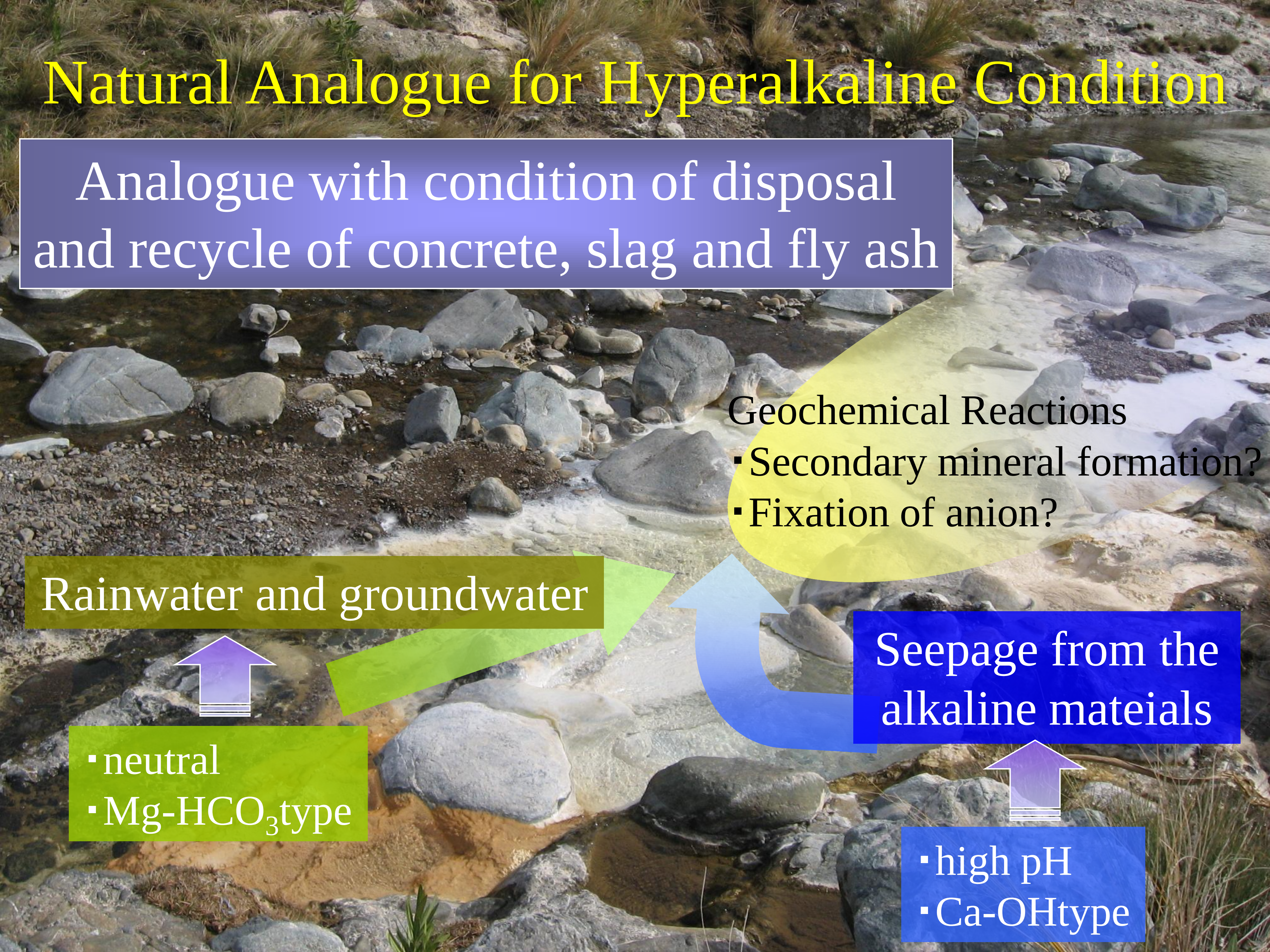
For better understanding of geochemistry at hyperalkaline condition

Hyperalkaline Spring at Oman Ophiolite

- pH11-12
- Ca-rich
- H_2 and CH_4 gas out

(Sano et. al.(1993) ,Neal and Stanger(1983))

Natural Analogue for Hyperalkaline Condition



Analogue with condition of disposal and recycle of concrete, slag and fly ash

Geochemical Reactions

- Secondary mineral formation?
- Fixation of anion?

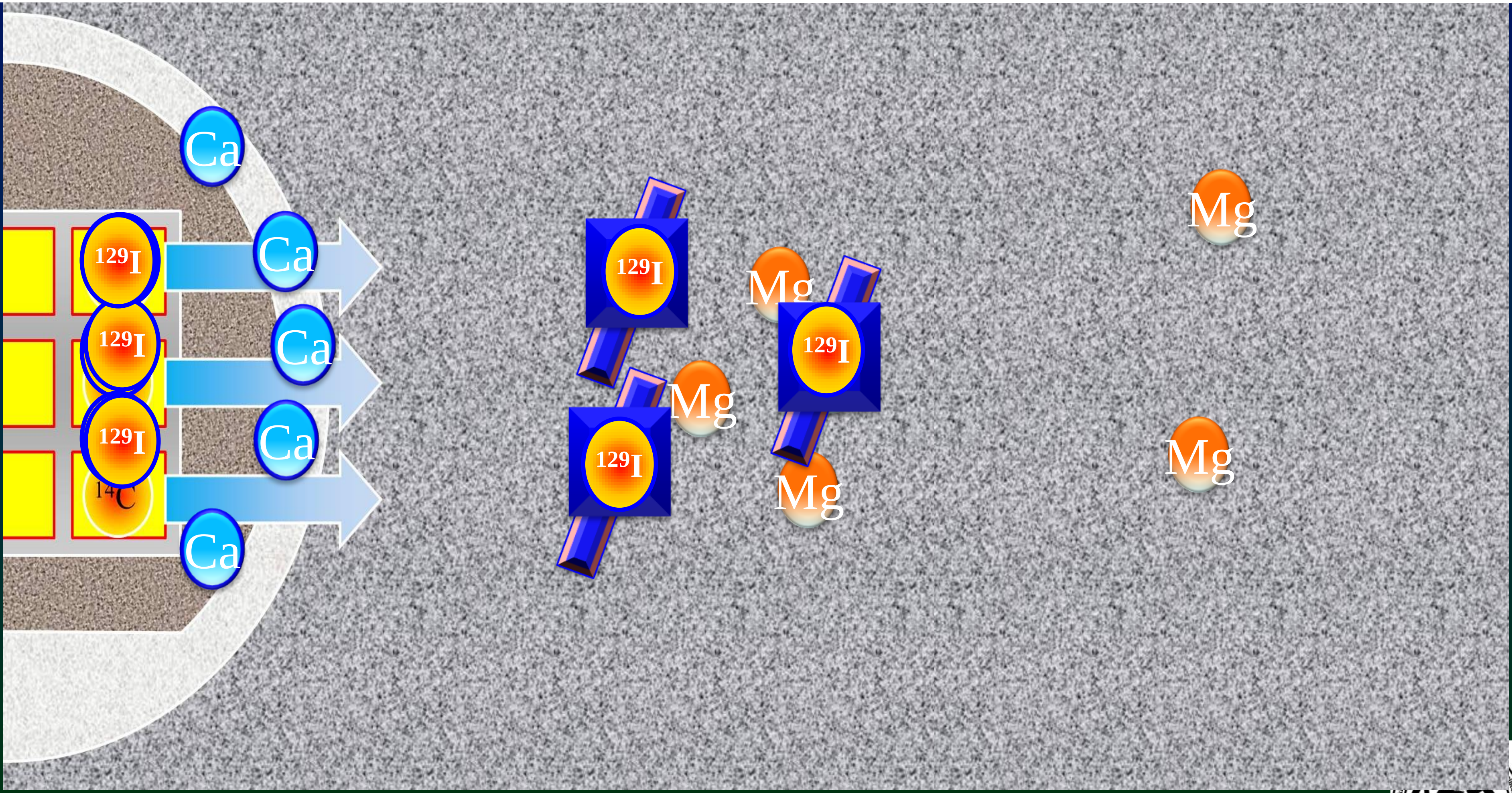
Rainwater and groundwater

- neutral
- Mg-HCO_3type

Seepage from the alkaline mateials

- high pH
- Ca-OHtype

Alkaline plume meet with groundwater at the near field



Minerals Formation at Hyperalkaline Springs


Hilti

Calcite


Hilti


Hayl

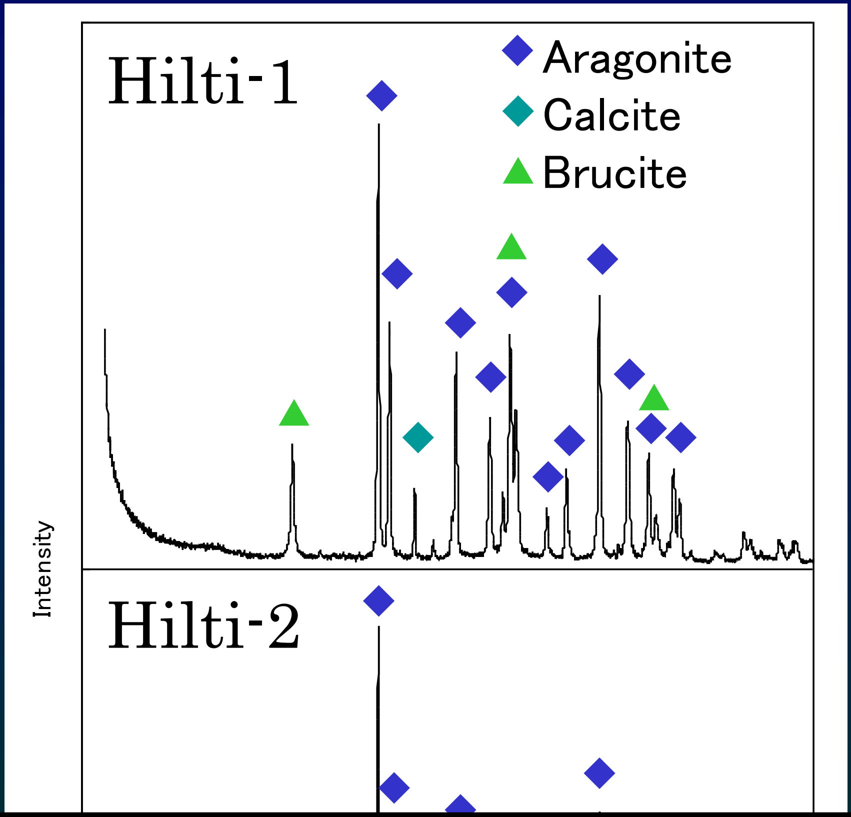
Aragonite

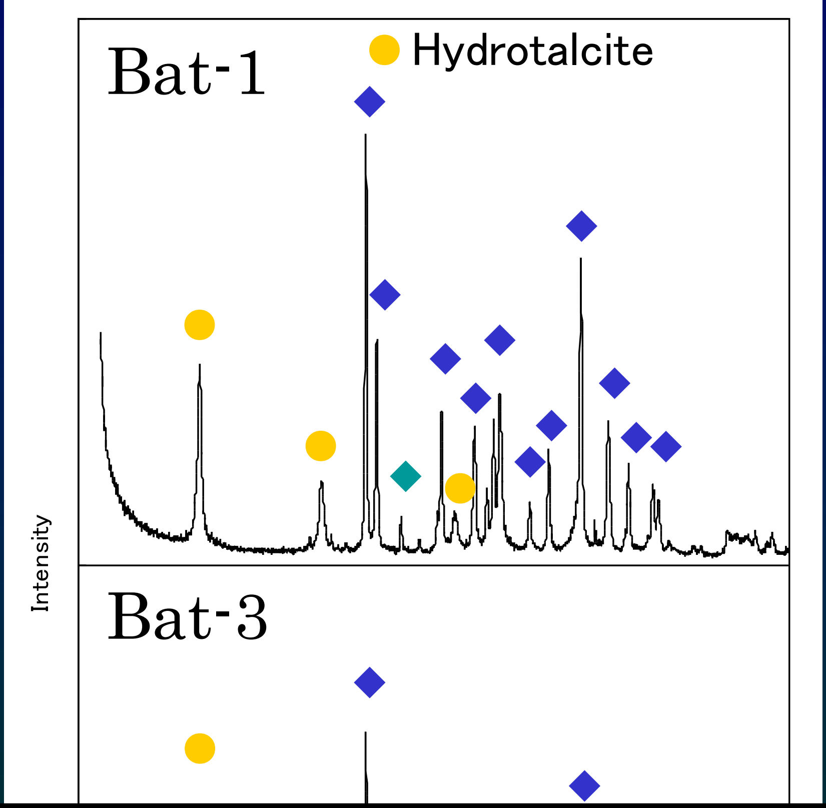
Aragoite + Brucite


Bat

Aragonite + Hydrotalcite like compound

XRD patterns of the precipitates





Minerals	Chemical Formulae
Hydrotalcite like compound (HTLc)	$Mg_6Al_2X(OH)_{16}\cdot 4H_2O$ X：anions
Aragonite	$CaCO_3$
Calcite	$CaCO_3$
Brucite	$Mg(OH)_2$

Morphology vs. Mineralogical Composition

Sample Name	Form	Mixing ratio of SW to HW	鉱物名				
			Aragonite	Calcite	HTlc	Brucite	Hydro-magnesite
t_Fizh①	Ice	I	○	◎			
t_Hayl-a	Ice	I	○	◎			
t_Hilti①-b	chimney	＊	◎	○	○	○	
t_Hilti①-c	terrace	＊	◎	○		○	
t_Hilti②-a	Ice	＊	◎	○		○	○
t_Hilti②-b	mousse	＊	◎			○	
t_Hilti②-c	mousse	＊	◎			○	
t_Hayl-c	mousse	＊	◎	○		○	
t_Fizh②-a	chimney	＊	◎	○	○		
t_Faydh②-a	Ice	＊	◎	○	○		
t_Fizh②-b	chimney	＊	◎	○	○		
t_Faydh②-b	needle	＊	◎	○	○		
t_Faydh②-c	mousse	＊	◎	○	○		
t_Farfar-a	Ice	＊	○	◎		○	
t_Farfar-b	mousse	＊	◎	○		○	
t_Farfar-c	mousse	＊	◎	○		○	○
t_Bat③-a	terrace	＊	◎	○	○		
t_Bat③-b	terrace	＊	◎		○		
t_BaniA-a	mousse	＊	◎	○	○		
t_Hilti②-d	mousse	＊＊＊	◎				
t_Hilti②-e	mousse	＊＊＊	◎				
t_Hayl-b	needle	＊＊＊	◎	○			
t_Bat③-c	chimney	＊＊＊	◎				
t_BaniA-b	chimney	＊＊＊	◎	○			

I・・・ Isolated from surface water
＊・・・・・ mixed with small amount of surface water
＊＊＊・・mixed with large amount of surface water

