

Stability of smectite under hyperalkaline fluids including Fe, Mg, Al ions

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This research was initiated within a project to develop Geological Disposal Technologies in Japan using Natural Analogue, which was funded by the Ministry of Economy Trade and Industry (METI), Japan.

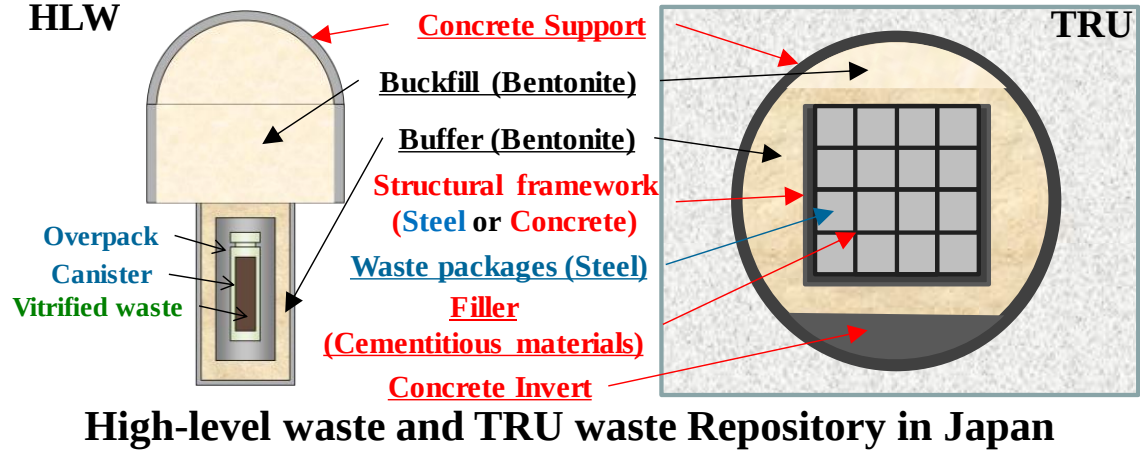
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1. Background

Influence of Hyperalkaline Fluid

- **Much of Cement Materials** are used for TRU waste disposal system in Japan.
- **High pH cement leachate** affects bentonite (dissolution/alteration of smectite), as a result, may cause the loss of its favorable properties.
- **The long-term phenomenon** of the hyperalkaline influence is a key issue of the safety assessment of waste disposal.



Natural Evidence

- **Hyperalkaline Groundwater** evolved by **Serpentinization** of **Ultramafic rocks** in **Ophiolite** is **high pH**, **high Ca**, reducing and **30~40°C**.
- Many serpentinizing ophiolites are distributed in the Philippines. Palawan ophiolite is one of the typical ophiolites.

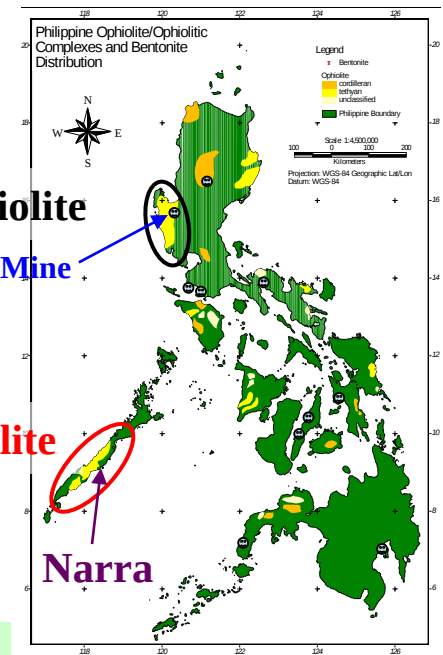
⇒ Hyperalkaline groundwater generated by serpentinization is regarded as a natural analogue of the cement leachate

Zambales ophiolite

Saile Mine

Palawan ophiolite

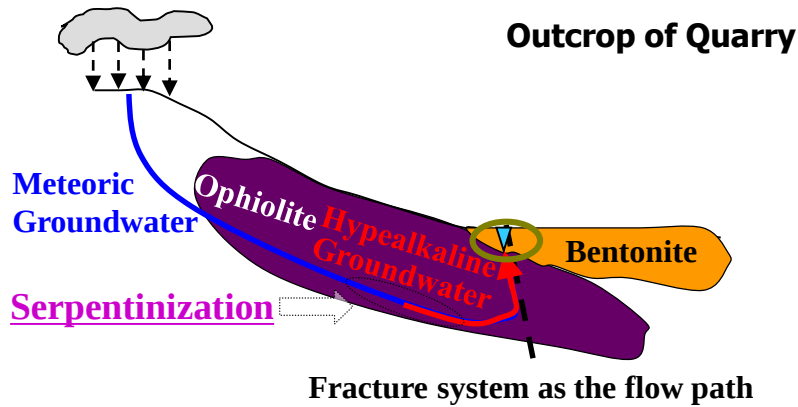
Narra



Distribution of Ophiolite and Bentonite deposits in the Philippines

2. Survey sites

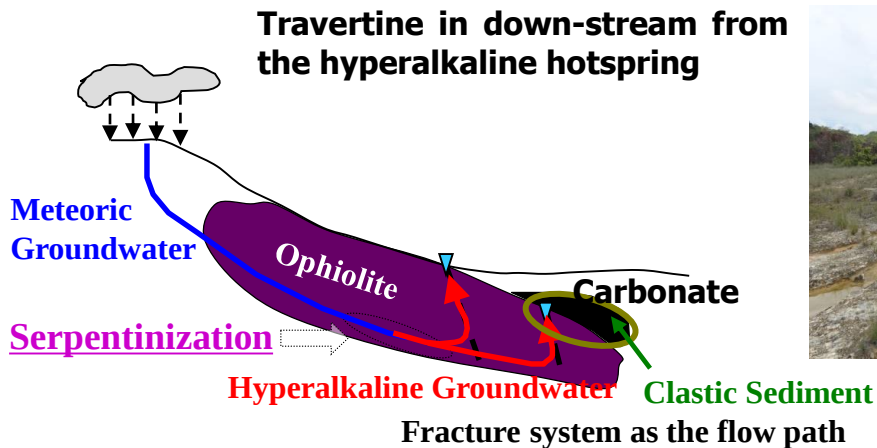
Natural Analogue in Saile Mine



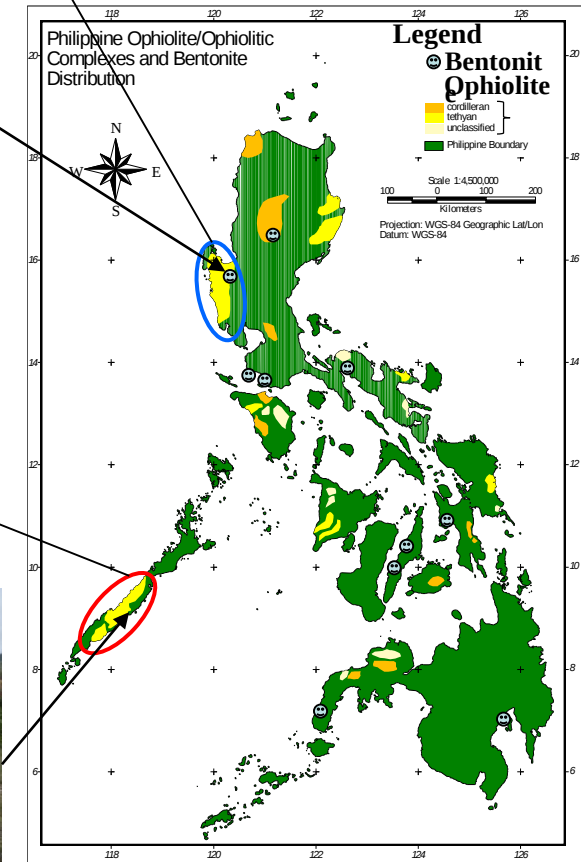
Zambales Ophiolite



Natural Analogue in Narra



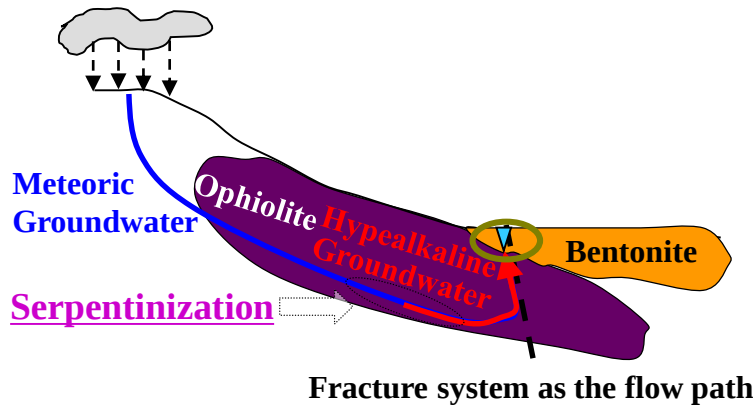
Palawan Ophiolite



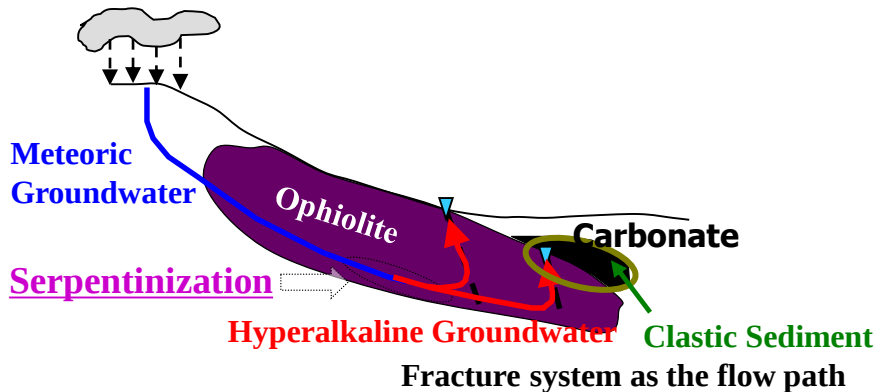
Distribution of Ophiolite and Bentonite deposits in the Philippines

2. Survey sites

Natural Analogue in Saile Mine



Natural Analogue in Narra



Advantages of Narra

- **Hyperalkaline groundwater have been seeping into overlying clastic sediment still now.**

We can directly measure **properties of hyperalkaline groundwater**, and observe **metastable reactions** between the groundwater and sediment, and estimate **the reaction time** by C-14 dating.

No hyperalkaline groundwater flow in Saile mine now.

- **pH > 11**

It is the required condition as cement analogue.

pH at Manleluag hot spring near Saile mine is under 11.

Disadvantages of Narra

- **The sediment is not bentonite.**

Sediment is smectite-rich clay, but the smectite is not montmorillonite.

It is impossible to observe Natural analogue of **bentonite buffer system** only at Narra site.



However, we can study several important **reaction processes** concerning alkaline alteration of bentonite in Narra.