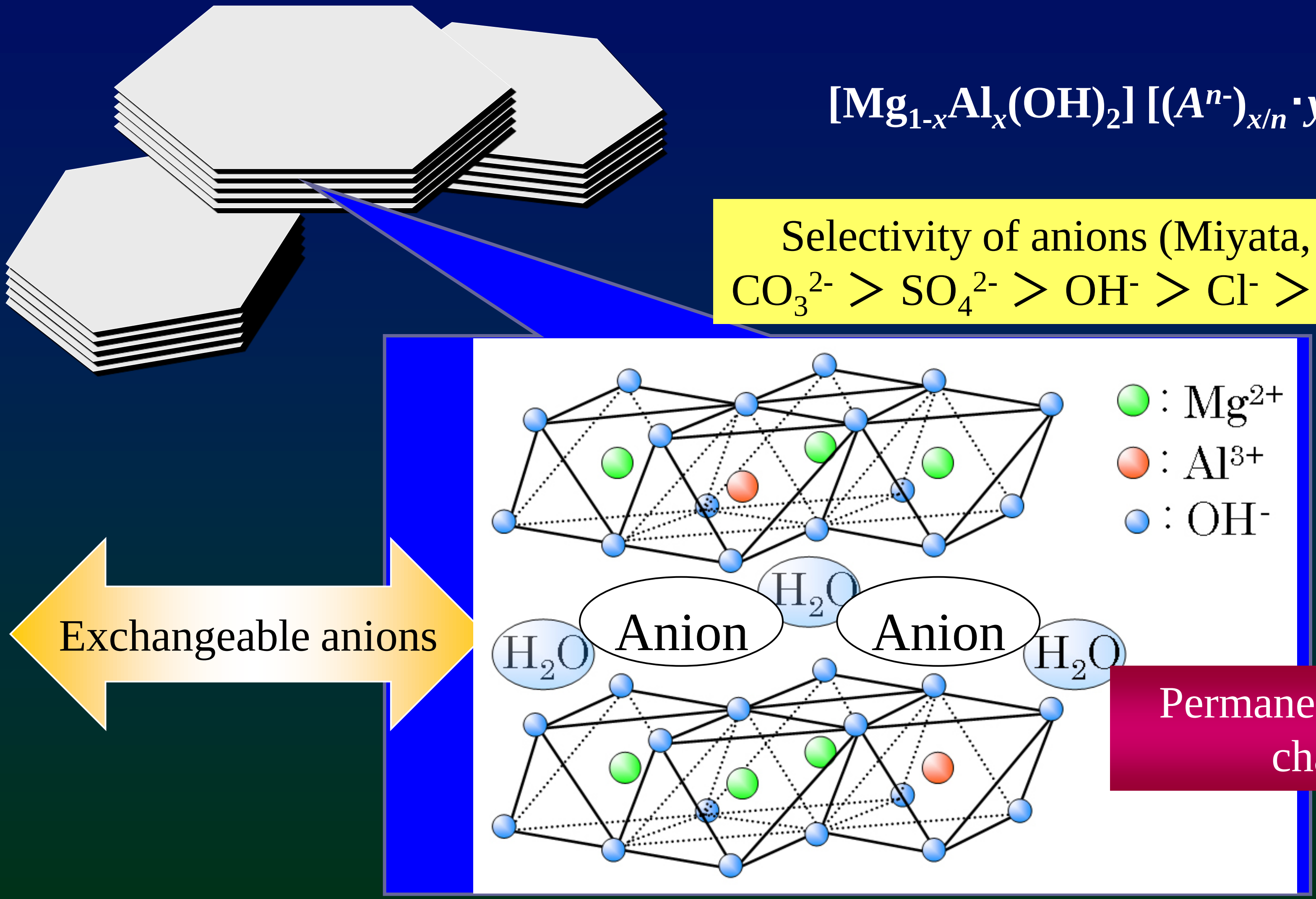
◎・・・dominant in XRD pattern
○・・・detected in XRD pattern

pH and Aluminum Content vs. Mineralogy

Site	Vent No.	pH	Al (μmol/L)	HTlc	Brucite
Feydh	4	9.41	4.3	X	X
Feydh	1	9.36	5.9	X	X
Feydh	6	10.38	1.0	X	X
Feydh	2	11.1	11.2	O	X
Feydh	7	10.96	31.4	O	X
Jaja	2	11.04	25.9	O	X
Fizh	2	10.88	25.8	O	X
Hilti	1	11.63	0.4	X	O
Hilti	8	11.43	0.5	X	O
Bani	1	11.18	0.5	X	O

Crystal Structure of Hydrotalcite

$[\mathrm{Mg}_{1-x}\mathrm{Al}_x(\mathrm{OH})_2]\,[(A^{n-})_{x/n}\cdot y\mathrm{H_2O}]$

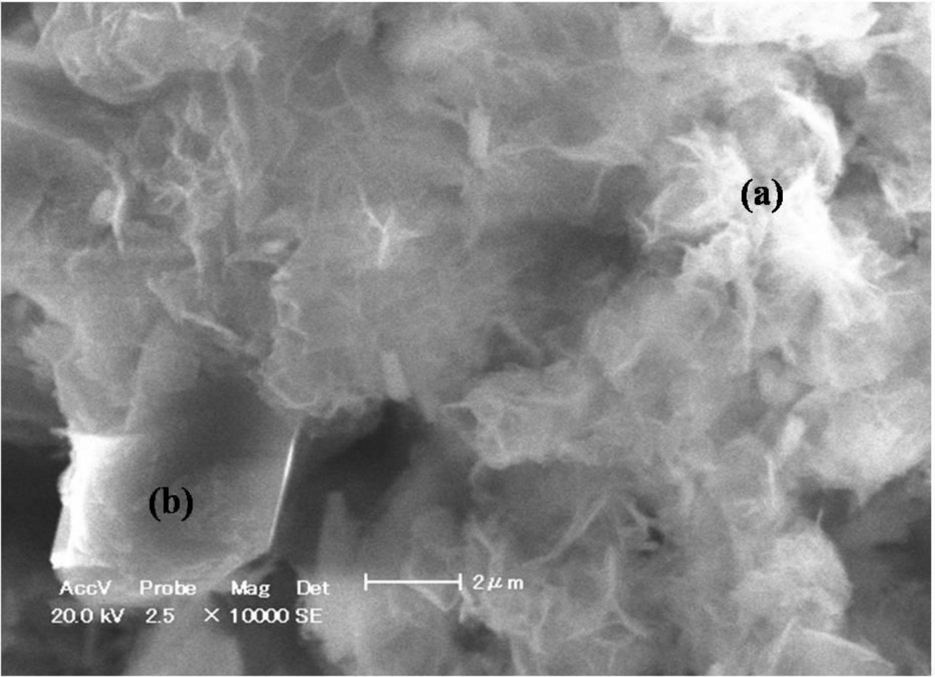


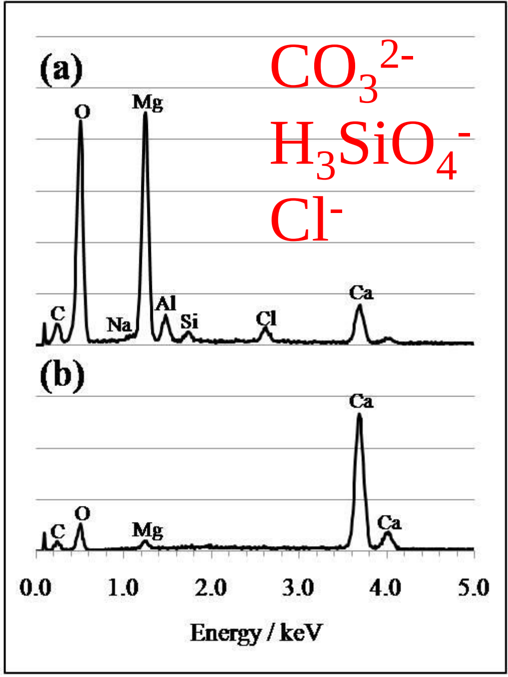
Selectivity of anions (Miyata, 1983)
$CO_3^{2-} > SO_4^{2-} > OH^- > Cl^- > NO_3^- > I^-$

Exchangeable anions

Permanent positive charge

SEM images and EDX spectra

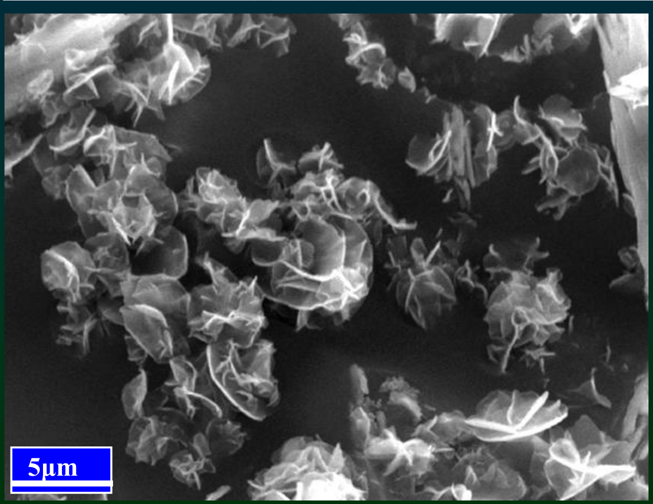


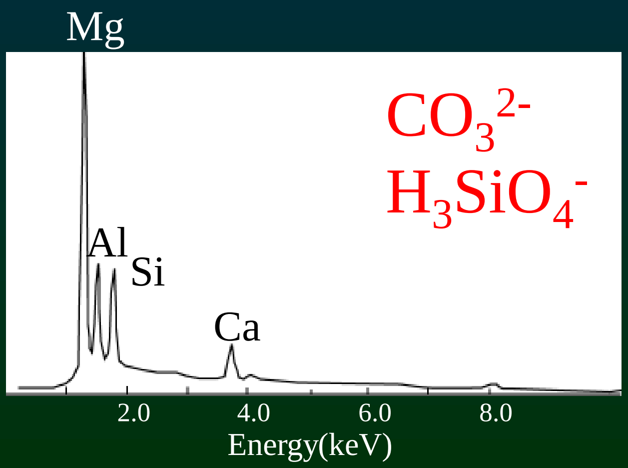


CO_3^{2-}

$H_3SiO_4^-$

Cl^-





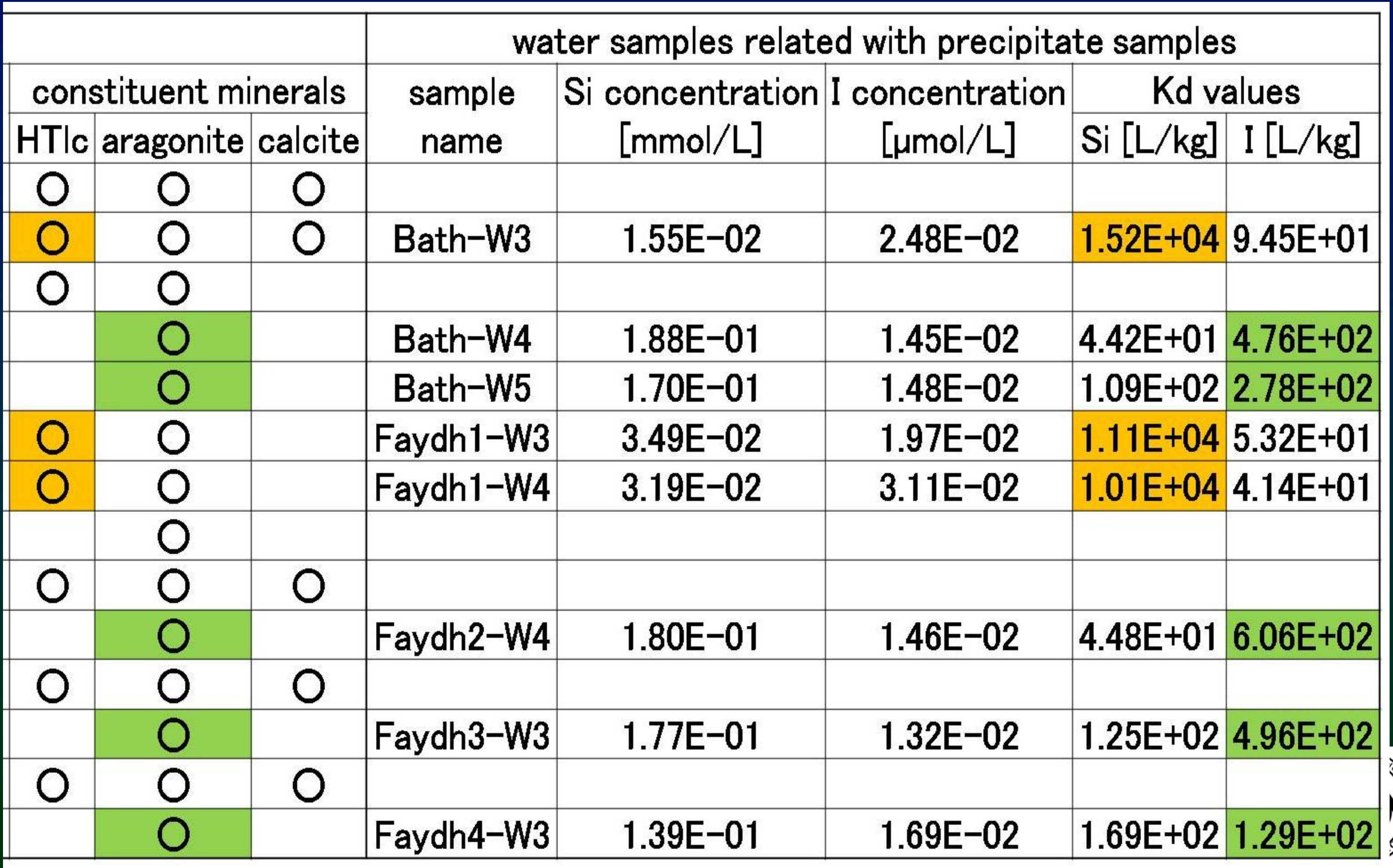
CO_3^{2-}

$H_3SiO_4^-$

Constituent Minerals and Iodine Concentrations in the Precipitates

Sample	Constituent minerals			Iodine conc. µmol-I/kg-precip.
	Hydrotalcite	Aragonite	Calcite	
Bath-P1		○	○	2.85
Bath-P2	○	○	○	2.56
Bath-P3	○	○		2.00
Bath-P4		○		7.12
Bath-P5		○		4.33
Faydh1-P1	○	○		1.27
Faydh1-P2	○	○		1.50
Faydh1-P3		○		8.19
Faydh2-P1	○	○	○	3.60
Faydh2-P2		○		9.05
Faydh3-P1	○	○	○	1.99
Faydh3-P2		○		6.79
Faydh4-P1	○	○	○	0.92

Relationship between Kd values of Si and I and Mineral Composition of the Precipitates (Anraku et al., *ICEM*, 2009)



			water samples related with precipitate samples				
constituent minerals			sample name	Si concentration [mmol/L]	I concentration [μmol/L]	Kd values	
HTlc	aragonite	calcite				Si [L/kg]	I [L/kg]
○	○	○					
○	○	○	Bath−W3	1.55E−02	2.48E−02	1.52E+04	9.45E+01
○	○						
	○		Bath−W4	1.88E−01	1.45E−02	4.42E+01	4.76E+02
	○		Bath−W5	1.70E−01	1.48E−02	1.09E+02	2.78E+02
○	○		Faydh1−W3	3.49E−02	1.97E−02	1.11E+04	5.32E+01
○	○		Faydh1−W4	3.19E−02	3.11E−02	1.01E+04	4.14E+01
	○						
○	○	○					
	○		Faydh2−W4	1.80E−01	1.46E−02	4.48E+01	6.06E+02
○	○	○					
	○		Faydh3−W3	1.77E−01	1.32E−02	1.25E+02	4.96E+02
○	○	○					
	○		Faydh4−W3	1.39E−01	1.69E−02	1.69E+02	1.29E+02