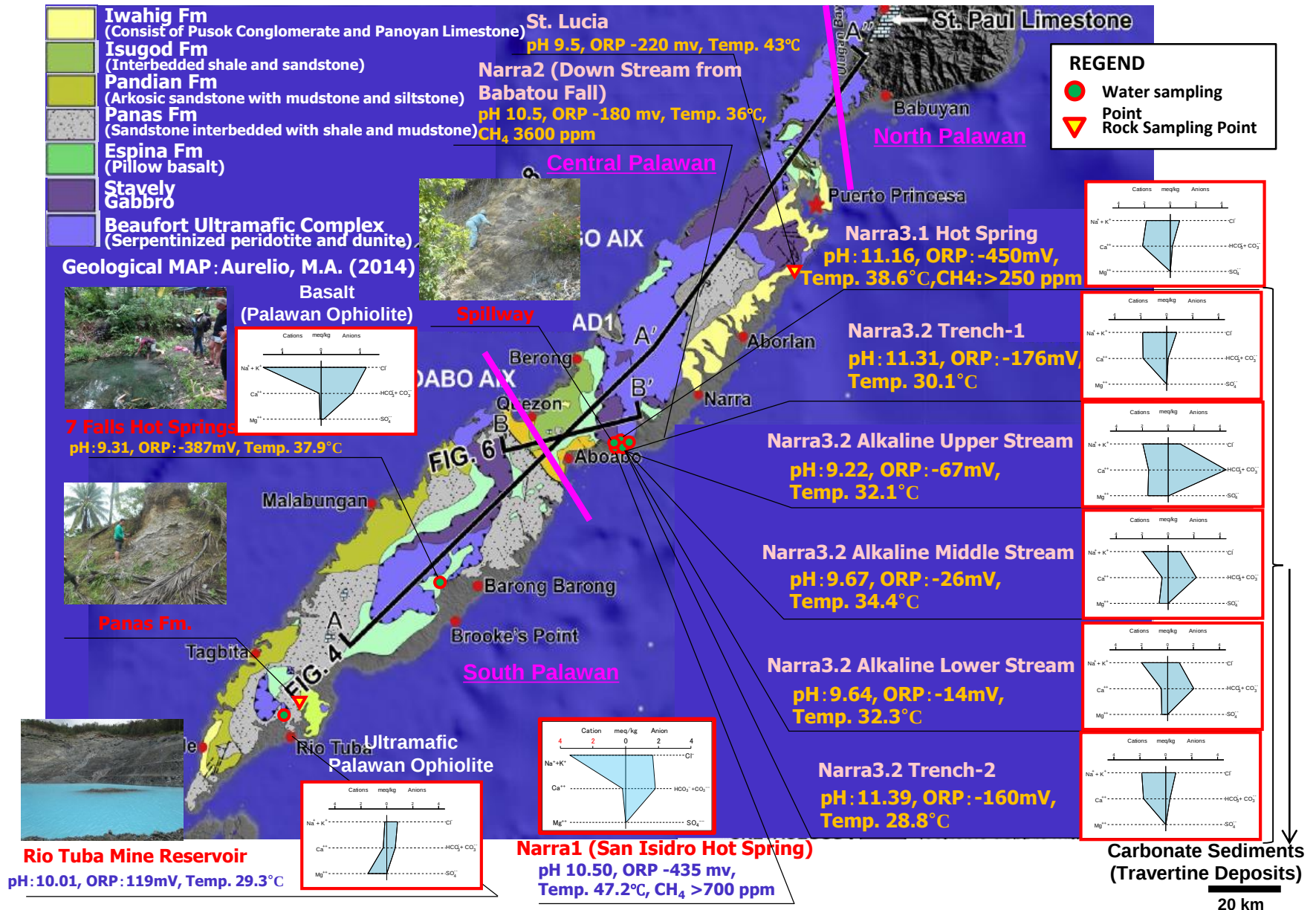
3. Objectives

This NA project has field survey at the Narra site in central Palawan, SW Philippines and chemical and mineralogical analysis,

- **To better understand alteration process under hyperalkaline conditions.**
 - **Dissolution/Formation reactions by hyperalkaline fluid**
 - **Mass balance of Fe, Mg, Si, Al, Ca in mineral formation**
 - **Stability of smectite**
- **To establish comprehensive scenario of bentonite reaction under realistic hyperalkaline environment.**



4.1 Groundwater Chemistry and Geology in Palawan Island



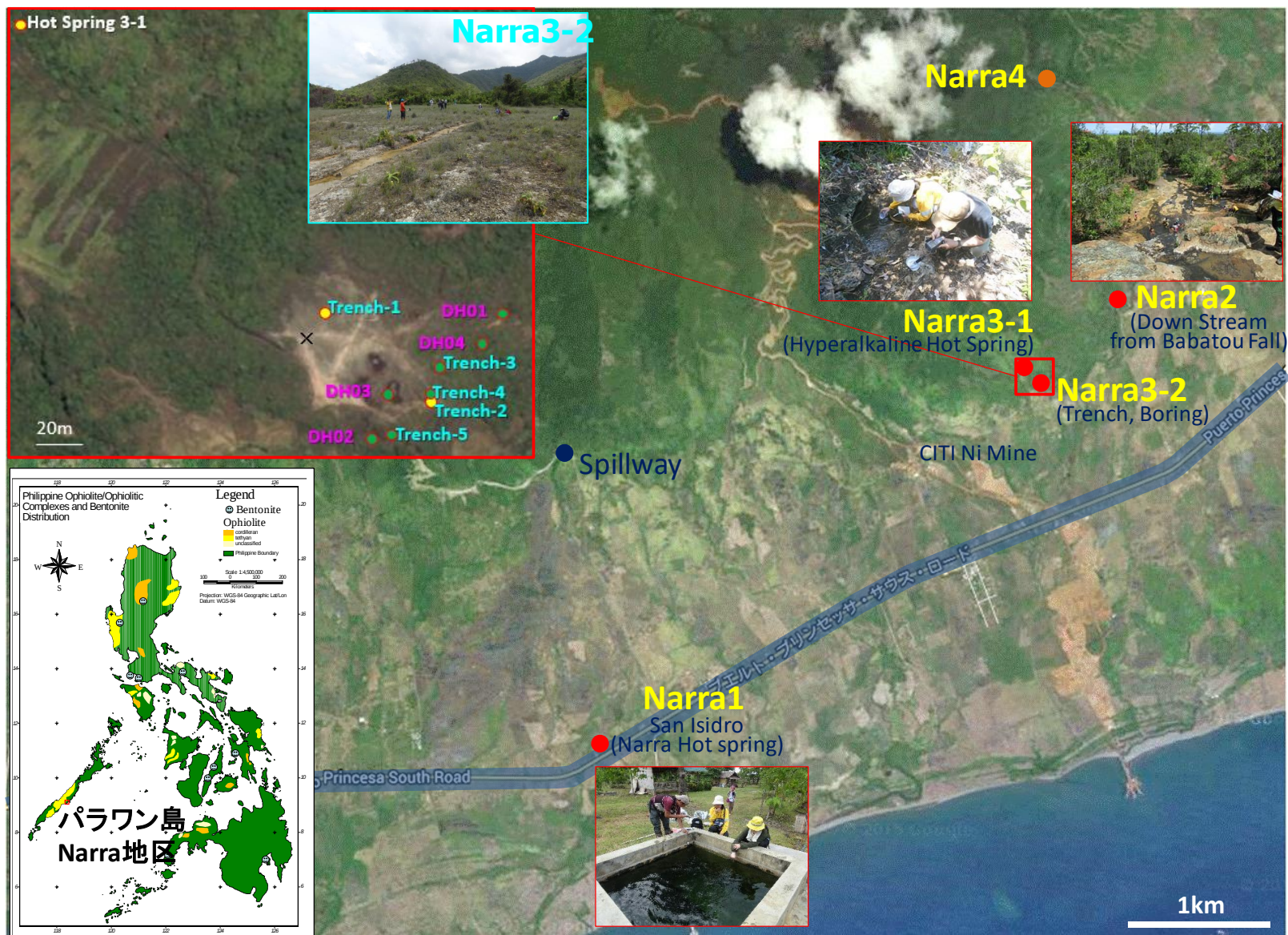
4.1 Groundwater Chemistry in Palawan

Site	Palawan Narra -1 Hot Spring	Palawan Narra -3.2 Trench5	Palawan Narra -3.2 Trench4	Palawan Narra -3.2 Trench3	Palawan Narra -3.2 Trench2	Palawan Narra -3.2 DH04	Palawan Narra -3.1 Hot Spring	Luzon Poonbato	Luzon Manleluag Hot Spring – M1*	Luzon Bigbiga - Well-1	Low alkali cement leachates (PNC 1997)**
採取年 Sample No.	2016 Narra1 San Isidro O	2016 Narra3-2 Trench5 O	2016 Narra3-2 Trench4 O	2016 Narra3-2 Trench3 O	2015 Narra3-2 Trench2 O	2016 PW-DH04 O	2016 Narra3-1 O	2013 P-2 G	2013 M1 G	2014 Well1 G	1997
pH	10.64	11.36	11.17	11.37	11.39	11.39	11.37	11.41	10.80	9.52	11.09
ORP(Eh) [mV]	-270	-152	-30	-111	-160	-119	-867	-111	-420	8	-
Temp [°C]	39.3	29.9	33.4	33.7	28.8	33.0	38.5	28.0	32.9	29.2	60
CH ₄ [ppm]	>700	0	0	0	0	0	200	> 5000	2090	0 (0~560)	-
H ₂ [ppm]	0	0	0	0	0	0	0	50~1320	0 (0~62)	0 (0~130)	-
Na ⁺ [ppm]	78.0	48.2	47.1	50.4	46.1	51.8	50.4	24.3	26.3	100.6	43
K ⁺ [ppm]	0.60	2.24	2.54	2.39	2.32	2.96	2.36	1.45	0.375	1.05	13
Ca ²⁺ [ppm]	3.70	44.8	36.4	48.5	26.9	22.4	50.6	92.5	29.9	1.63	16.8
Mg ²⁺ [ppm]	0	0	0.02	0.01	0.02	0.02	0.01	0.24	0.03	0.02	-
Si ²⁺ [ppm]	38	4.1	2.3	2.5	2.5	2.9	0.29	11	17	72.3	
Al ³⁺ [ppm]	0.29	0.13	0.10	0.08	0.08	0.06	0.13	1.41	1.05	0.97	0.3
Fe ⁽²⁺⁺³⁺⁾ [ppm]	0.01	0.01	0.03	0.05	0.02	0.03	0.01	0.18	< 0.001	0.0058	-
Cl ⁻ [ppm]	58.8	27.8	28.5	27.0	27.3	21.1	28.0	12.9	17.8	4.50	-
SO ₄ ²⁻ [ppm]	2.56	0	0.21	0.02	0.13	0.14	0.05	0.05	0.364	48.0	-
HCO ₃ ^{-*} [ppm]	11.3	3.6	2.1	0	0.67	2.8	0.5	1.6	30.0	135.6	-