Previous study on halogen anion distribution to calcite and aragonite

(Kitano & Okumura, 1973)

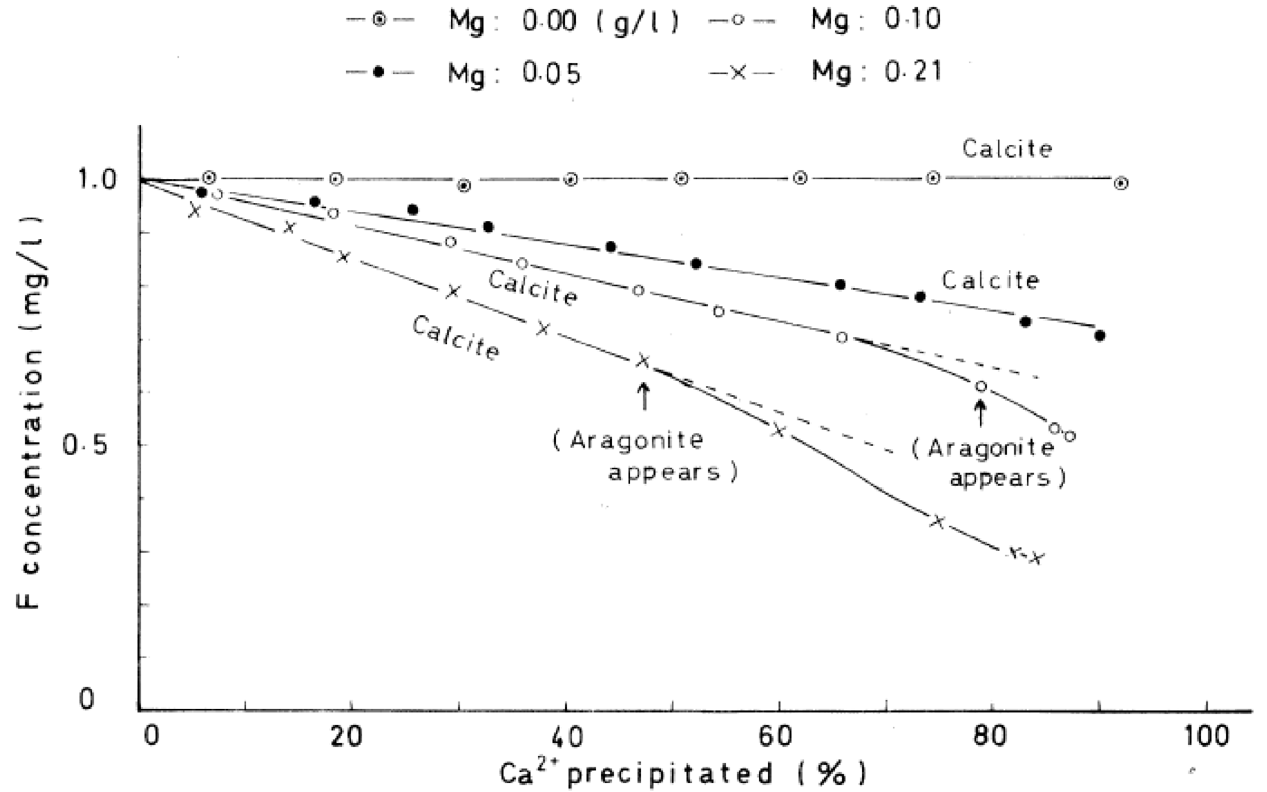
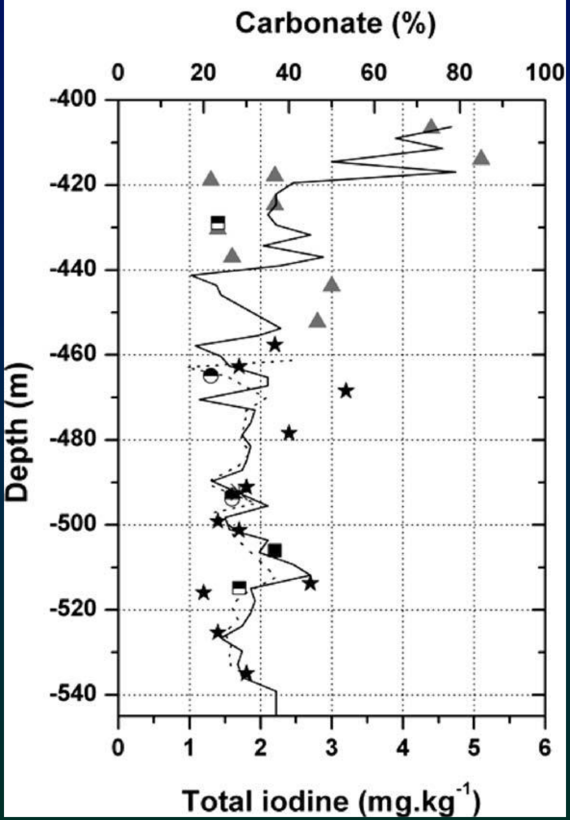


Fig.2. Change in fluoride concentration in a parent solution with per cent calcium precipitated (25±1°C) in the system: $Ca(HCO_3)_2$ + $MgCl_2$ + NaF → calcite + aragonite; or calcite

Correlation between total iodine* and carbonate content at Callovian Oxfordian argillite (Claret et al. 2010)



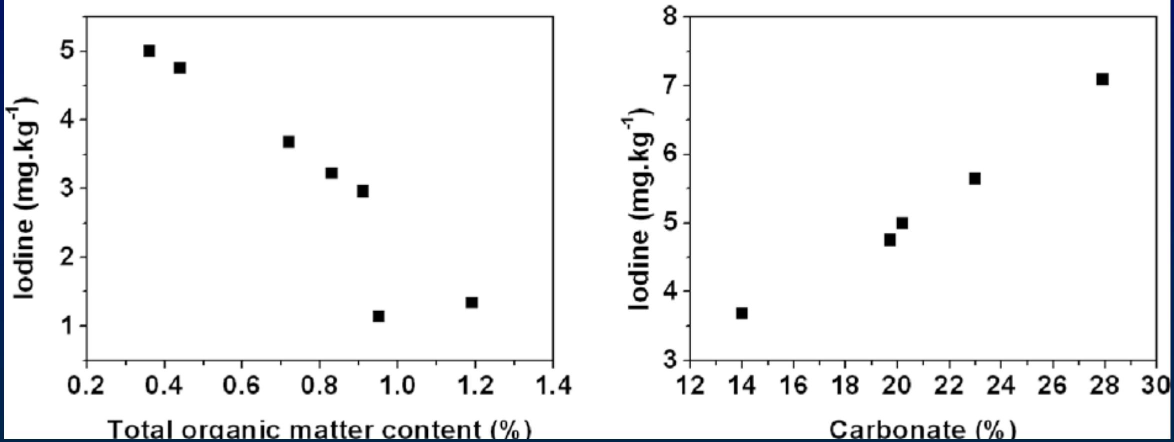


Fig. Total iodine* content as a function of organic matter content (left) and carbonate content (right) of the reference COx sample.

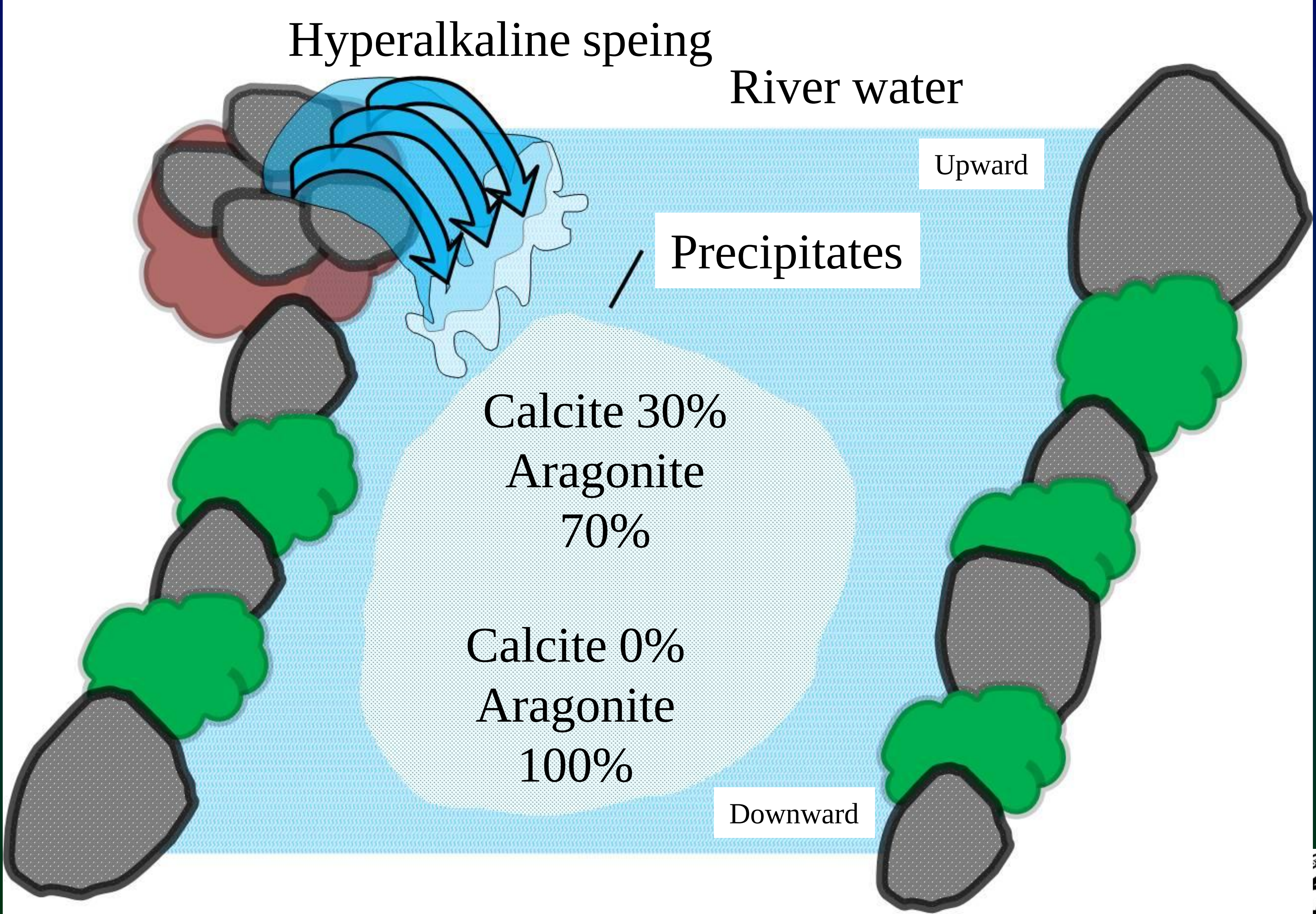
This finding is potentially in conflict with the usual assumption that iodine* is mainly associated with the organic matter of rock or sediment (Schlegel et al. 2006; Tournassat et al. 2007).

Fig. Total iodine* content (symbols, measured after HNO3 digestion at 90 C overnight) and carbonate content (lines) as a function of depth.

Summary of the Study at Oman

- Aragonite was dominant phase in the observed precipitates at the mixing points of the springs and surface water, due to high Mg content in the surface water .
- Hydrotalcite (Mg-Al hydroxides) was also observed as accessory minerals when the hyperalkaline springs was comparatively rich in Al.
- During formation of the minerals at the mixing points, HCO_3^- in the surface water was mainly fixed as carbonate minerals such as aragonite and calcite.
- $H_3SiO_4^-$ and Cl^- in the surface water were fixed into interlayers and/or surface of the hydrotalcite.
- Iodine in the springs and surface water was mainly associate with the aragonite.

CaCO$_3$ polymorphs at hyperalkaline spring



Hyperalkaline speing

River water

Upward

Precipitates

Calcite 30%
Aragonite 70%

Calcite 0%
Aragonite 100%

Downward

Synthesis experiment in the field

Spring Water

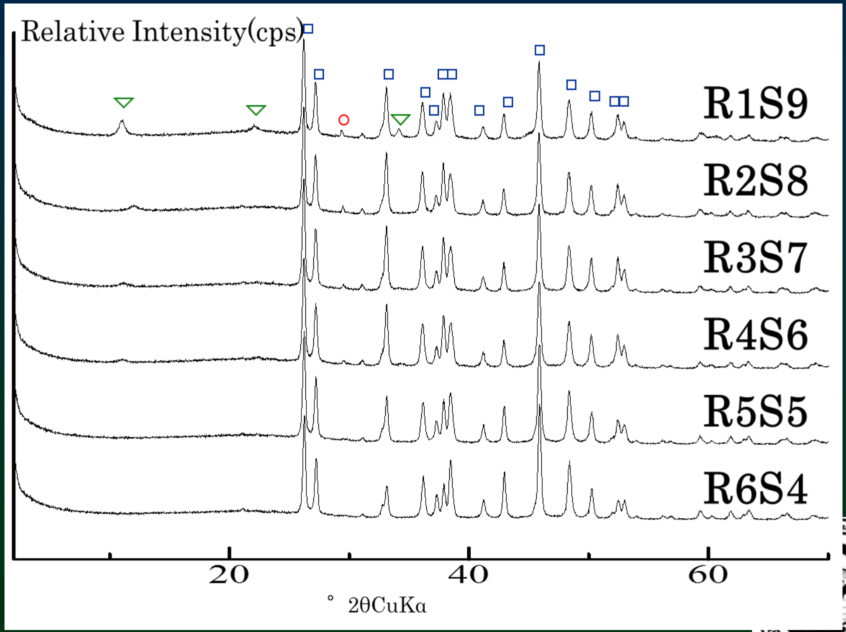
River Water

KI

- 0.5mM
- 0.05mM
- 0.005mM

Spring water and river water were mixed in particular ratio to reveal the relationship between the mixing ratio and the secondary mineral phases.

Iodide reagent also added in deferent concentration to know the dominant phase of iodide uptake.



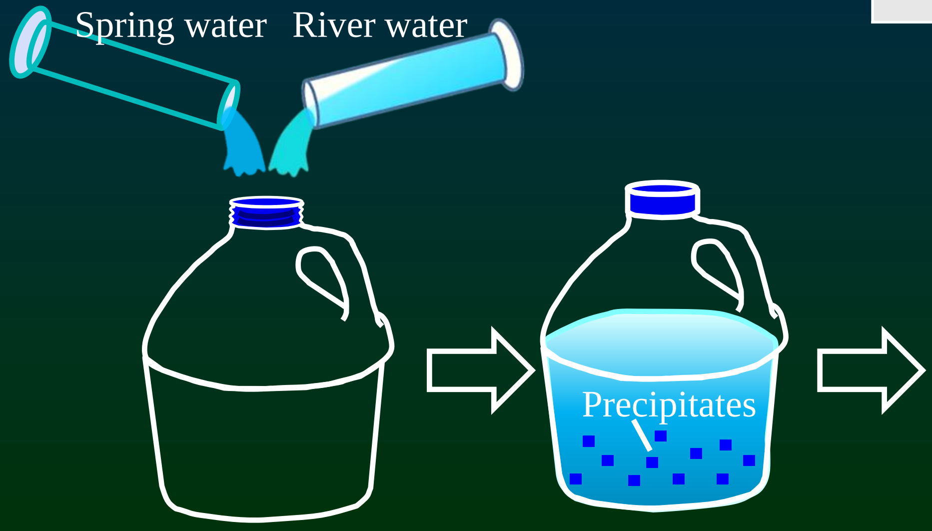
Synthesis experiment in the field

Sample names and mixing ratios between spring water (S) and river water (R)

Sample name	River water (%)	Spring water (%)
R5S95	5	95
R10S90	10	90
R20S80	20	80
R40S60	40	60
R60S40	60	40

Chemical compositions and temperatures of the river water and the spring water

	River water	Spring water
pH	9.1	11.1
Ca (mM)	0.48	1.32
Mg (mM)	1.53	0.01
Al (mM)	nd	0.02
CO_3^{2-}+HCO_3^- (mM)	2.87	0.39
Temp. (℃)	22.6	37.9

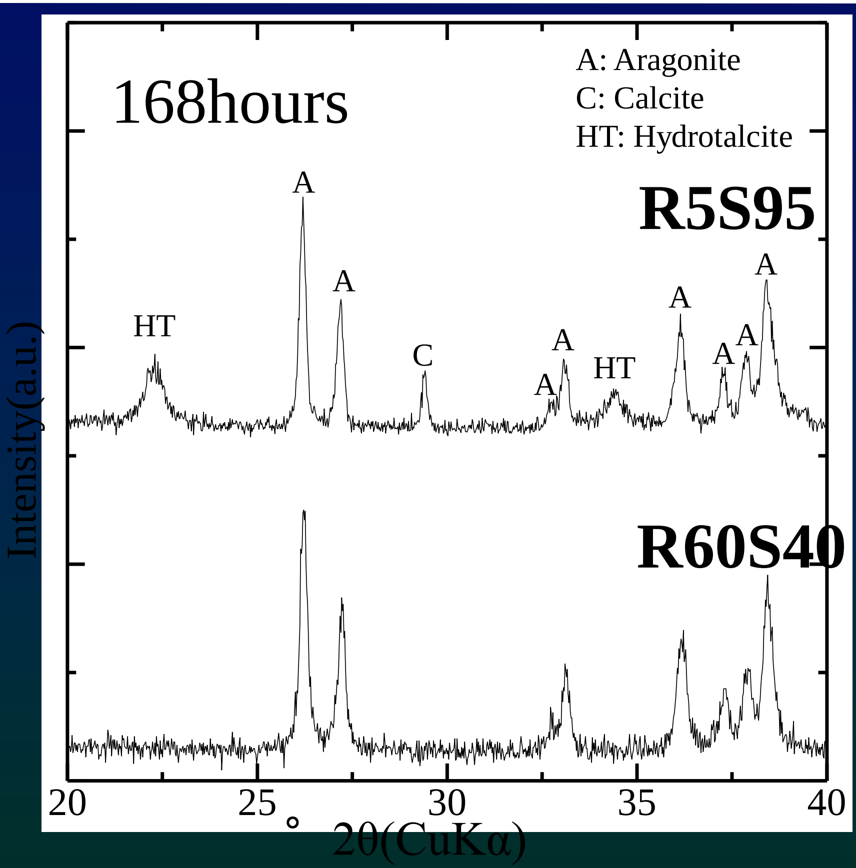


Dry up

Analyses

Solid	XRD, FT-IR, SEM
Liquid	ICP-AES, IC, UV-BIS

Mineral phases of the synthesized precipitates



XRD patterns of the samples collected from the precipitates in the in-situ experiment.

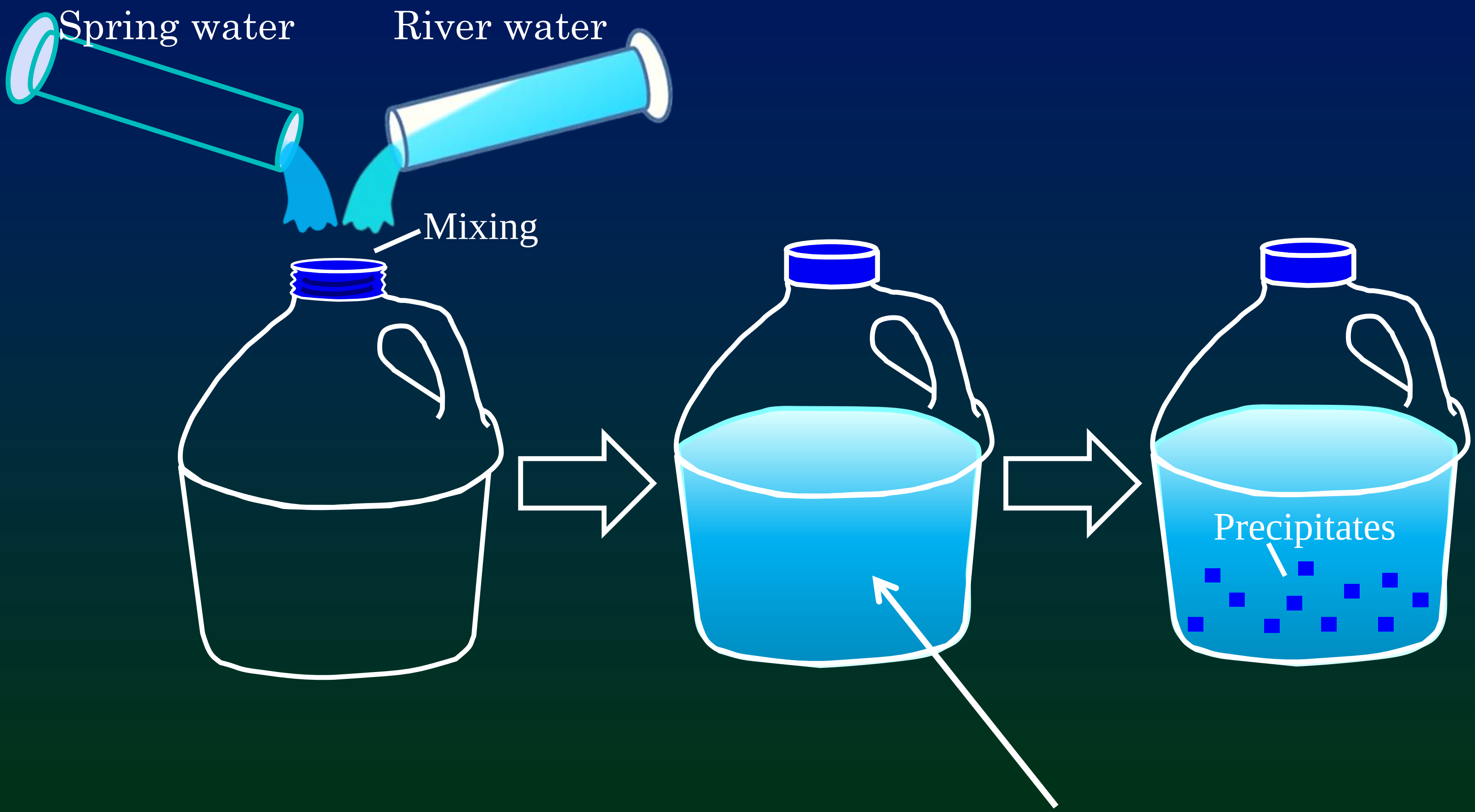
Mineral components and ratios between calcite and aragonite for different samples collected from the in-situ experiments. The ratios were obtained by Rietveld method.

Sample	Hydrotalcite	Calcite (mg)	Aragonite (mg)	Cal/Ara (%)
R5S95	4.8	1.0	12.8	7.6
R10S90	4.8	0.6	25.4	2.3
R20S80	7.6	0.4	51.6	0.7
R40S60	3.5	0.4	83.9	0.5
R60S40	nd	nd	74.1	0.0

Aragonite is dominant phase when mixing ratio of river water is higher.

Geochemical modelling for formation of the precipitates

Code : The Geochemist's Workbench®9.0 Database: thermoddem (BRGM)



Kinetics: Calcite and Aragonite formation
Equilibrium: Other chemical reaction

Growth rate of calcite and aragonite (Gutjahr *et al*., 1996)

$$R_0 = p(S-1)^n$$

- p is the rate constant($\mathrm{mol/cm^2 \cdot s}$), n obtained from fitting with the experiment.
- S is saturation ratio of $CaCO_3$.
- R_0 is the crystal growth rates in the absence of Mg^{2+}.

Inhibition of crystallization of calcite by Mg^{2+} (Lin and Singer, 2009)

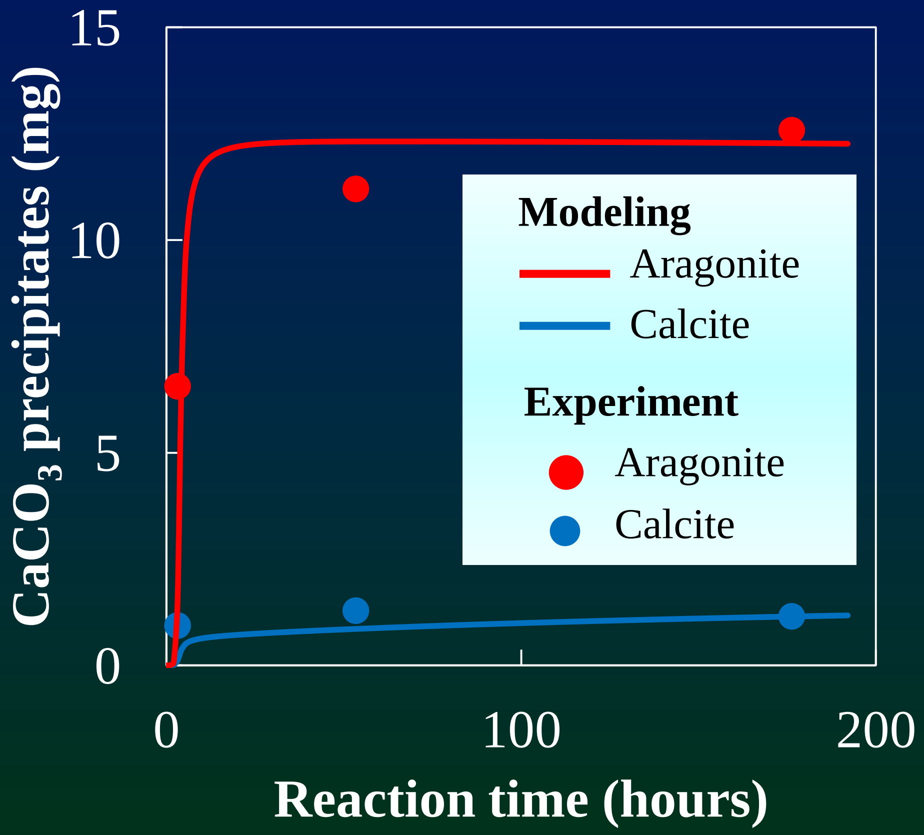
$$R_i = R_0 \times \left(\frac{[Ca^{2+}]}{[Ca^{2+}] + K_{Mg/Ca}[Mg^{2+}]} \right)$$

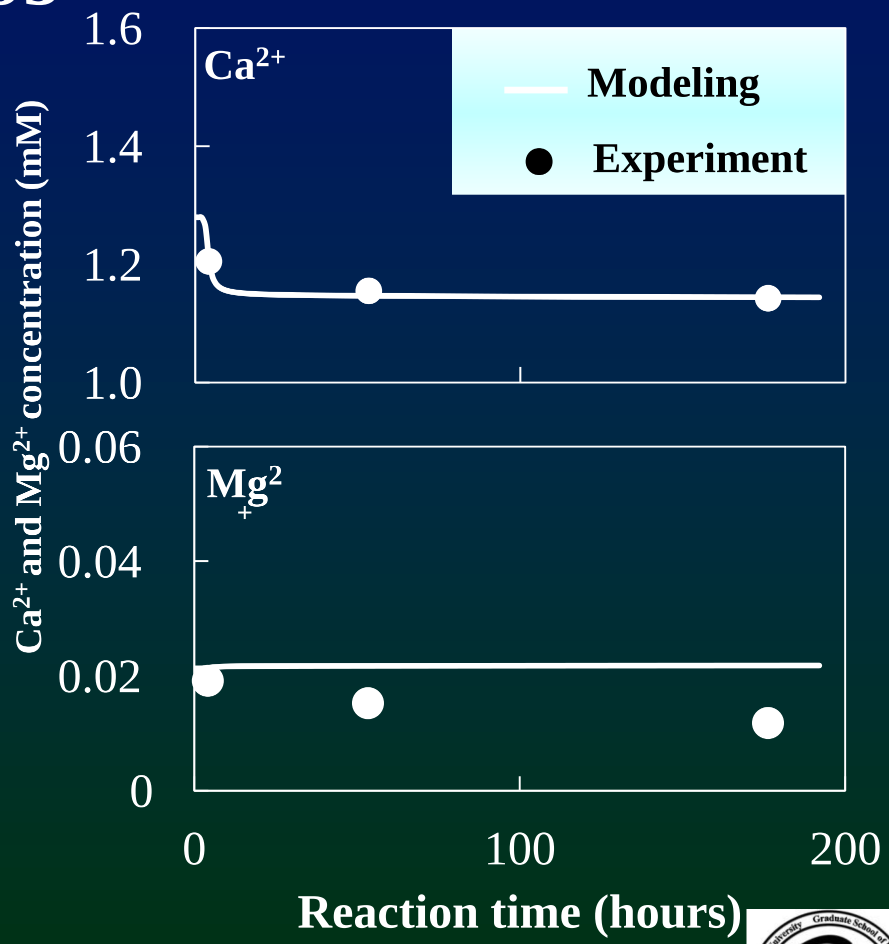
$$K_{Mg/Ca} = K_{Mg}/K_{Ca}$$

- R_0 *and* R_i are the calcite crystal growth rates in the presence and absence of Mg^{2+}, respectively.
- K_{Ca} and K_{Mg} represent the respective adsorption constants for Ca^{2+} and Mg^{2+} on the calcite surface in the competitive adsorption system.