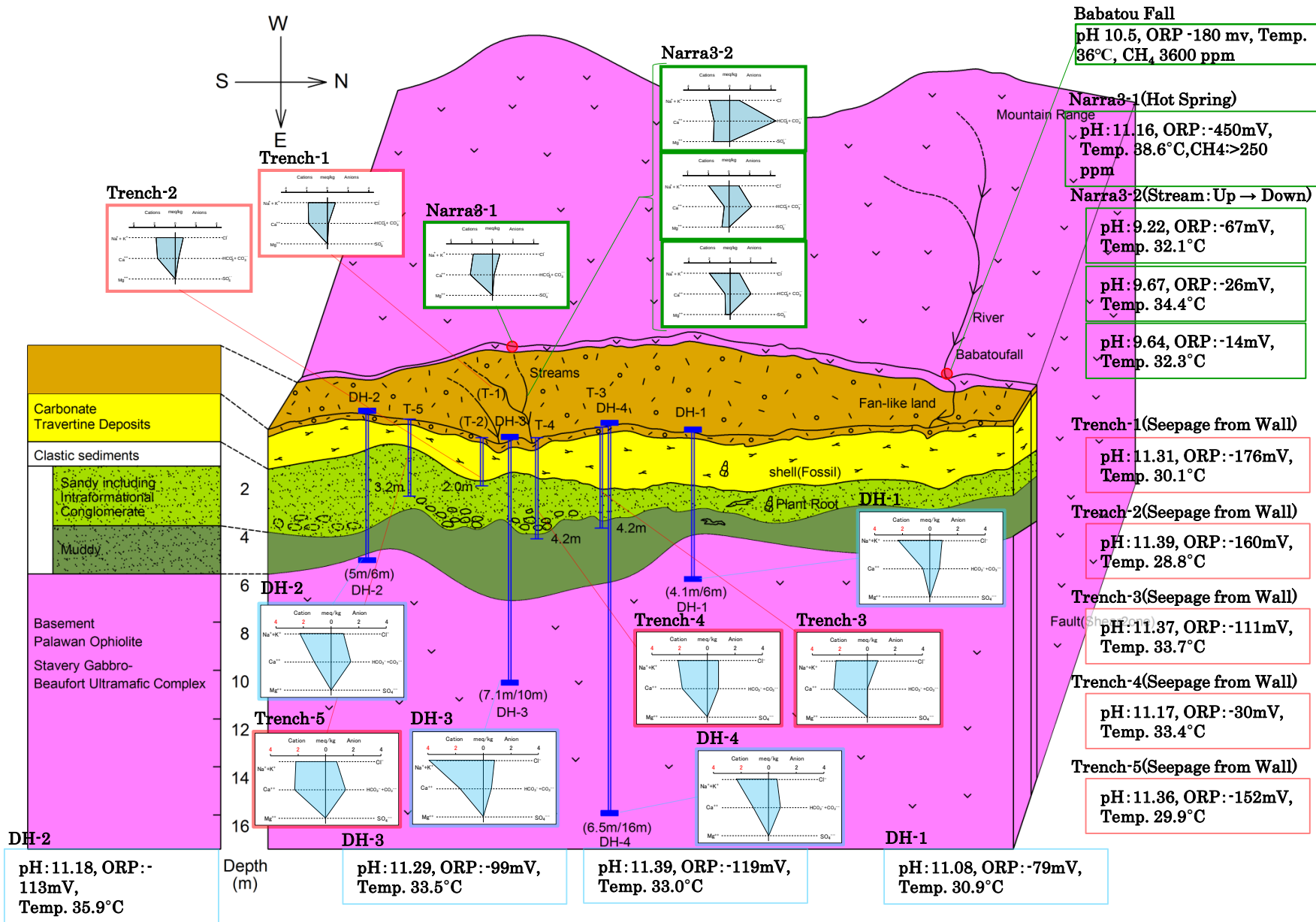
* wt % - Manleluag hot spring is located in the 2.7km SW of Saile mine

** wt % - Portlandite Cement: Silica Fume: Fly Ash=40: 20: 40

4.2 Narra Site – Investigation Points of Trench and Borehole



4.3 Conceptual Cross-Section at Narra site in central Palawan - Geological Structure and Groundwater Chemistry -



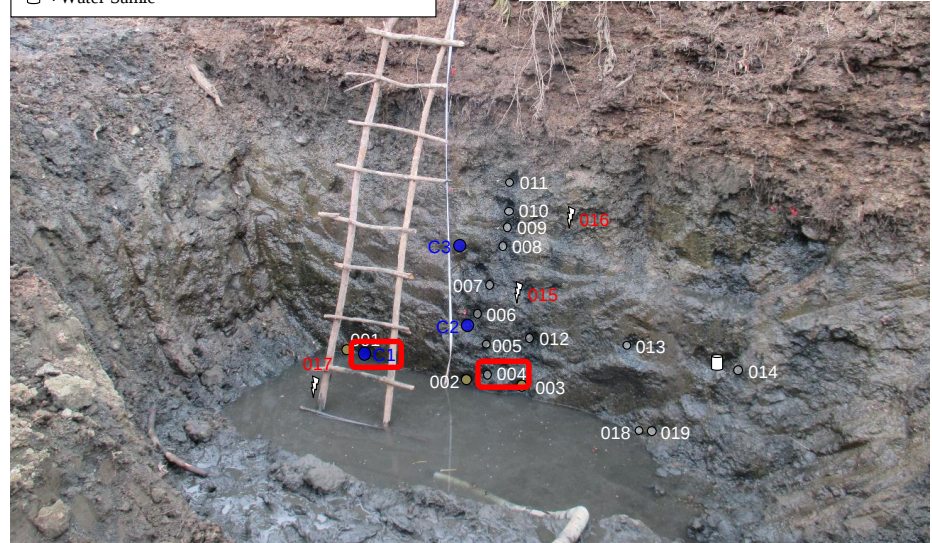
4.4 Trench Survey

Trench-3



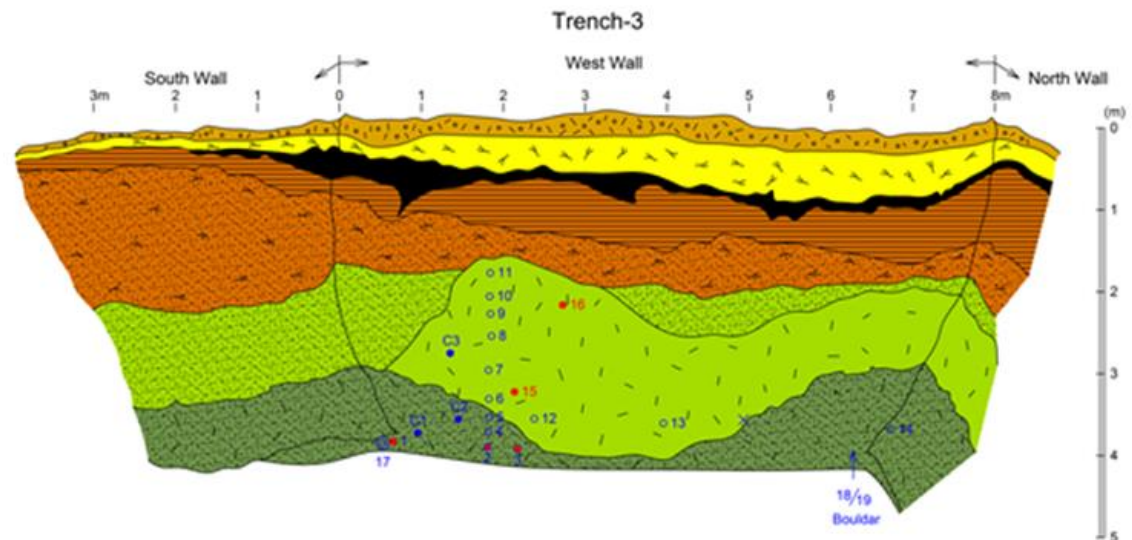
- : Clay Sample PWT03-16-Rh-004~014, 018~019
- : Clay Sample PWT03-16-Rh-001~003
- ⚡ : Dating Sample PWT03-16-Rh-015~017
- : Core Sample PWT03-16-C1-C3-001~005
- : Water Sample

Seepage water from Wall
pH: 11.37, ORP: -111 [mv]
Temp.: 33.7[°C]



Summary of Lithological Units and Legend in Narra

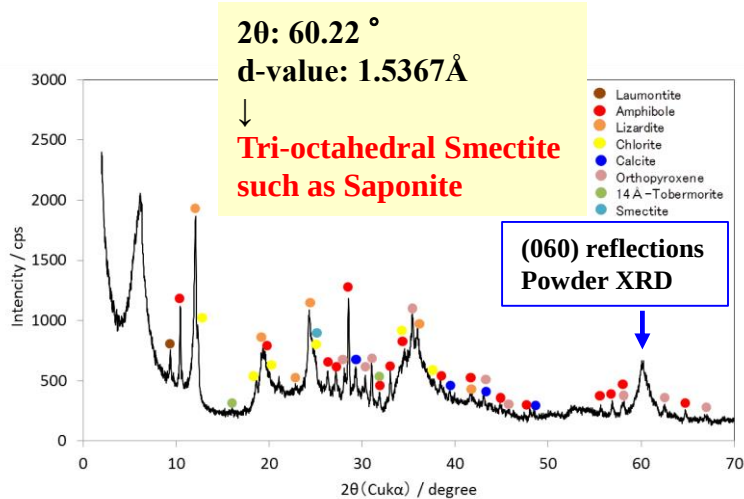
- | | | |
|----|--|---|
| 1 | | Alluvium unconsolidated deposits |
| 2 | | Pale brownish [or pale gray] and loosed Carbonate Sediment |
| 2A | | Pale brownish bedded(laminated) Carbonate Sediment |
| 2B | | Dark and pale brownish Massive Carbonate Sediment |
| 3A | | Carbonaceous and Sandy Clastic sediment |
| 3B | | Carbonaceous and Coarse-grained Sandy Clastic sediment |
| 4 | | Blackish Sandy Clastic sediment with patchy clayey matrix including boulder and pebble of Palawan Ophiolite |
| 5 | | Blackish Sandy Clastic sediment including granule of Palawan Ophiolite |
| 6 | | Blackish and fine-grained Sandy Clastic sediment with patchy clayey matrix |
| 7 | | Palawan Ophiolite(Harzbergite Basement) |
| 8 | | Organic Matter, likely buried Plant-Roots |
| 9 | | Occurrence of Living Shells |
| 10 | | Poorly sorted interformational Conglomerate (Conglomeratic Sandy Sediment) |



4.4 Trench Survey -XRD-

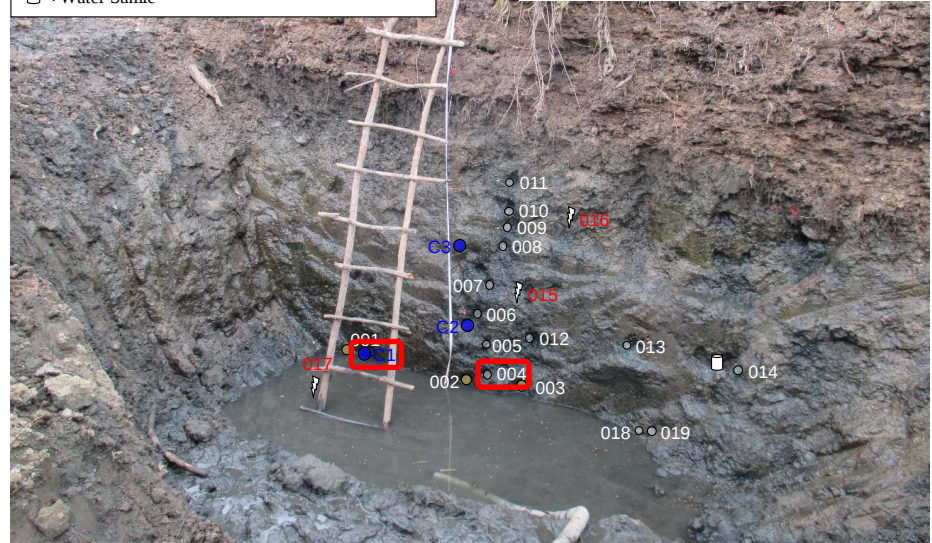
Trench-3

PWT03-16-Rh-004
(Powder XRD)

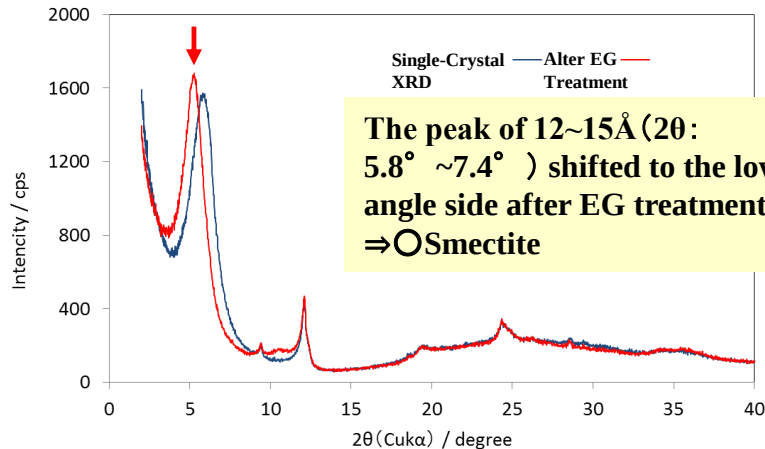


- : Clay Sample PWT03-16-Rh-004~014, 018~019
- : Clay Sample PWT03-16-Rh-001~003
- ⚡ : Dating Sample PWT03-16-Rh-015~017
- : Core Sample PWT03-16-C1-C3-001~005
- : Water Sample