Comparison between Results of Experiments and Modelling

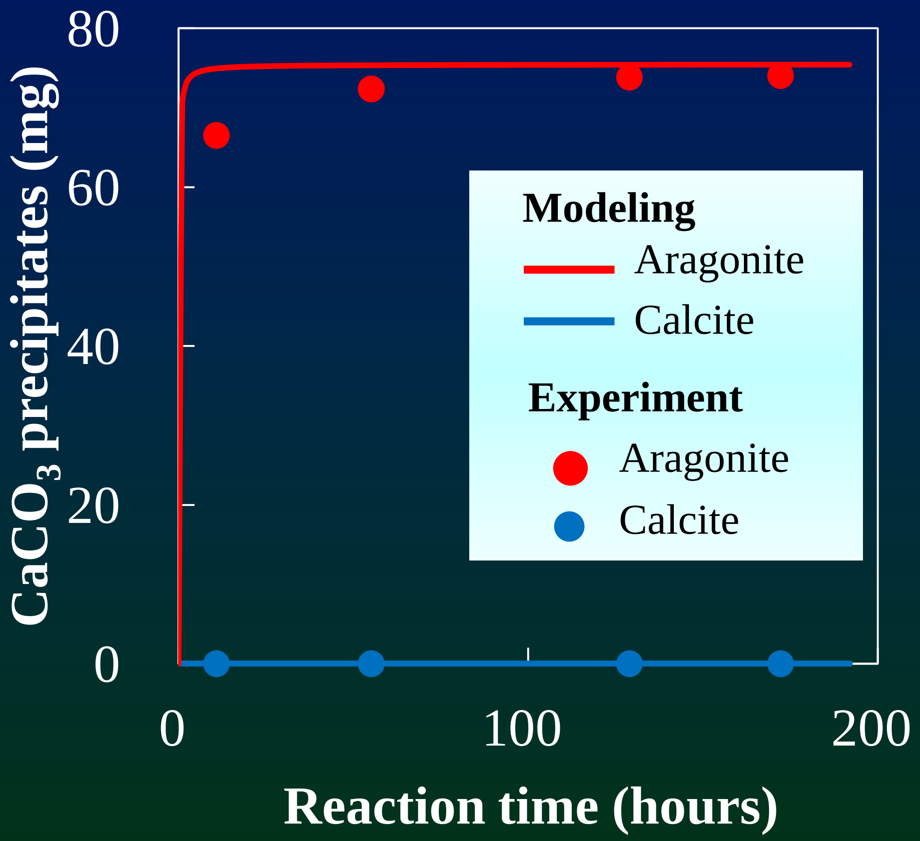
R5S95

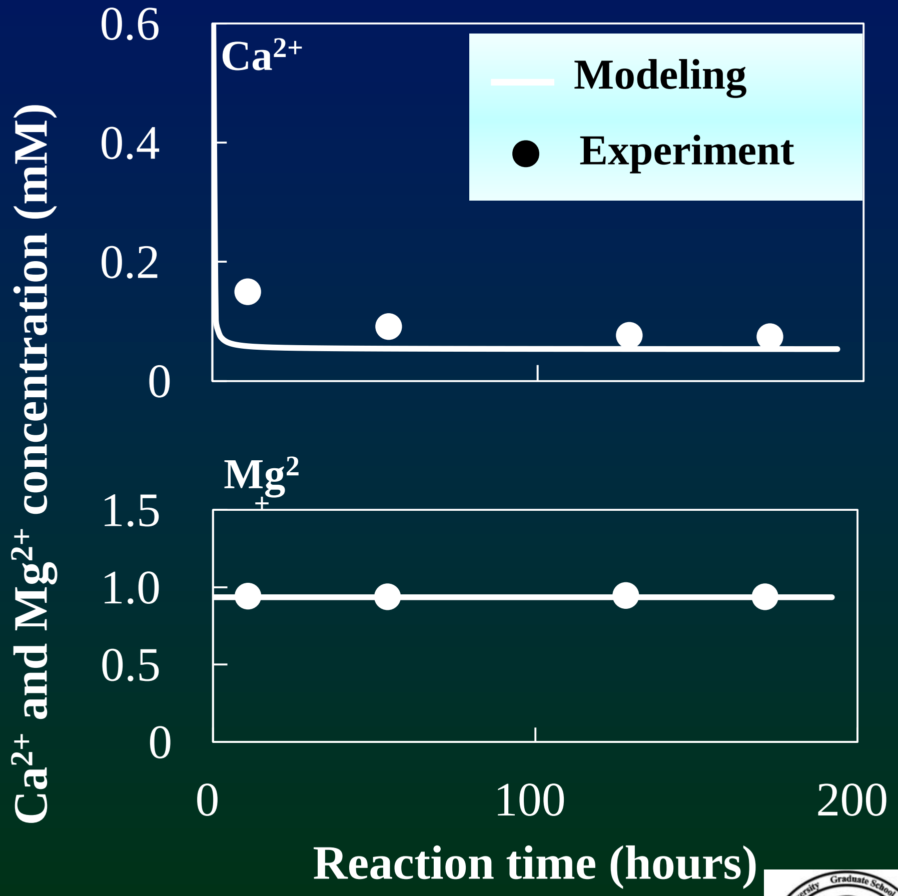




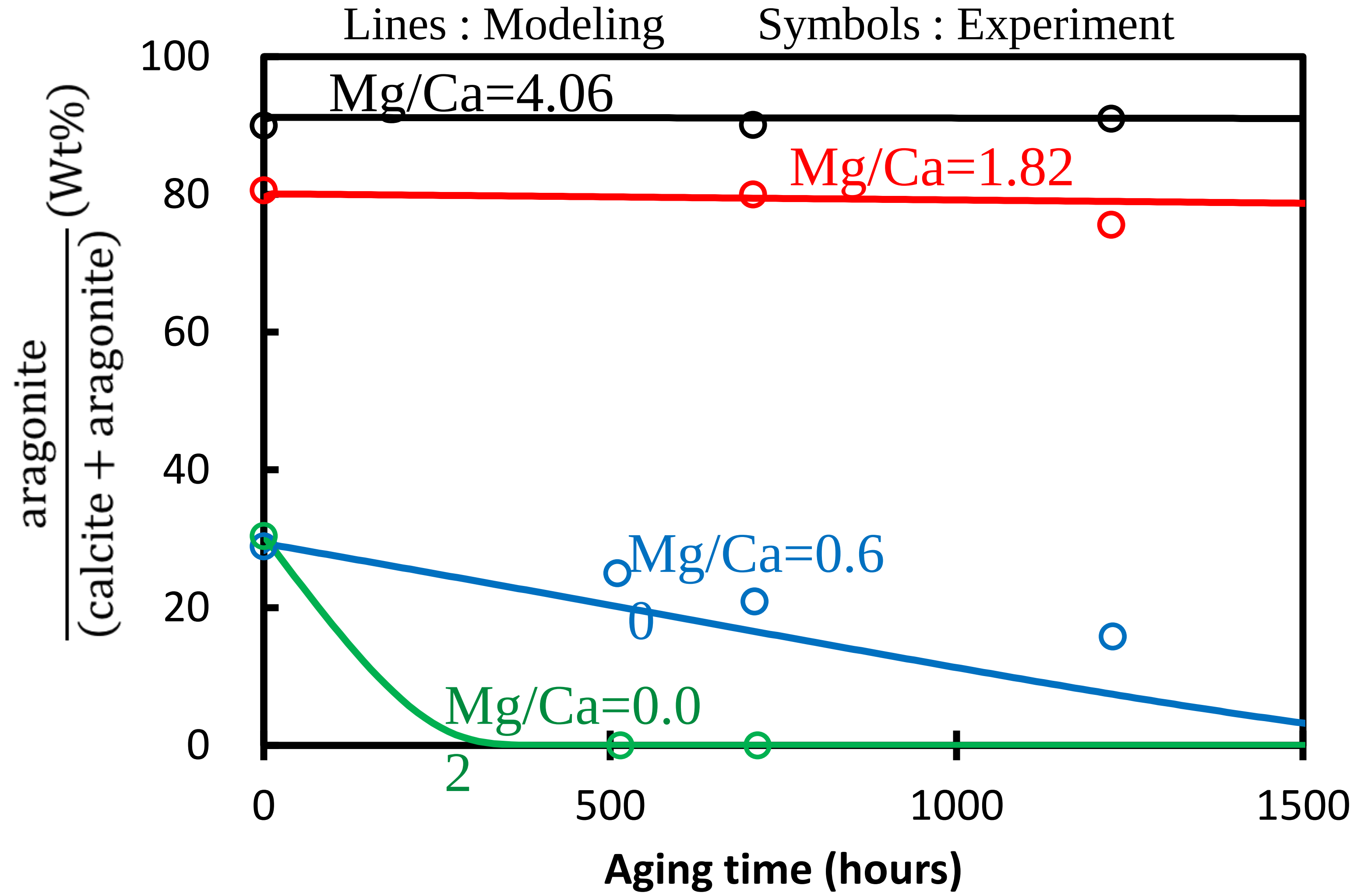
Comparison between Results of Experiments and Modelling

R60S40





Kinetics of aragonite-calcite transformation with different initial Mg/Ca ratios of the solution



Synthesis experiment in the field

Spring Water

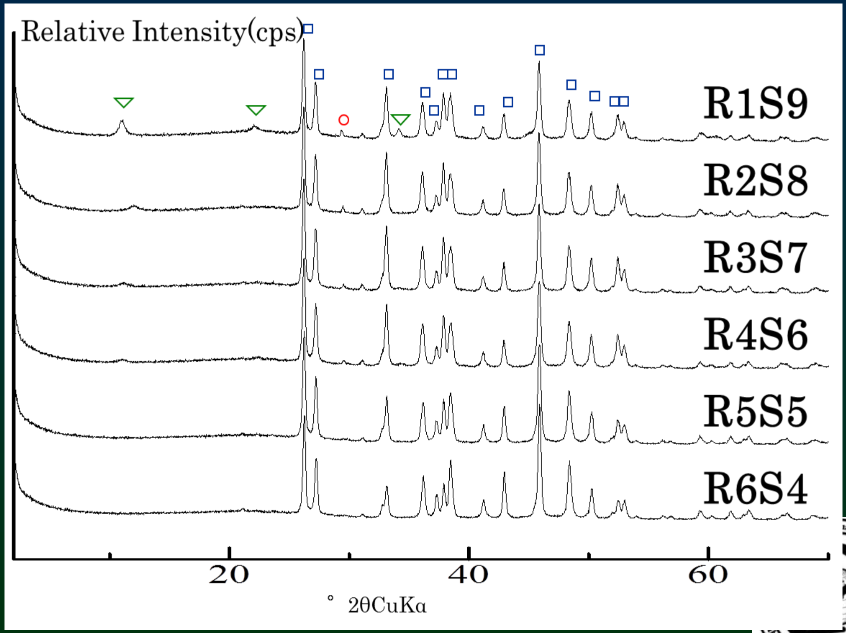
River Water

KI

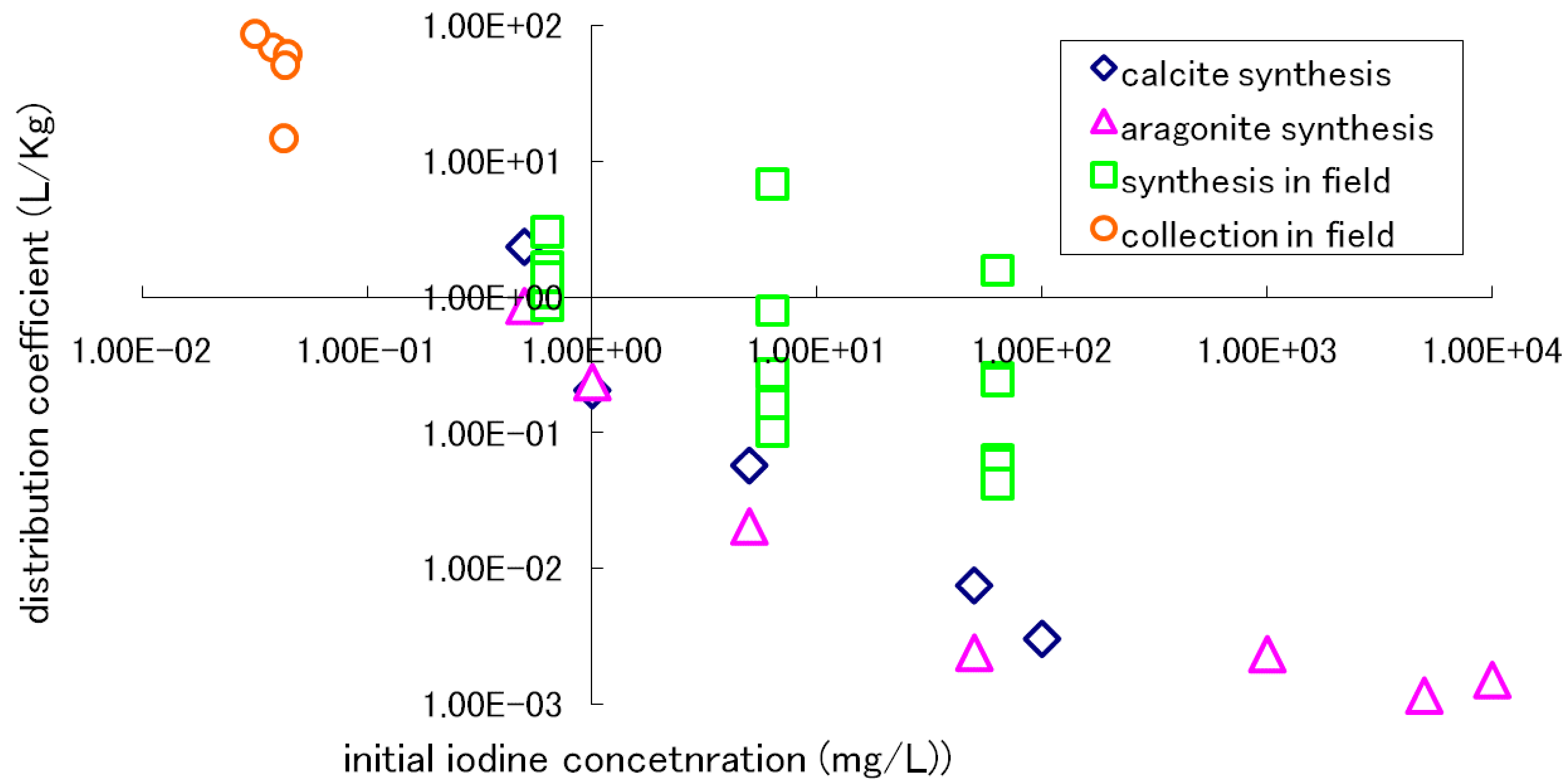
- 0.5mM
- 0.05mM
- 0.005mM

Spring water and river water were mixed in particular ratio to reveal the relationship between the mixing ratio and the secondary mineral phases.

Iodide reagent also added in deferent concentration to know the dominant phase of iodide uptake.



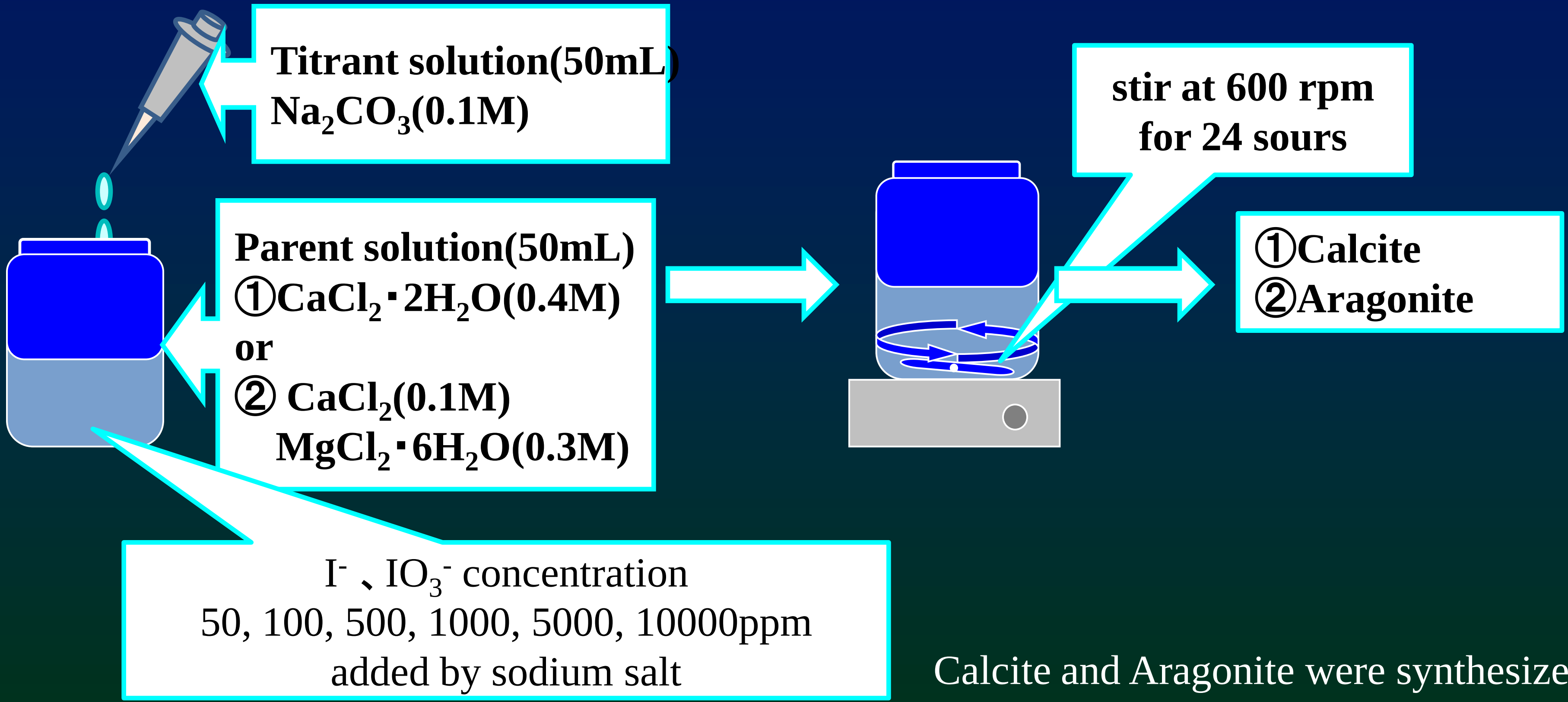
Kd values of iodide for the precipitates in the field and laboratory



Batch co-precipitation experiments in laboratory

✓Synthesis method

Stirred in the oven at 25 ℃



Titrant solution(50mL)
Na_2CO_3(0.1M)

Parent solution(50mL)
①$CaCl_2 \cdot 2H_2O$(0.4M)
or
② $CaCl_2$(0.1M)
$MgCl_2 \cdot 6H_2O$(0.3M)

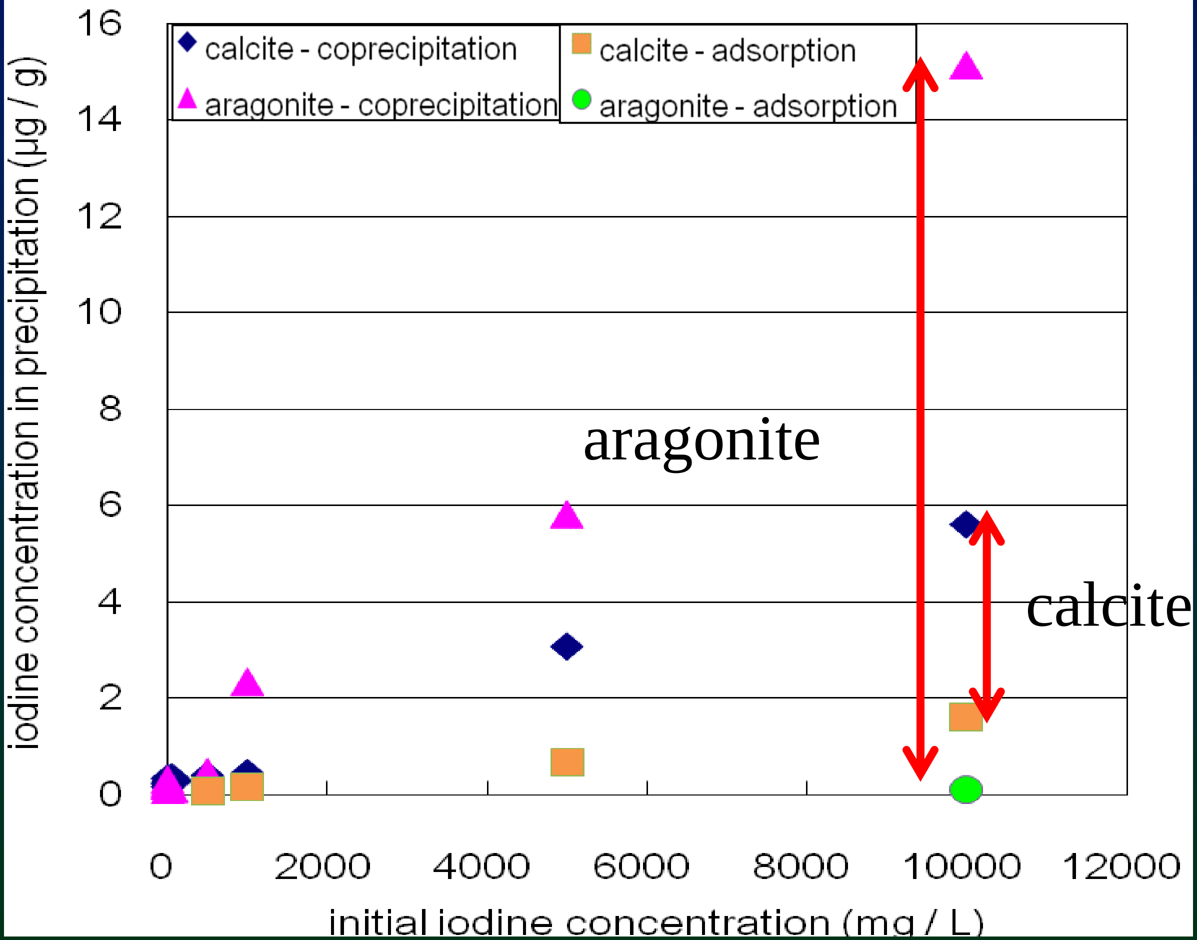
stir at 600 rpm
for 24 sours

①Calcite
②Aragonite

I^- 、IO_3^- concentration
50, 100, 500, 1000, 5000, 10000ppm
added by sodium salt

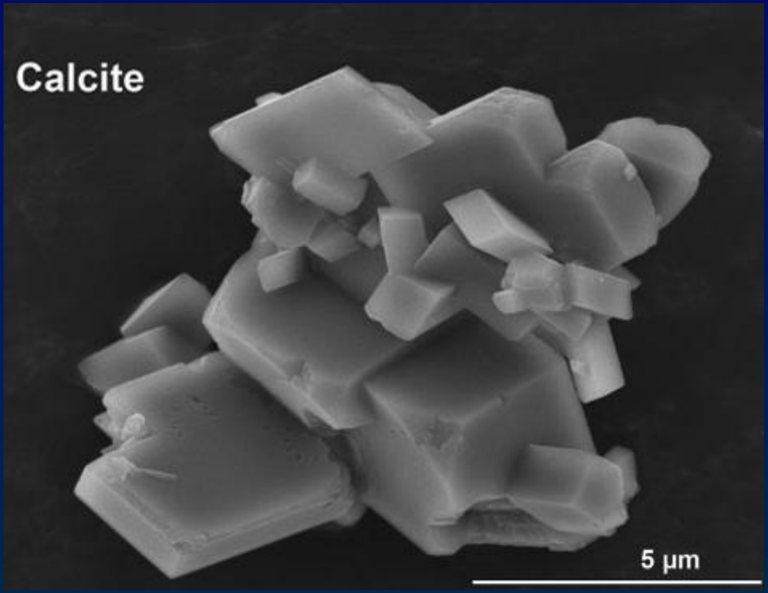
Calcite and Aragonite were synthesized by the difference of Mg content in the reaction solution

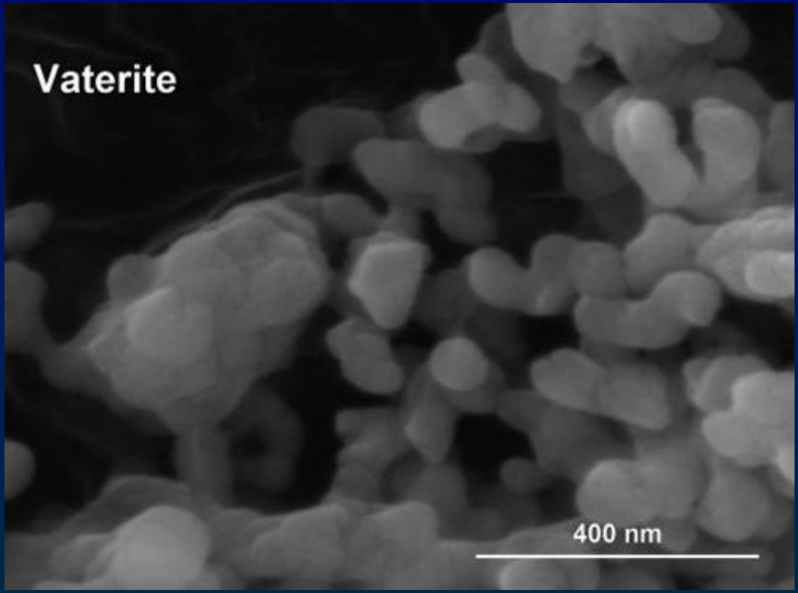
Iodide ion uptake in the experiments for adsorption and coprecipitation



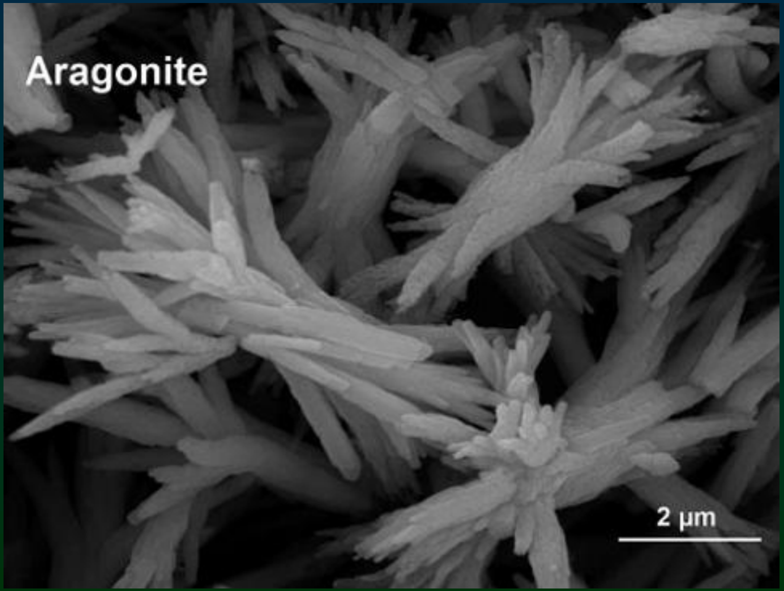
Aragonite has greater uptake capacity of iodide. Greater uptake of iodide is observed in the coprecipitation process.

Polymorphs of $CaCO_3$ minerals





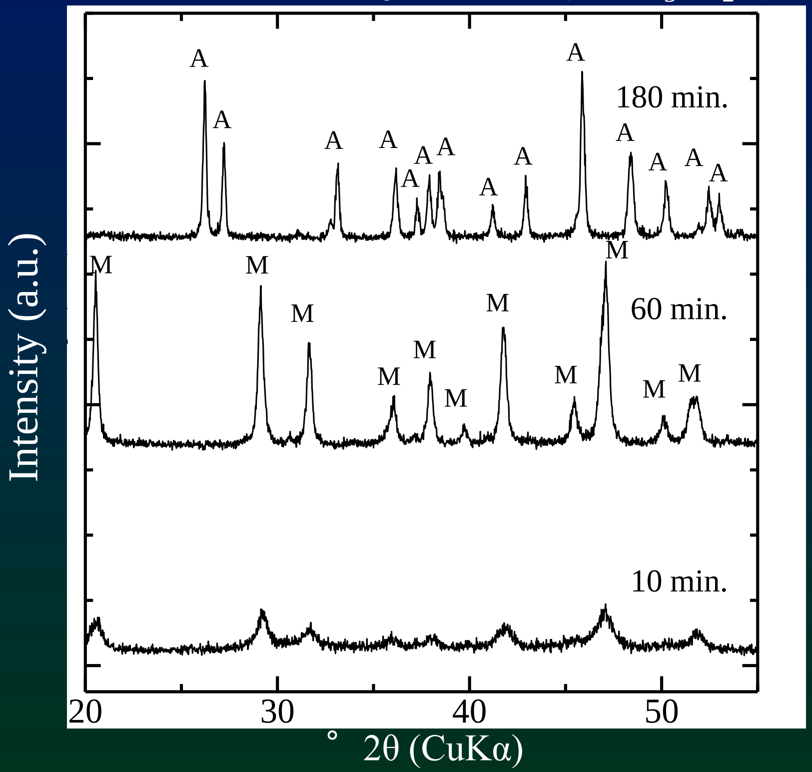
(Nebel and Epple 2008)



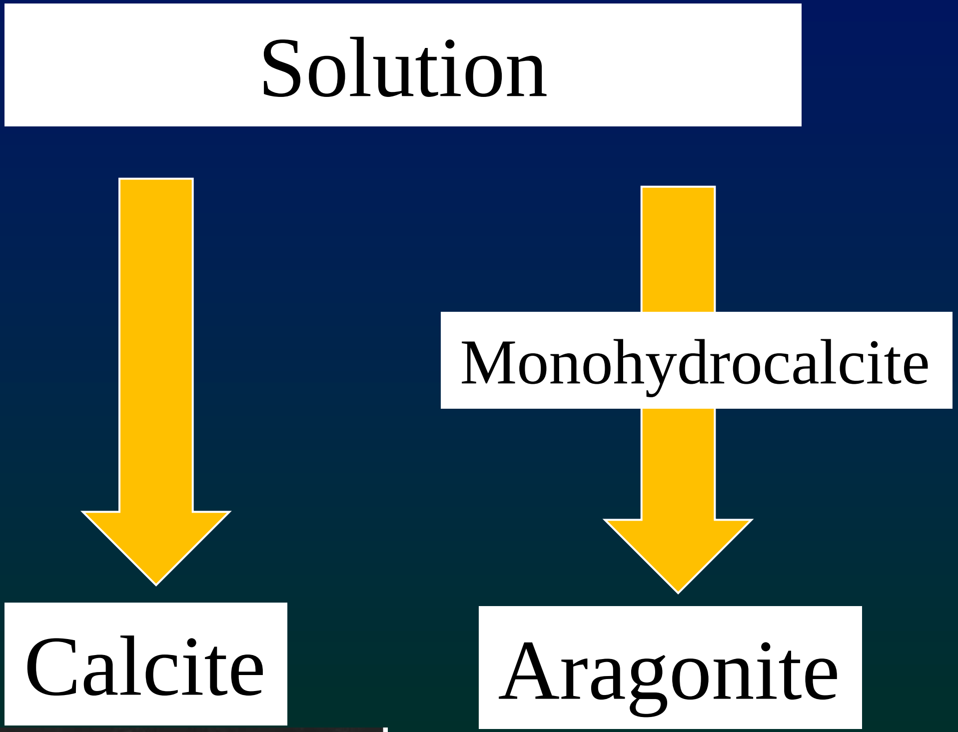
Name	chemical formula	Density (g/cm^3)	log Ksp
calcite	$CaCO_3$	2.71	-8.35
aragonite	$CaCO_3$	2.93	-8.22
vaterite	$CaCO_3$	2.54	-7.91
monohydrocalcite	$CaCO_3 \cdot H_2O$	2.43	-7.54
ikaite	$CaCO_3 \cdot 6H_2O$	1.77	-7.12

Monohydrocalcite: Precursor of aragonite

A: Aragonite
M: Monohydrocalcite ($CaCO_3 \cdot H_2O$)



XRD patterns of the precipitates collected from a synthesis experiment as a function of reaction time.