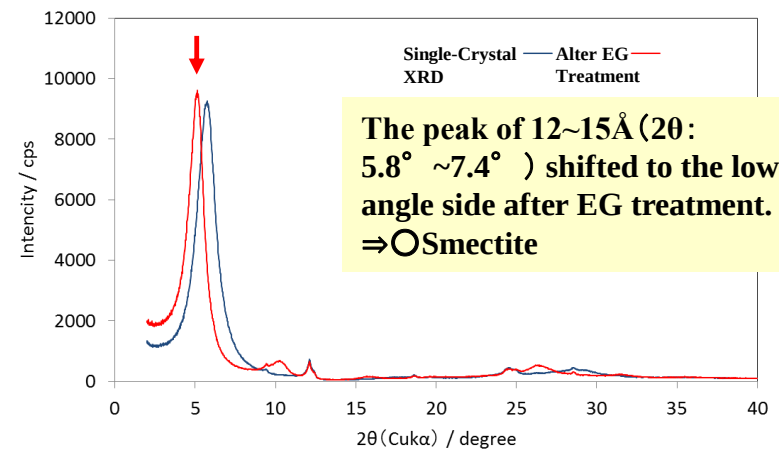
Seepage water from Wall
pH: 11.37, ORP: -111 [mv]
Temp.: 33.7[°C]



PWT03-16-Rh-004 (Single-Crystal XRD)



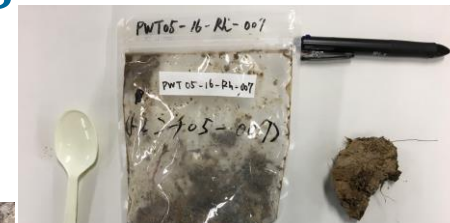
PWT03-16-C1-002 (Single-Crystal XRD)



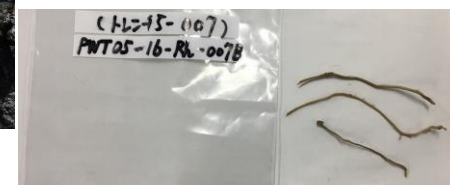
4.4 Trench Survey - ^{14}C Dating - Trench-5



- : Clay Sample PWT05-16-Rh-001~004
- : Clay Sample PWT05-16-Rh-008~013, 015, 016
- ⚡ : Dating Sample PWT03-16-Rh-005~007, 014
- : Core Sample PWT03-16-C1~C2-001
- : Water Sample



PWT05-16-Rh-007
Carbonate
 ^{14}C age: 1965 ± 46 year



PWT05-16-Rh-007B
Wooden Root (in Carbonate)
 ^{14}C age: 1209 ± 46 year



PWT05-16-Rh-005
Wooden branch (in Sediment)
 ^{14}C age: 2443 ± 46 year

PWT05-16-Rh-014
Clastic Sediment (Bottom)
 ^{14}C age: 9587 ± 56 year : Humic acid
 ^{14}C age: 9647 ± 56 year : Humin

PWT05-16-Rh-006
Shell (Semisulcospira libertina)
 ^{14}C age: 2401 ± 46 year

5.1 Mineralogical Evolution in Narra site

-Identified Minerals and Reactions with regard to Smectite Formation-

Magmatic Evolution and Tectonics of Palawan Ophiolite			Formation of Smectite in Ultramafic-originated Clastic Sediments		
Magmatic Differentiation	Rock Type	Emplacement Main Alteration	Weathering	Interaction between Mafic Minerals, Weathered Minerals and Alkaline Fluids	
Formation of Ultramafic Complex onto Oceanic Crust	Palawan Ophiolite (Ultramafic Complex) ◁mainly, Harzburgite, Gabbro▷	①Primary Serpentinization Opx(Ol, Cpx)→SP Br Tc (Mt) (Cc)	○Primary Minerals ◁Mafic Minerals▷ Opx Mg, (Fe, Al) Ol Mg, (Fe) (Cpx) Mg, (Fe), Ca (Amph*) Mg, (Fe), Al ◁Feldspathic Minerals▷ Plag Al, Ca ○Altered Minerals SP Mg Chl Al	Mg·Fe-Sap Tri-octahedral Smectite (Di-octahedral Smectite) Major Ion Mg, Fe, Al, Si	$\text{ExFe}^{3+}_2(\text{Al}_{0.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ Nont [Di-octahedral Smectite] Cal $\text{Ex}(\text{Mg,Fe})_3(\text{Al}_{0.33}\text{Si}_{3.67})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ Fe-Sap [Tri-octahedral Smectite] Fe-Sap[ppt] [Tri-octahedral Smectite] C-S-H $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot n\text{H}_2\text{O}$ Tobermolite $\text{Ca}_2\text{Si}_6\text{O}_8 \cdot 2\text{H}_2\text{O}$ Gyrolite M-S-H $\text{ExMg}_{5.84}\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ Stev[ppt] [Tri-octahedral Smectite] Sepiolite
		②Primary Chloritization Opx, Ol, Cpx, (Amph*) →Chl			*Si[from all minerals]

Legend

Sap: Saponite Nont: Nontronite Stev: Stevensite

Cc: Calcite C-S-H: Calcium Silicate Hydrate

M-S-H: Magnesium Silicate Hydrate

Qz: Quartz Plag: Plagioclase Mt: Magnetite

SP: Serpentine Ol: Olivine Br: Brucite

Opx: Orthopyroxenes Cpx: Clinopyroxenes

Tc: Talc Chl: Chlomite Amph: Amphibole

Cr: Cr-Spinel

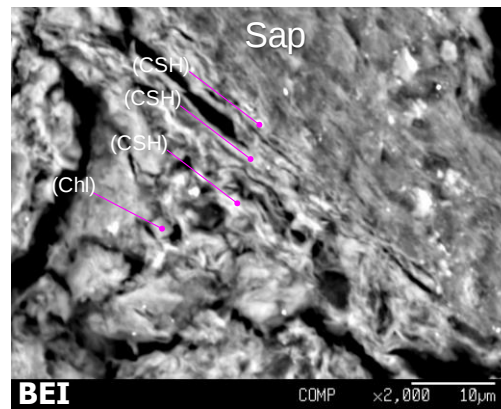
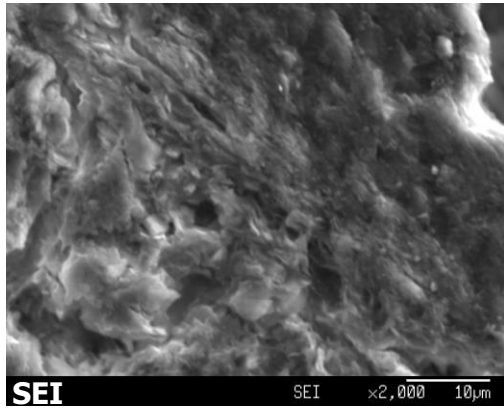
Legend

Sap: Saponite	Nont: Nontronite	Stev: Stevensite
Cc: Calcite	C-S-H: Calcium Silicate Hydrate	
M-S-H: Magnesium Silicate Hydrate		
Qz: Quartz	Plag: Plagioclase	Mt: Magnetite
SP: Serpentine	Ol: Olivine	Br: Brucite
Opx: Orthopyroxenes		Cpx: Clinopyroxenes
Tc: Talc	Chl: Chlomite	Amph: Amphibole
Cr: Cr-Spinel		

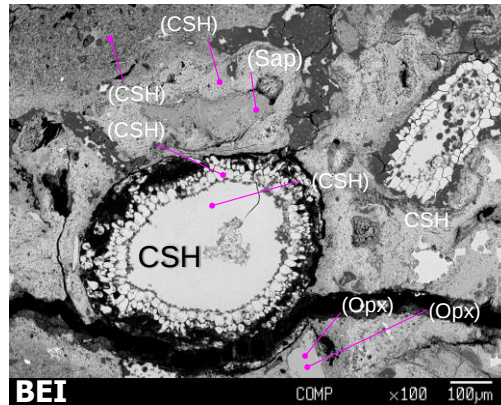
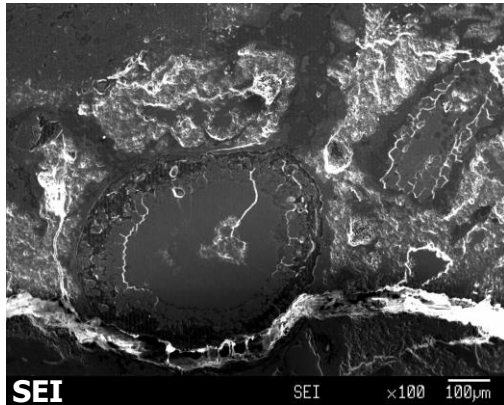
Amph*: Pargasite, (Cumingtonite, Actinolite, Tremolite) ppt: precipitation

5.1 Mineralogical Evolution in Narra site - Smectite coprecipitated with C-S-H -

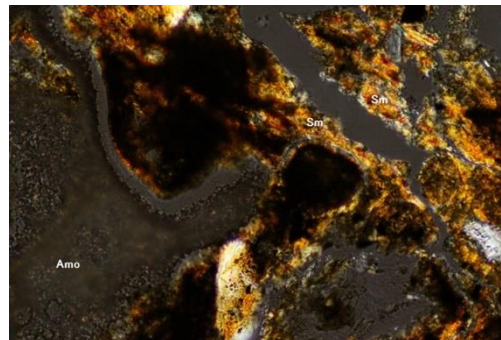
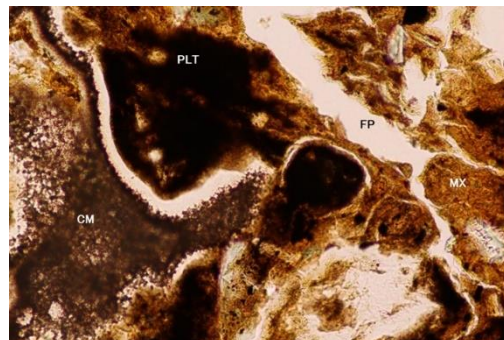
PWT02-15-
Rh-016



PWT02B-15-
C2-2-001

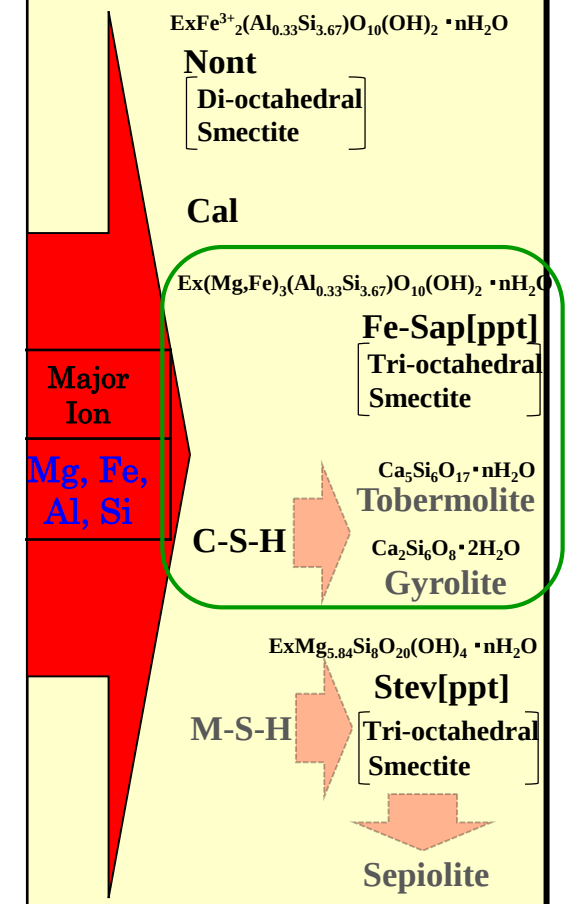


PWT03-16-
C2-001



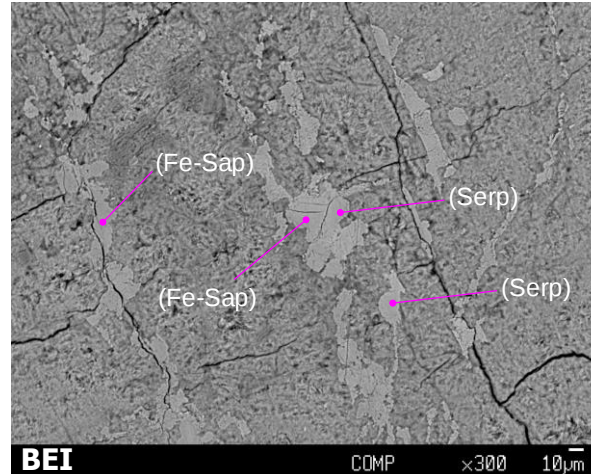
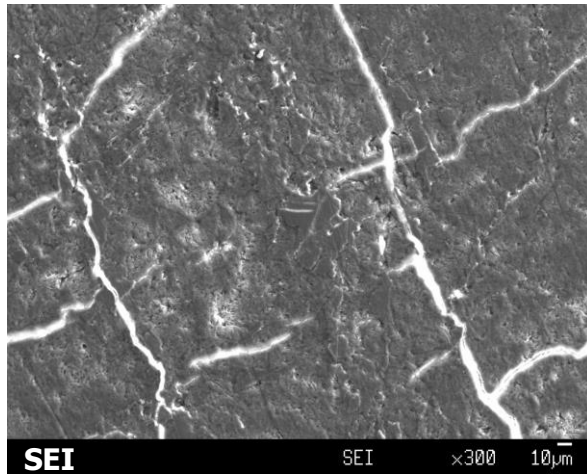
afic-originated Clastic Sediments

Interaction between Mafic Minerals,
Weathered Minerals and Alkaline
Fluids



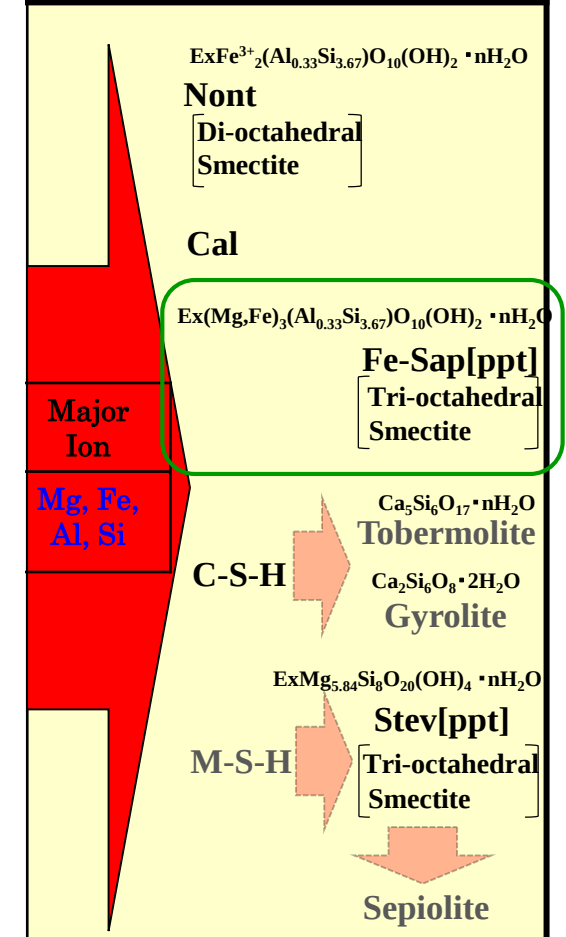
5.1 Mineralogical Evolution in Narra site - Smectite precipitated in grain boundary -

PWT02B-15-C2-2-001



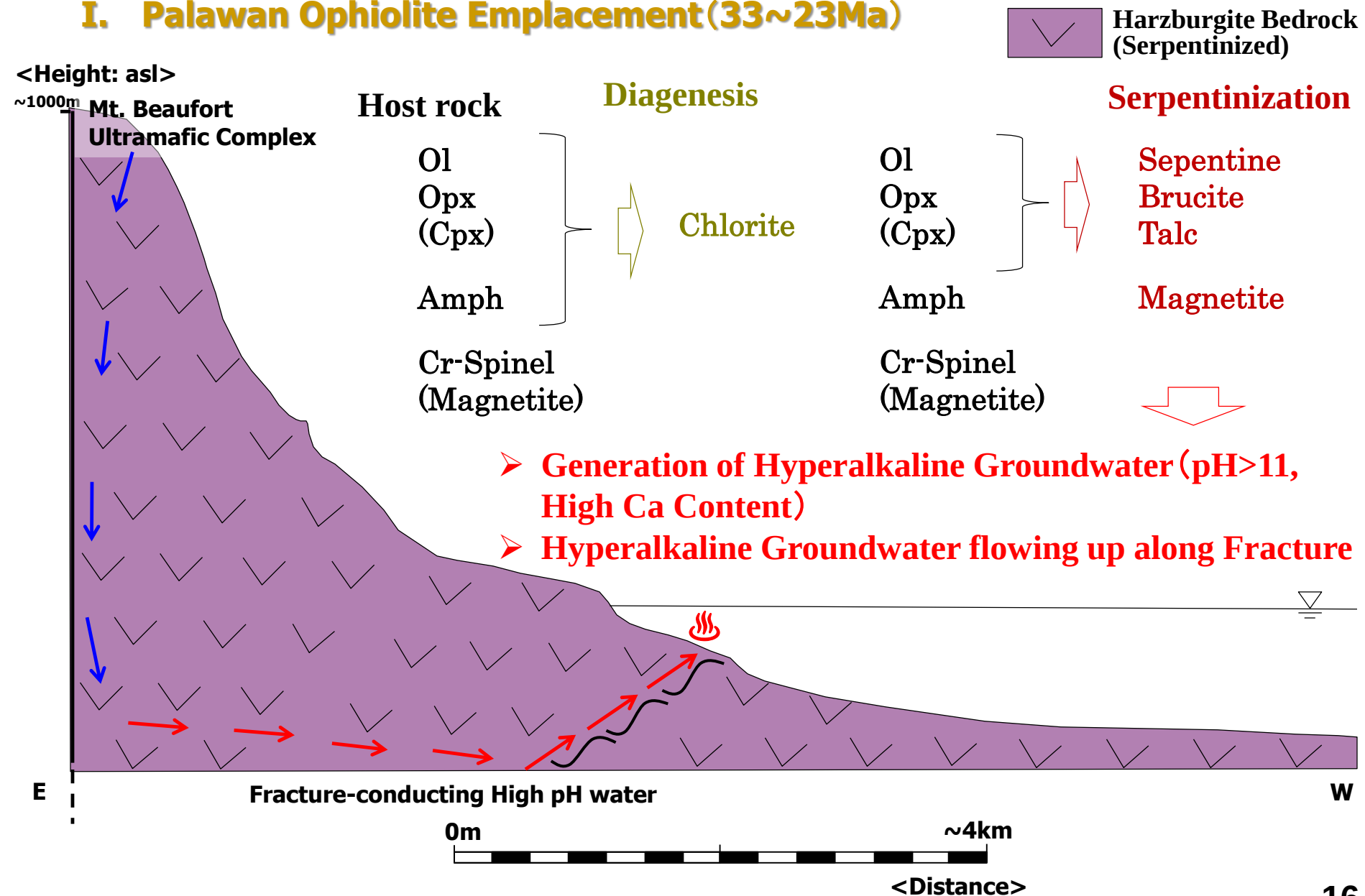
afic-originated Clastic Sediments

Interaction between Mafic Minerals,
Weathered Minerals and Alkaline
Fluids



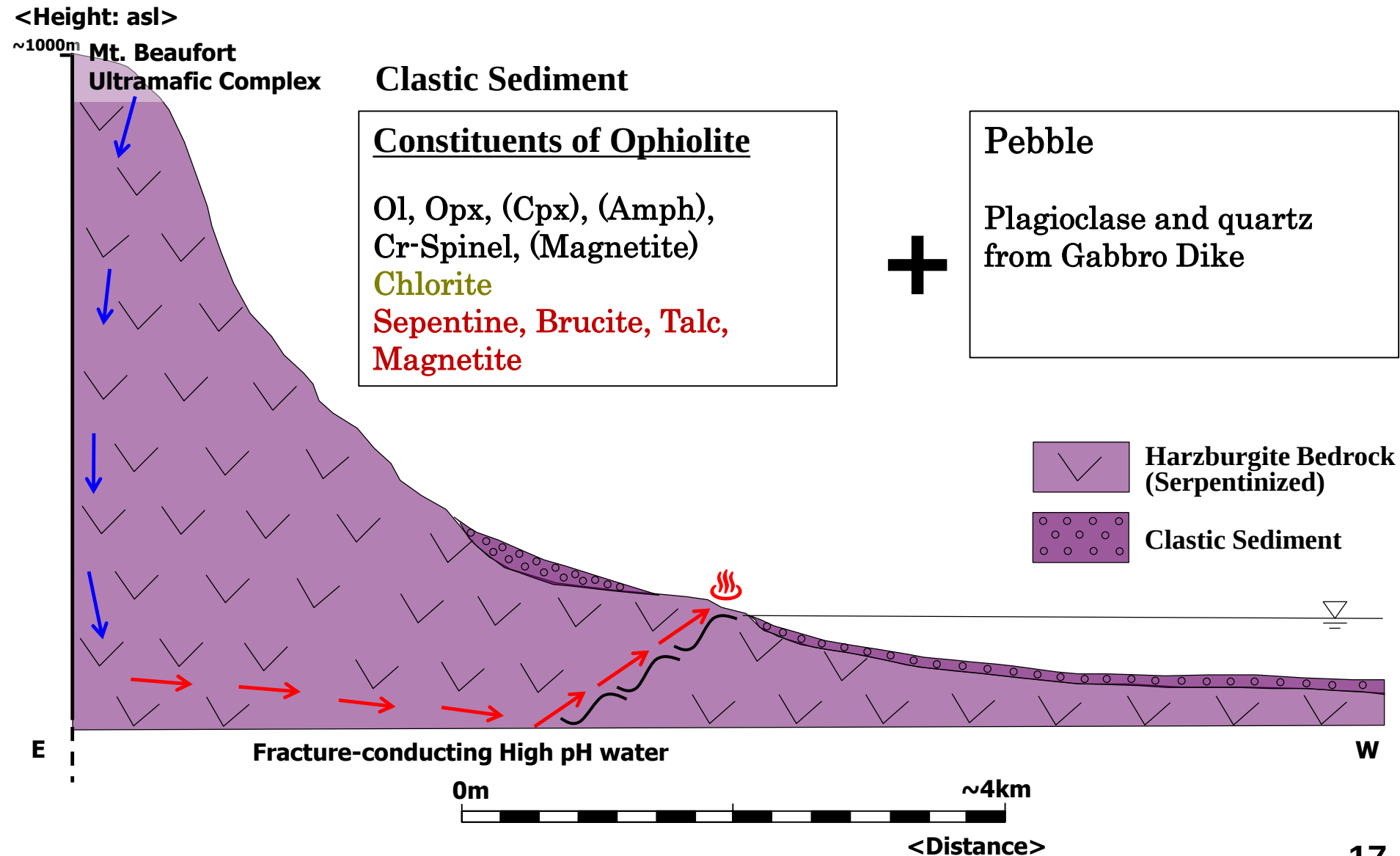
5.2 Tectonic Evolution of the Palawan Ophiolite and Smectite Formation in Clastic Sediment