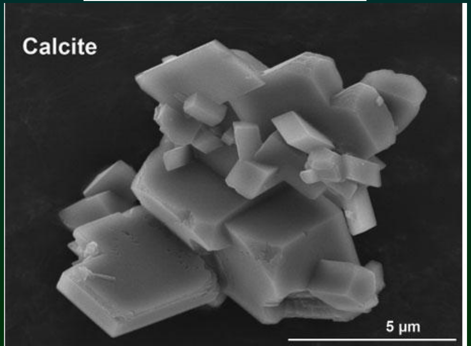


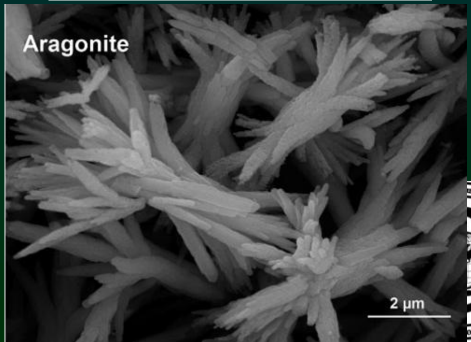
Solution

Calcite

Monohydrocalcite

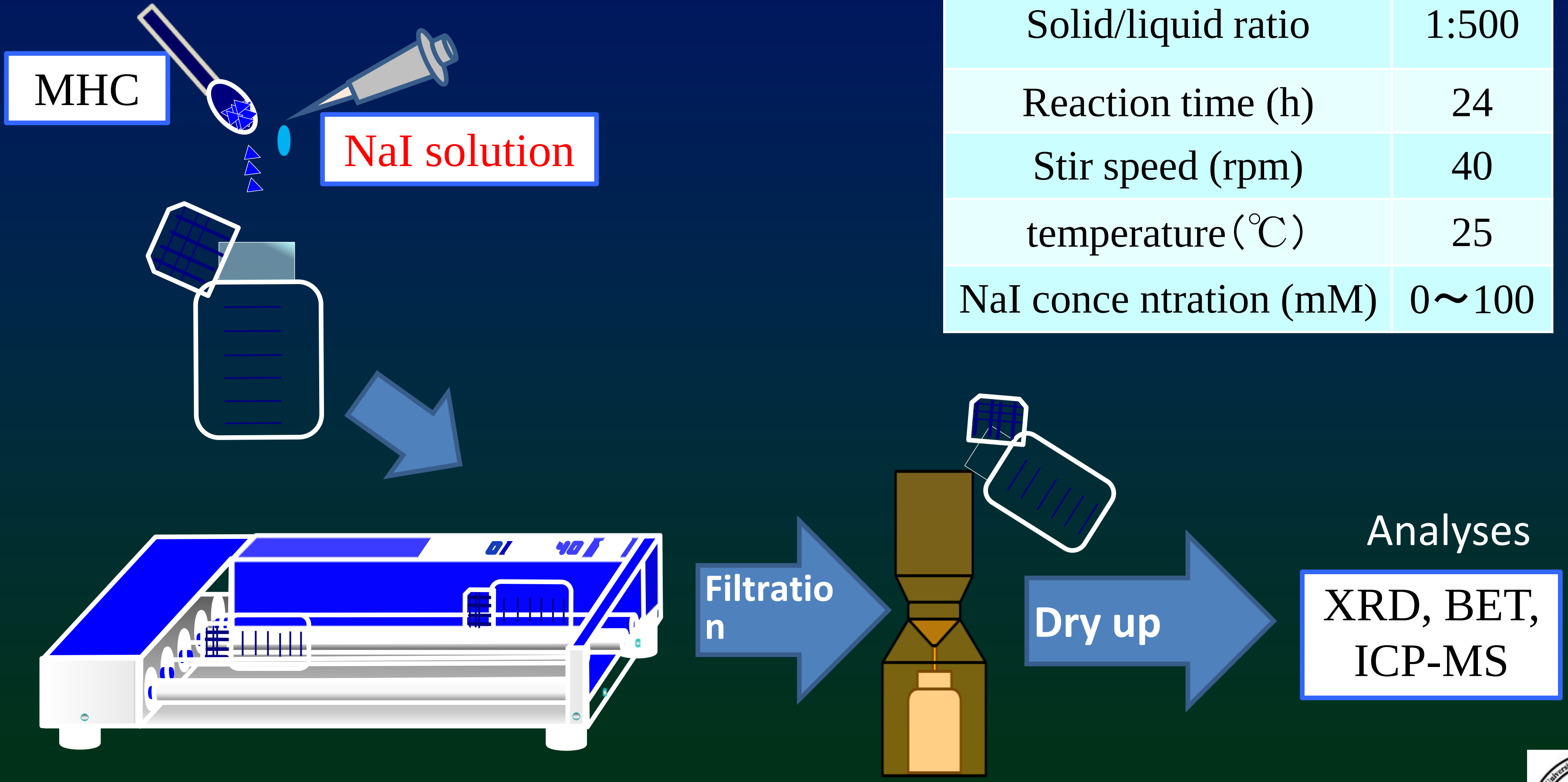
Aragonite





Adsorption experiments of iodide ion for monohydrocalcite

Experimental condition	
Solid/liquid ratio	1:500
Reaction time (h)	24
Stir speed (rpm)	40
temperature（℃）	25
NaI conce ntration (mM)	0～100



MHC

NaI solution

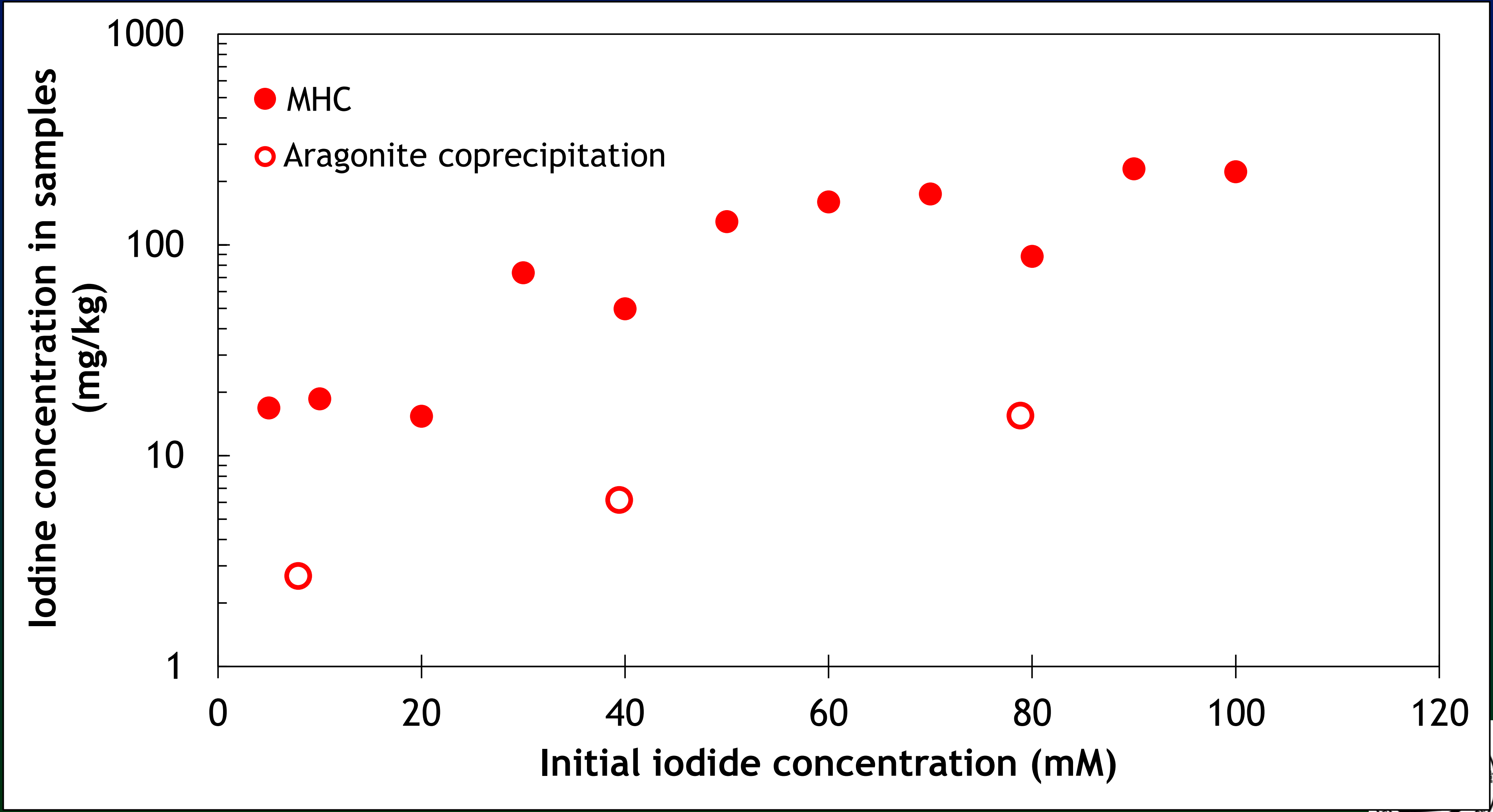
Filtration

Dry up

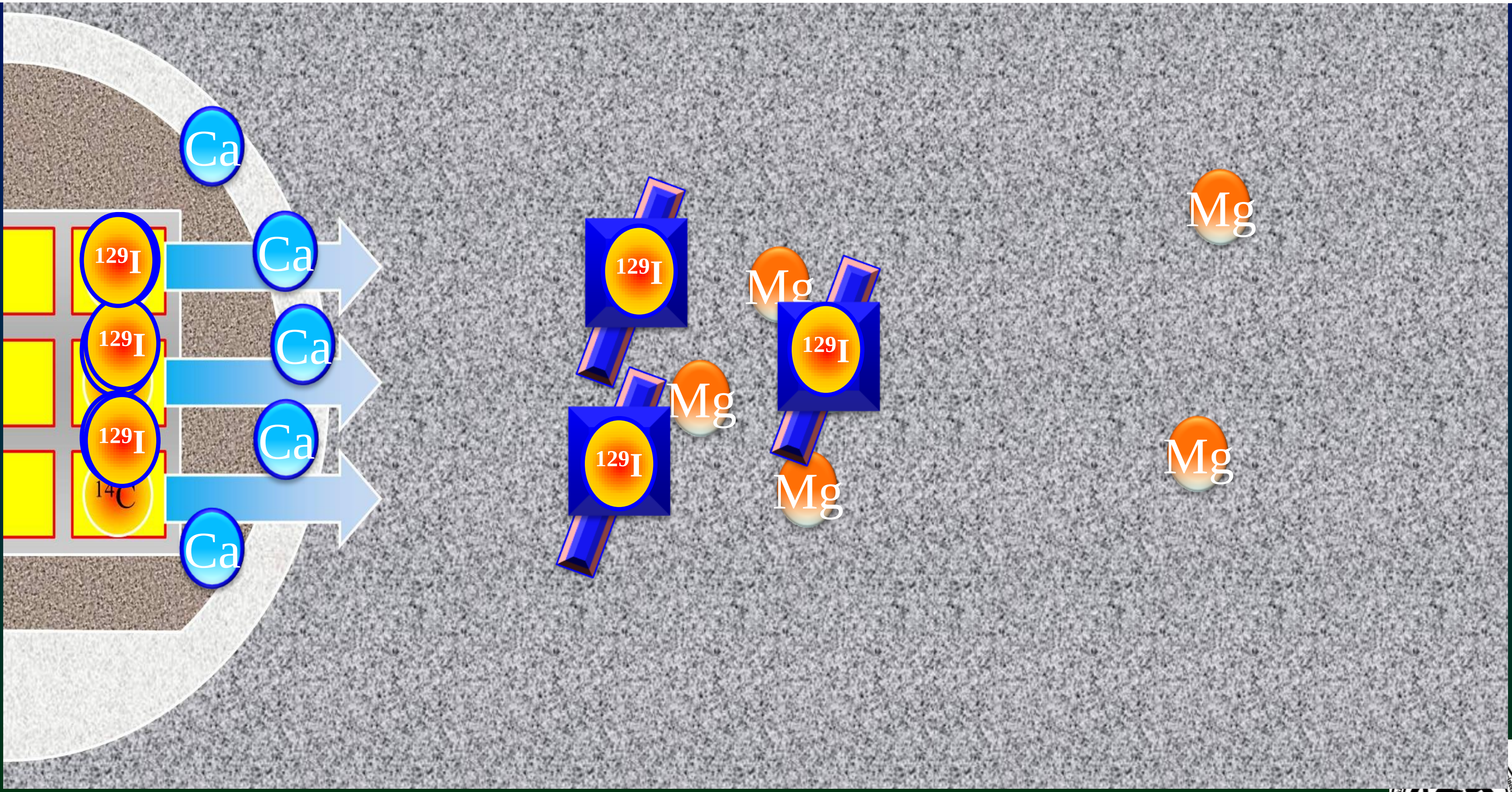
Analyses

XRD, BET, ICP-MS

Comparison of iodide sorption in MHC adsorption with that in aragonite coprecipitation experiments



Alkaline plume meet with groundwater at the near field



環境地質学研究室

Laboratory of Environmental Geology

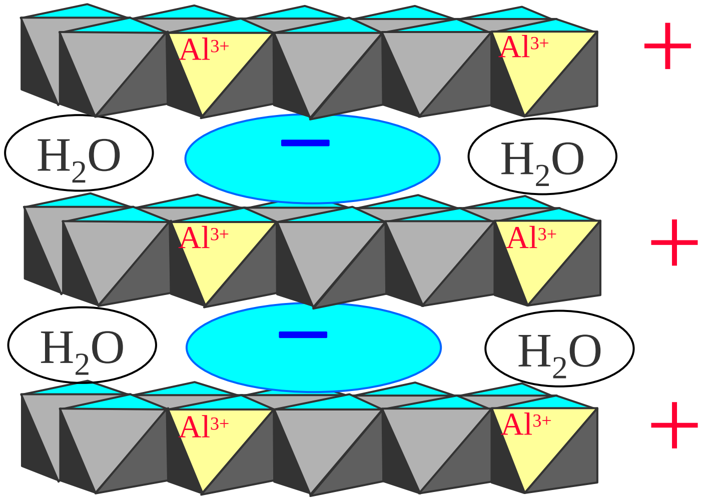
Natural analogue study of hyperalkaline geochemistry at Oman

Could we expect a retardation of anion migration at hyperalkaline condition?