I. Palawan Ophiolite Emplacement (33~23Ma)



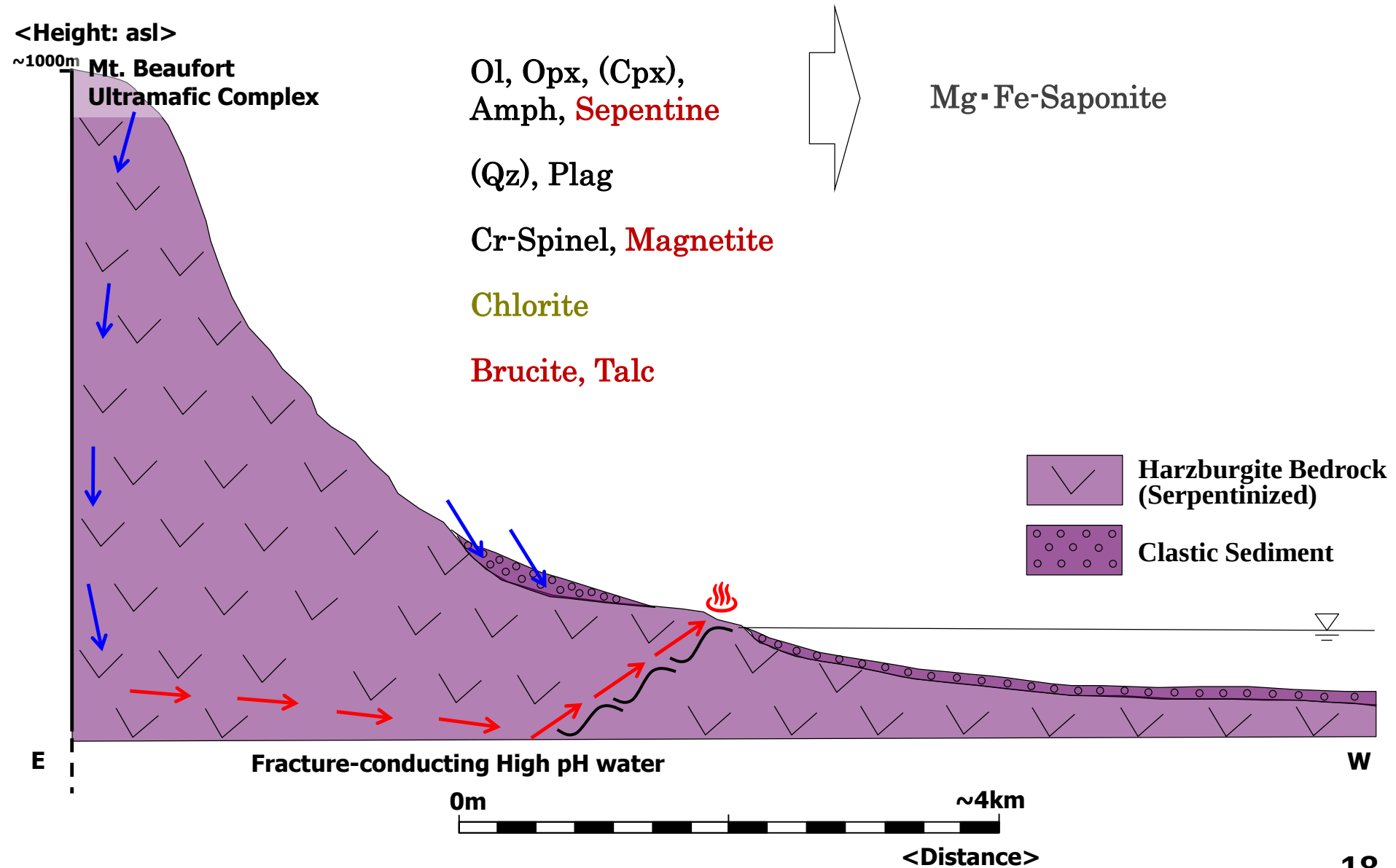
5.2 Tectonic Evolution of the Palawan Ophiolite and Smectite Formation in Clastic Sediment

II. Uplift-Erosion-Transport-Deposition(Clastic Sediment)



5.2 Tectonic Evolution of the Palawan Ophiolite and Smectite Formation in Clastic Sediment

III. Formation of Smectite by Weathering

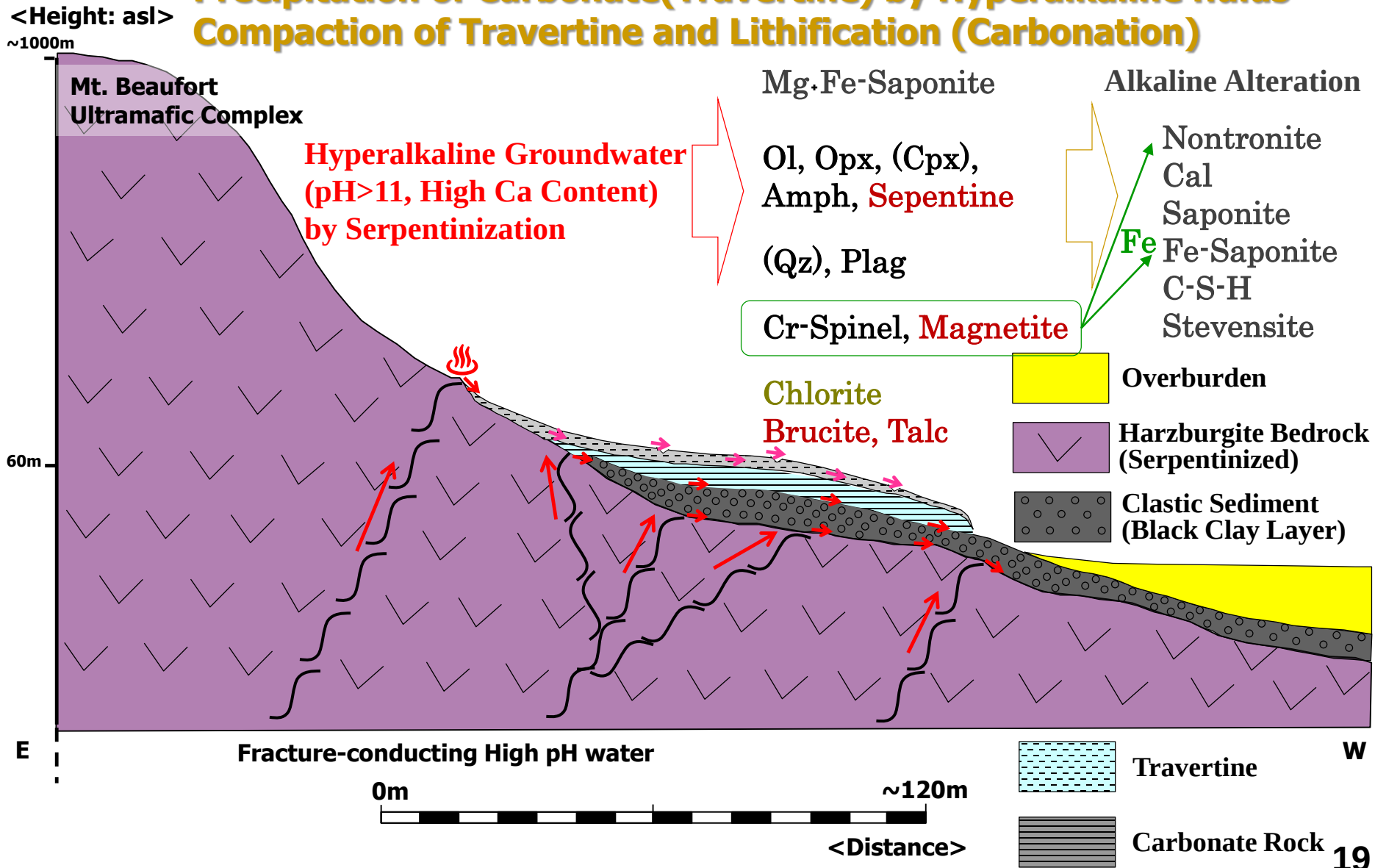


5.2 Tectonic Evolution of the Palawan Ophiolite and Smectite Formation in Clastic Sediment

IV. Formation of Smectite by Hyperalkaline Fluids

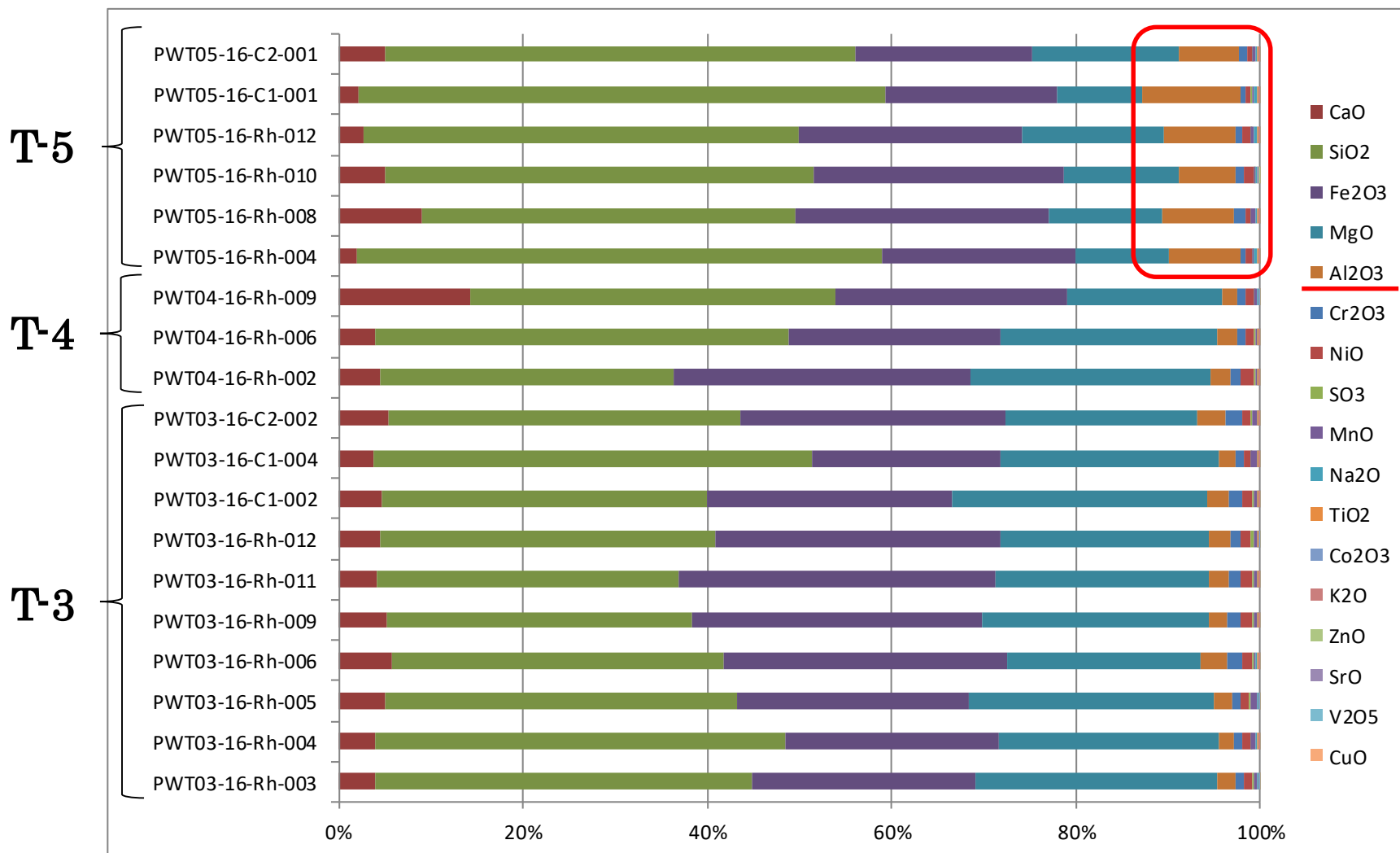
Precipitation of Carbonate(Travertine) by Hyperalkaline fluids

Compaction of Travertine and Lithification (Carbonation)



6.1 XRF

Trench-3~5



➤ The Sediment of Trench-5 has more Al_2O_3 and less MgO than that of Trench-3 and 4.

6.2 Mineral Assemblage - XRD (Trench) -



	Clay mineral		Amphibole	Pyroxene	Serpentine	C-S-H	Carbonate	Zeolite
	Smectite	Chlorite	Amphibole	Orthopyroxene	Chrysotile	14ÅTobermorite	Calcite	Laumontite
PWT02-15-Rh-016	● Tri-octahedral	▲	△	△	○	△	△	△
PWT03-16-Rh-004	● Tri-octahedral	●	○	△	○	△	△	△
PWT03-16-Rh-006	○ Tri-octahedral	○	△	○	○	△	△	△
PWT03-16-Rh-009	○ Tri-octahedral	○	△	△	○	△	△	△
PWT03-16-Rh-011	○ Tri-octahedral	○	○	△	○		○	△
PWT03-16-Rh-012	○ Tri-octahedral	○	○	○	○		△	△
PWT03-16-C1-002	●	●	○	○	○		△	△
PWT03-16-C1-004	●	●	○	○	○		△	△
PWT03-16-C2-002	○ Tri-octahedral	○	○	△	○	△	△	△
PWT04-16-Rh-002	○ Tri-octahedral	○	△	○	○		△	△
PWT04-16-Rh-006	○	○	○	△	○		△	△
PWT04-16-Rh-009	▲ Tri-octahedral	●	△	△	○	△	△	△
PWT05-16-Rh-004	○ Di-octahedral	○	○	△	△		△	△
PWT05-16-Rh-008	○ Tri-octahedral	○	○	○	△		○	△
PWT05-16-Rh-010	● Di-octahedral	●	△	△	△		△	△
PWT05-16-Rh-012	○ Di-octahedral	○	○	△	○		△	△

※Black Symbol means identification by Single-Crystal XRD with EG treatment.

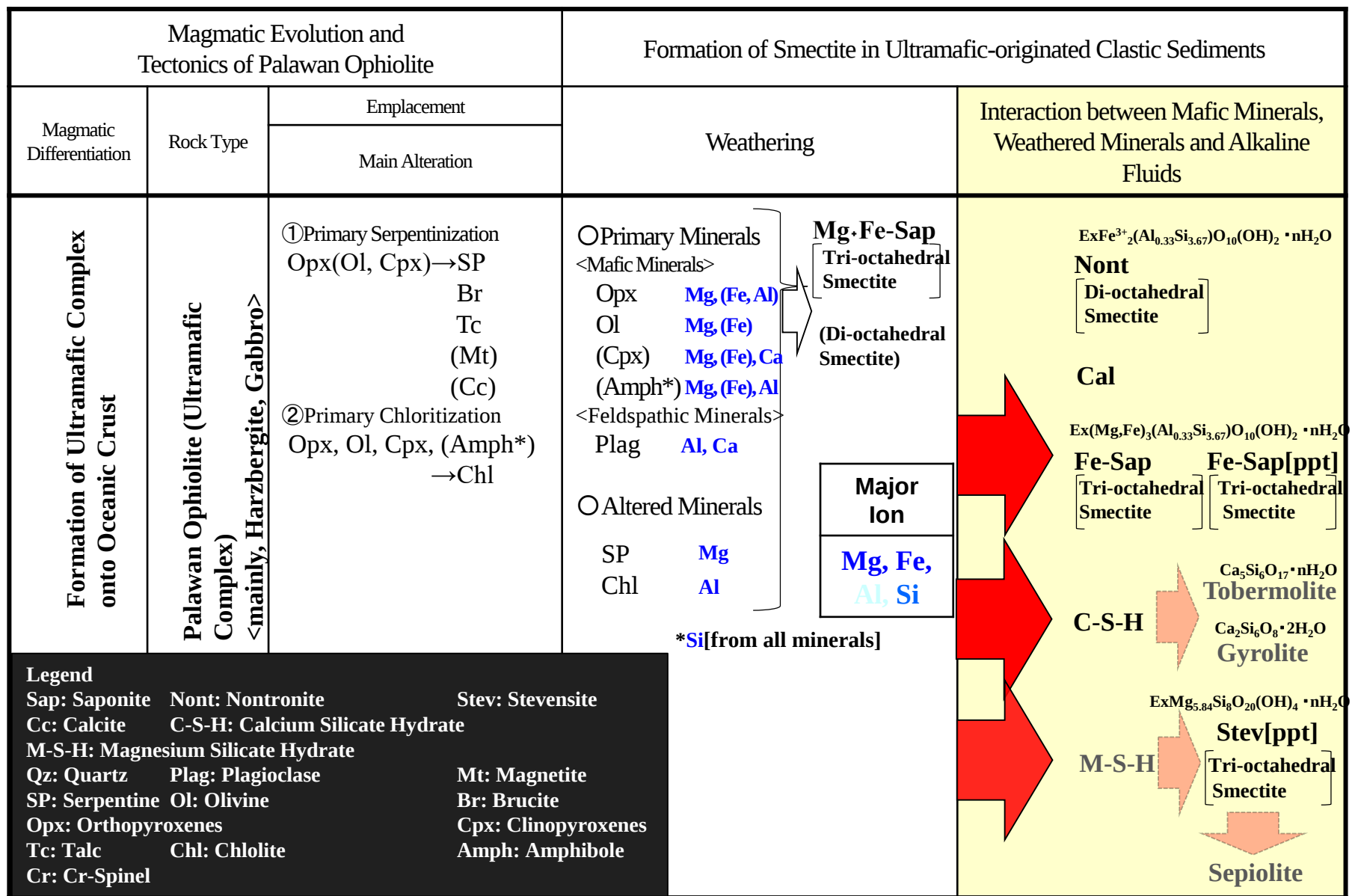
6.3 Mineral Assemblage - μ -XRD (Trench) -



Sample ID	Chrm	Mag	Cpx	Opx	Serp	Plag	Ca-Amph	Cum	Act	Chl	Stev	Sap	Nont	Cal	C-S-H	Unknown
Trench-3																
PWT03-16-Rh-004	○	○	×	⊙	○	×	○	○	○	⊙	○	⊙	×	×	⊙	
PWT03-16-C1-004	○	○	×	⊙	○	○	○	○	○	○	○	⊙	×	×	×	
Trench-4																
PWT04-16-Rh-006	○	○	×	⊙	○	○	○	○	○	×	○	⊙	×	×	×	
PWT04-16-Rh-009	○	○	×	⊙	○	○	○	○	○	×	×	⊙	×	○	⊙	
Trench-5																
PWT05-16-Rh-008	○	×	⊙	○	×	×	○	○	○	⊙	×	⊙	×	⊙	×	
PWT05-16-Rh-010	○	○	○	○	○	○	⊙	×	○	⊙	×	○	⊙	×	×	

6.4 Formation of Smectite under hyealkaline condtion in Narra site

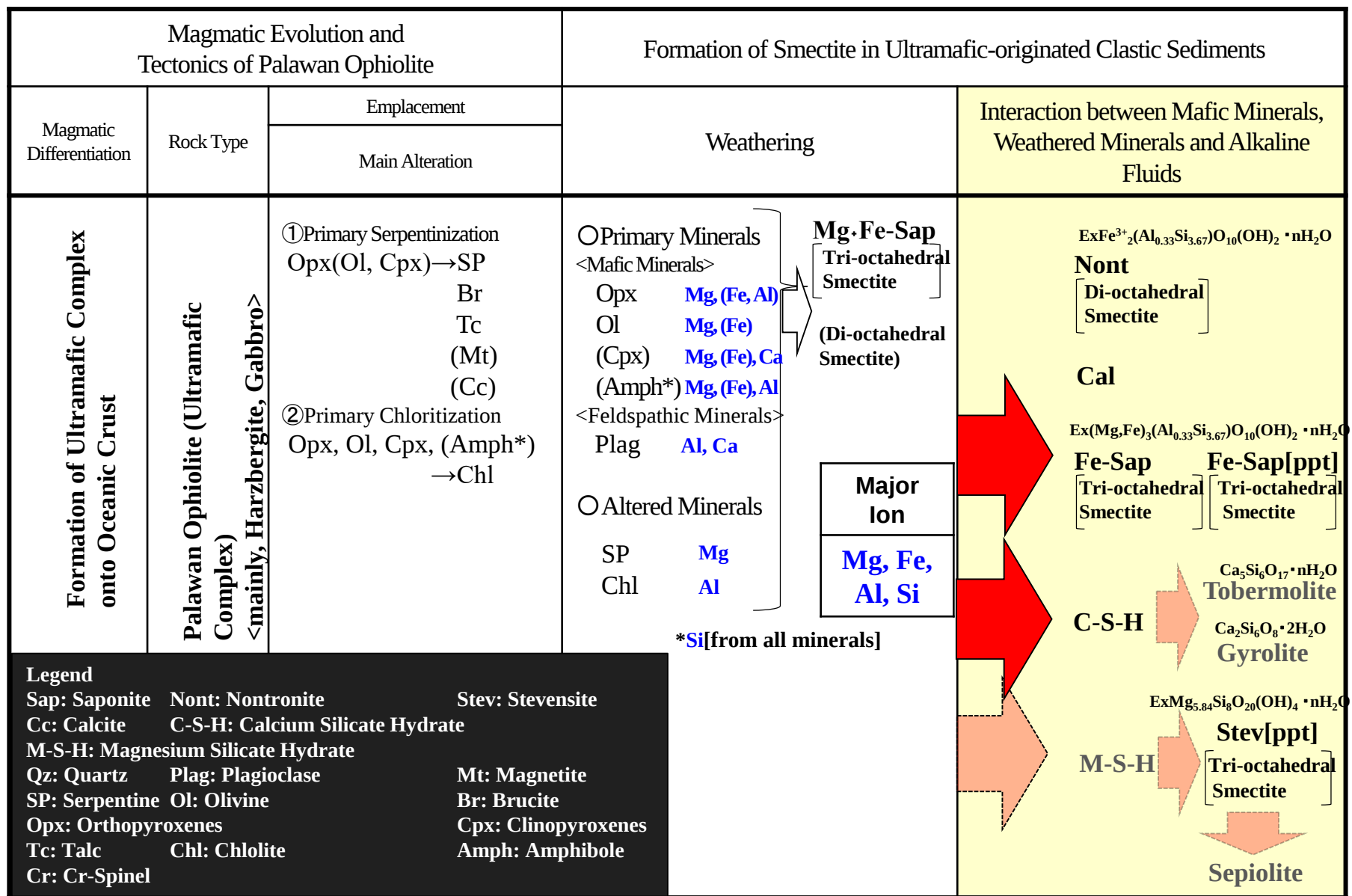
-Environment with little Al (Trench-3 and 4)-