Tsutomu Sato
Laboratory of Environmental Geology,
Faculty of Engineering,
Hokkaido University, Sapporo, Japan

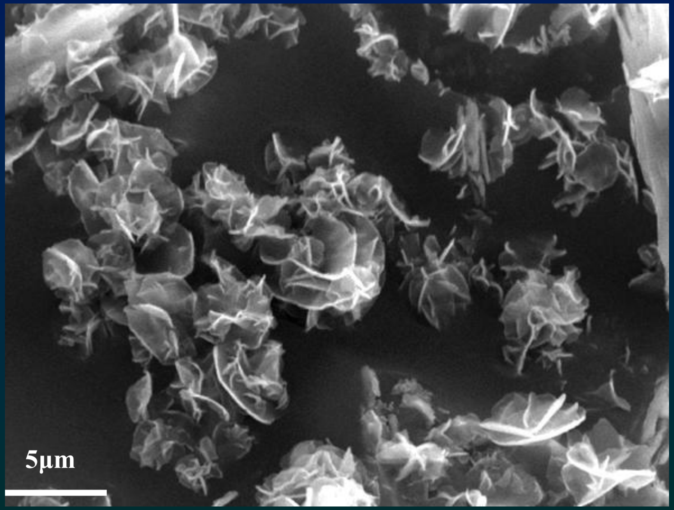
Layered Double Hydroxides
-Natural Anion Getter in Alkaline Condition-

$Mg_{0.67}Al_{0.33}(OH)_2(X^{-1})_{0.33}\cdot nH_2O$



Stracture of hydrotalcite

From Narita 2001



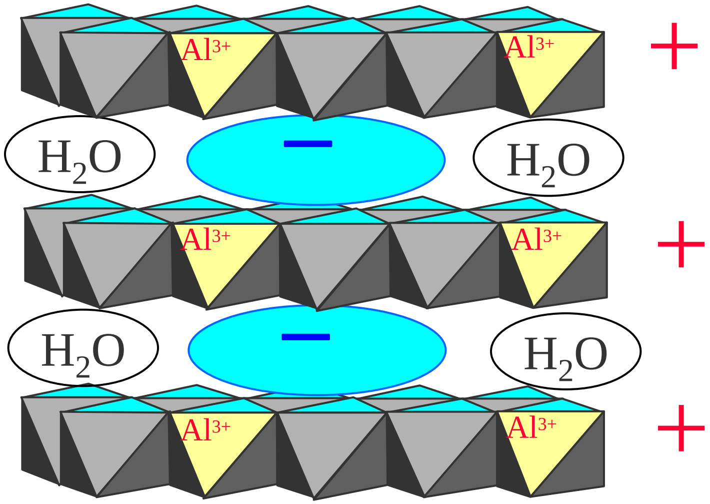
Anion selectivity

$CO_3^{2-} \gg SO_4^{2-} \gg OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$

Pyroaurite (green rust)-Anion Getter-

-Alteration Product of Carbon Steal-

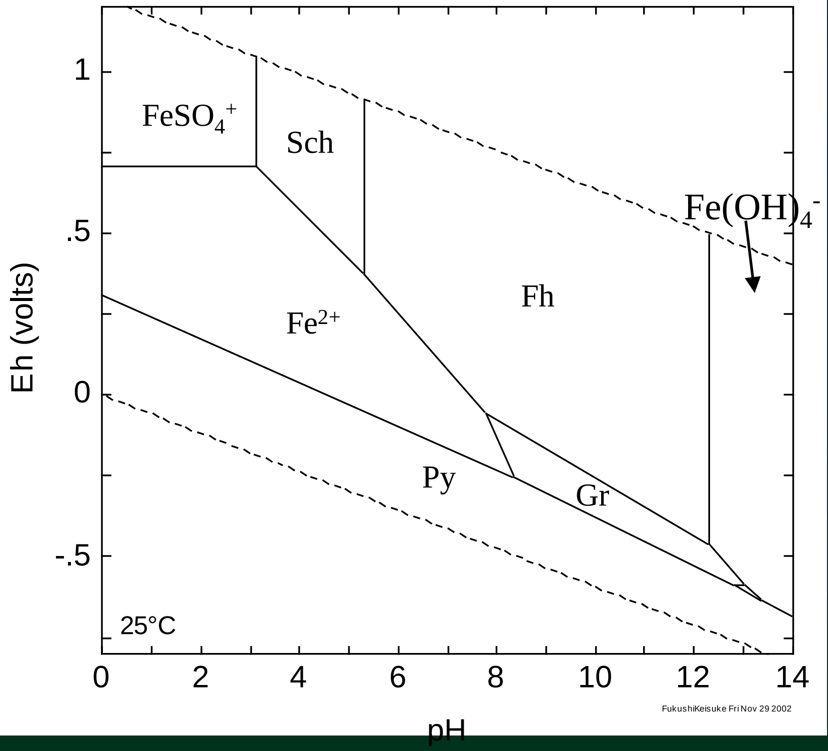
$Fe^{2+}_{0.67}Fe^{3+}_{0.33}(OH)_2(X^{-1})_{0.33}\cdot nH_2O$



Structure of pyroaurite (green rust)

Modified from Narita 2001

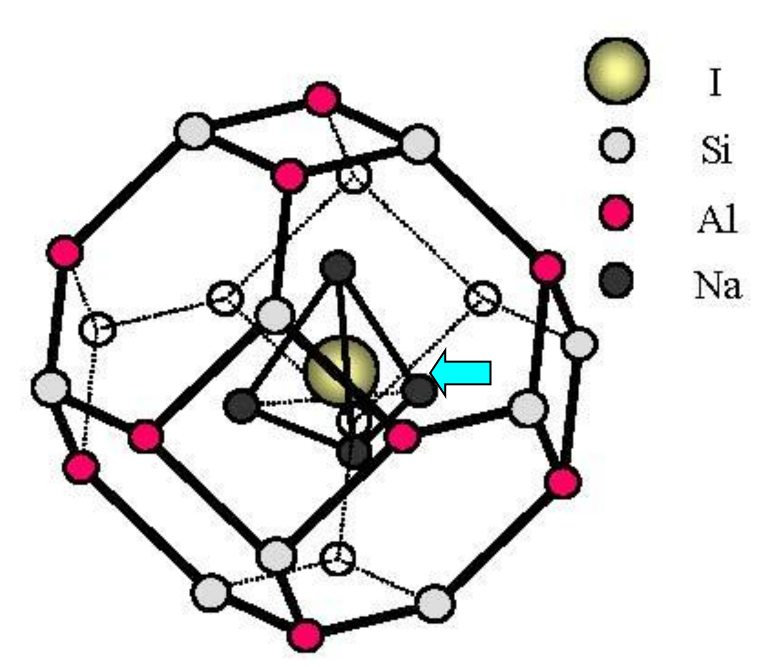
$Fe-S-O_2-H_2O$ system



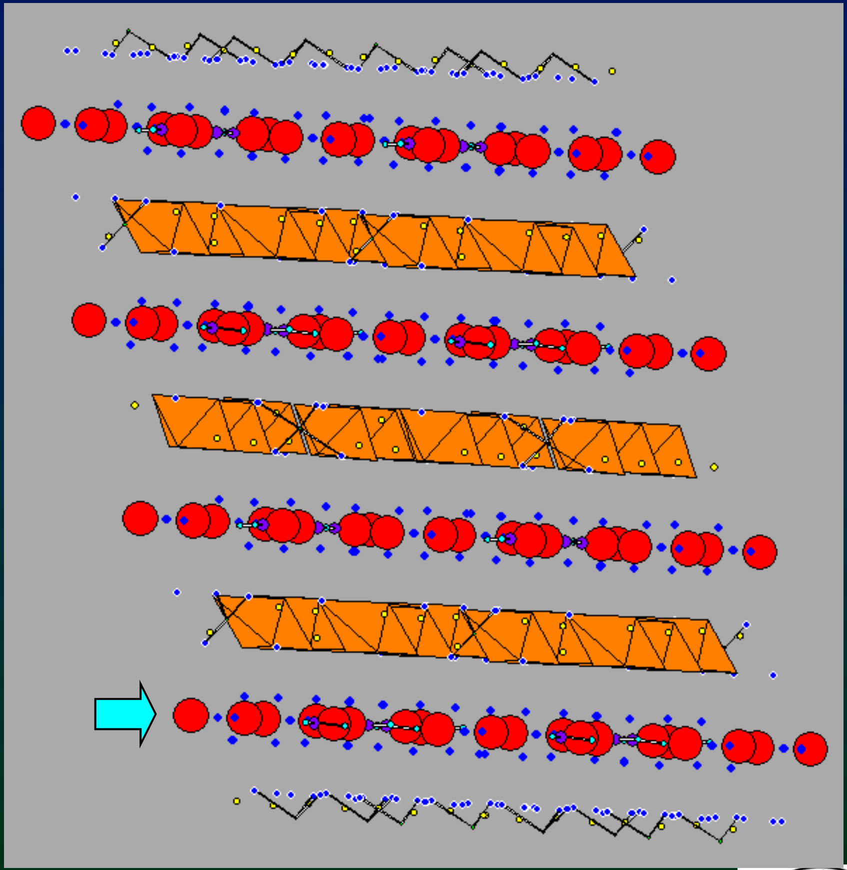
(Fukushi and Sato, 2003)

Other Candidates for Anion Retention

Sodalite, $[Na_4Cl_1(Al_3Si_3O_{12})]$

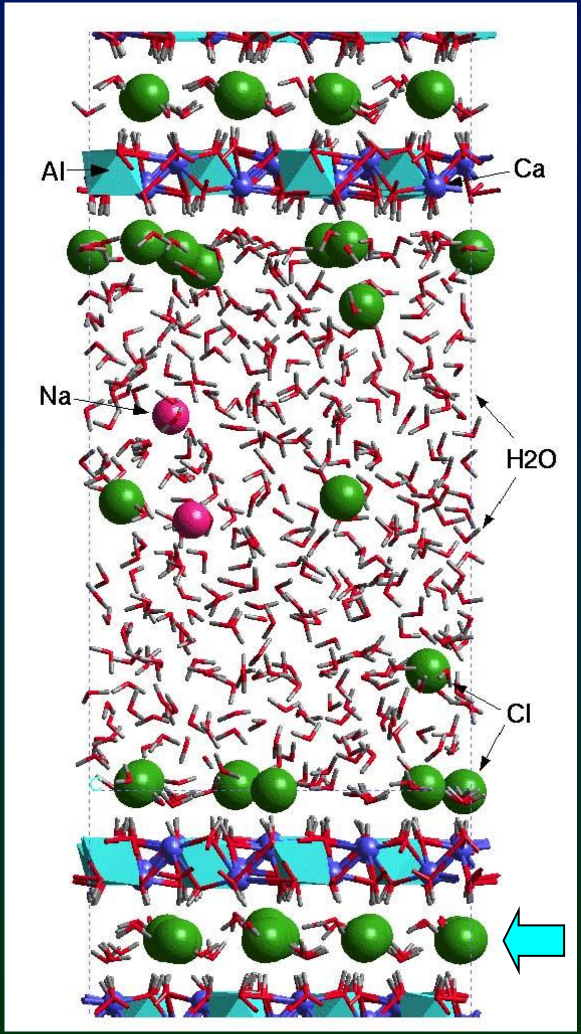


Hydrocalmite, $[Ca_2Al(OH)_{6.5}Cl_{0.5} \cdot 3H_2O]$

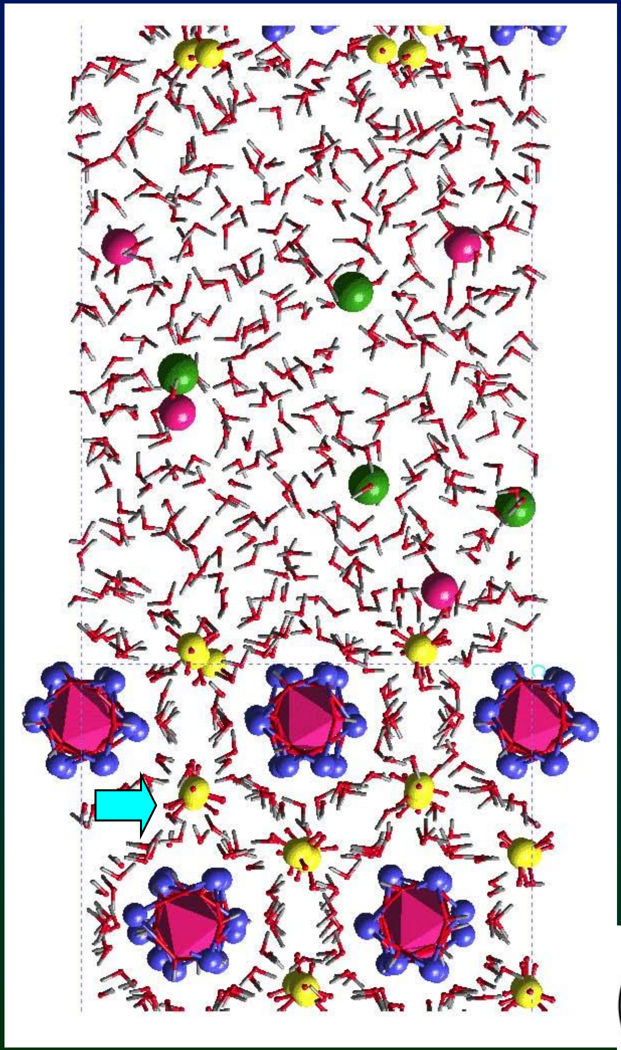


Other Candidates for Anion Retention

Friedel's salt, $[Ca_2Al(OH)_6]Cl \cdot 2H_2O$

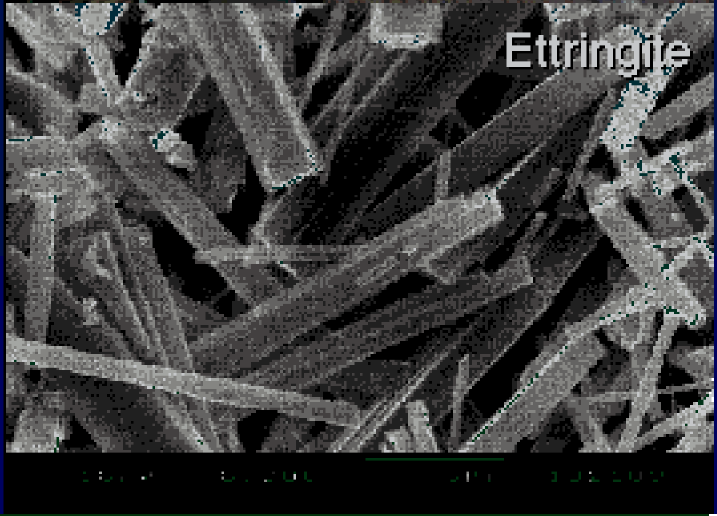


Ettringite, $Ca_6[Al(OH)_6]_2[SO_4]_3 \cdot 26H_2O$



Precipitation of Heavy Metal at Acid Mine Drainage

Disposal pond at Ogoya mine, Ishikawa



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- 21st COE Program, Hokkaido University, Japan

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- Prof. Michibayashi and Suzuki of Shizuoka Univ.
- Drs. Yanase of JAEA
- My students of Kanazawa and Hokkaido Univ.