Amph*: Pargasite, (Cumingtonite, Actinolite, Tremolite) ppt: precipitation

6.4 Formation of Smectite under hyealkaline condtion in Narra site

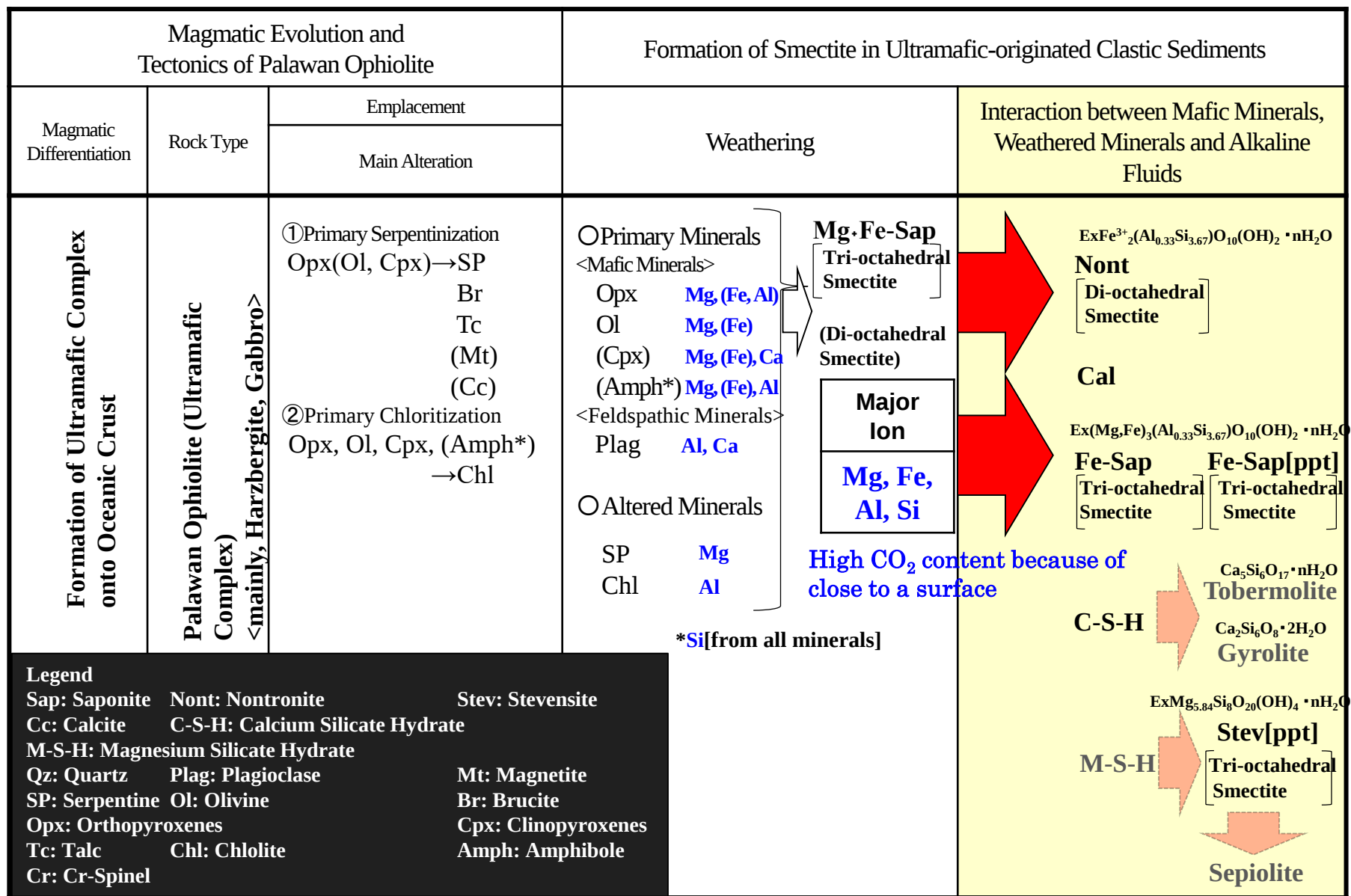
-Environment supplied Al from the pebbles of gabbro oringin (Trench-5)-



Amph*: Pargasite, (Cumingtonite, Actinolite, Tremolite) ppt: precipitation

6.4 Formation of Smectite under hyealkaline condtion in Narra site

-Environment with high CO₂ partial pressure (The upper part of Trench-5)-



Amph*: Pargasite, (Cummingtonite, Actinolite, Tremolite) ppt: precipitation

7. Summary

➤ Natural Evidences of Narra in Palawan

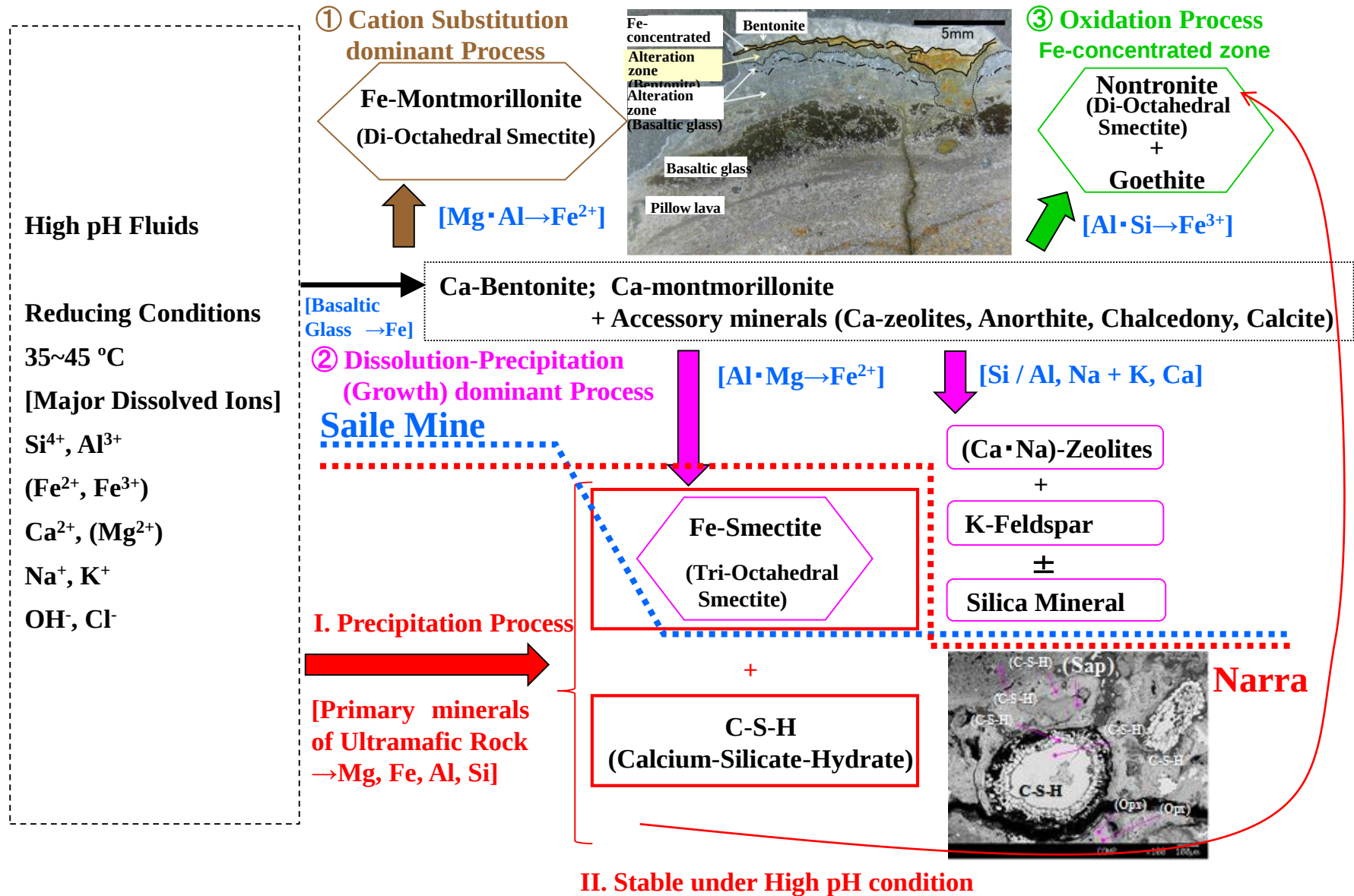
1. The smectite various type ((Mg-)Saponite, Stevensite, Fe-Saponite and Nontronite) was identified in clastic sediment under hyperalkaline (pH>11, low Eh, 35~45°C and high Ca content) condition by serpentinization.
2. C-S-H coprecipitated with (Fe-)Saponite. This evidence show that (Fe-)Saponite was precipitated from hyperalkaline groundwater.
3. Primary minerals of Clastic Sediment are olivine, orthopyroxenes, clinopyroxenes, amphibole of ultramafic rock origin and plagioclase in the pebbles of gabbro origin. Smectite was mainly formed as a result of the interaction between these minerals and hyperalkaline groundwater. A part of smectite may have been formed by weathering of these minerals.
4. Fe, Mg, Si, Al and Ca in the hyperalkaline fluid affected the formation of smctite.



- Could we use these natural evidences as a natural analogue of EBS system, especially analogous to bentonite?

7. Summary

— Alkaline Alteration Process shown from the natural analogues in the Philippines —



7. Summary

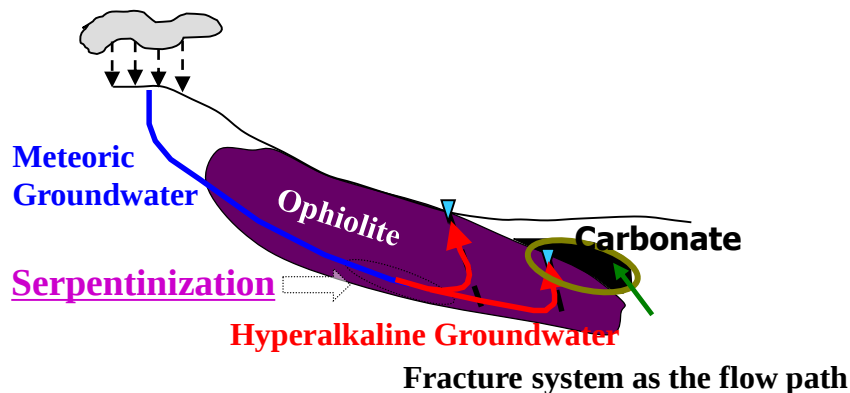
Hyperalkaline Fluids from much of cement materials in the TRU repository.

Decreasing the desirable functions of bentonite as a buffer from
Dissolution of Smectite (Montmorillonite)

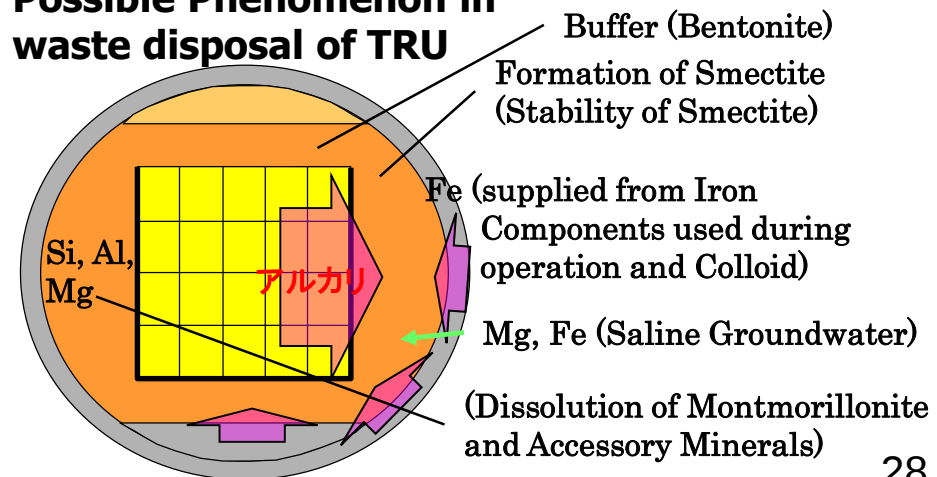
Formation and Stability of Smectite

- Natural Analogue at Narra site supports the latter, the positive reaction.
- The worst scenario is that montmorillonite alters non-swelling mineral (zeolite, chlorite and illite). Natural Analogues in the Philippines can show a type of Smectite (Montmorillonite) altered another type of smectite (Saponite, Nontronite etc) under hyperalkaline with Fe, Mg condition and that suggests Hyperalkaline fluid make not much decrease the desirable functions.

NA of Narra in Palawan



Possible Phenomenon in waste disposal of TRU



A photograph of a field site under a clear blue sky with scattered clouds. In the foreground, there is a muddy, uneven ground with some small pools of water. A person wearing a white shirt, light-colored pants, and a hat stands on the left side of the frame. In the background, there are green bushes and trees, and a few other people are visible further back. A large white text overlay is centered in the middle of the image.

Thank you for your kind attention.