The International Philippines Natural Analogue Project (IPNAP)

- NA studies for bentonite reaction under hyperalkaline conditions -

The 12th NAWG Workshop

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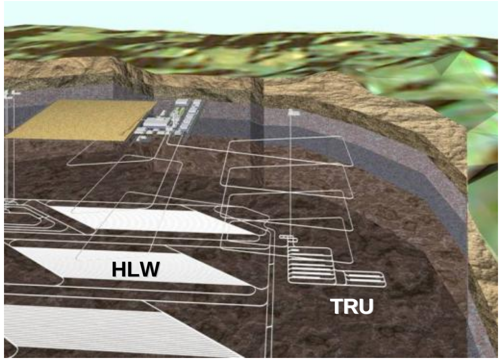
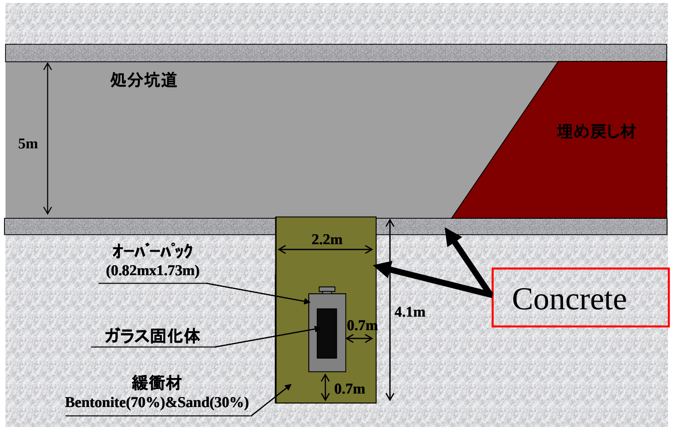
○N. Fujii, M. Yamakawa, J. Owada (RWMC, Japan)
T. Sato, K. Fujita(Hokkaido Univ., Japan)
N. Shikazono, M. Oi(Keio Univ., Japan)
C.A. Arcilla, C.S. Pascua(Univ. of the Philippines, Philippines)
K. Namiki, H. Kawamura(Obayashi Co., Japan)
R. Alexander(Bedrock Geosciences, Switzerland)

Contents

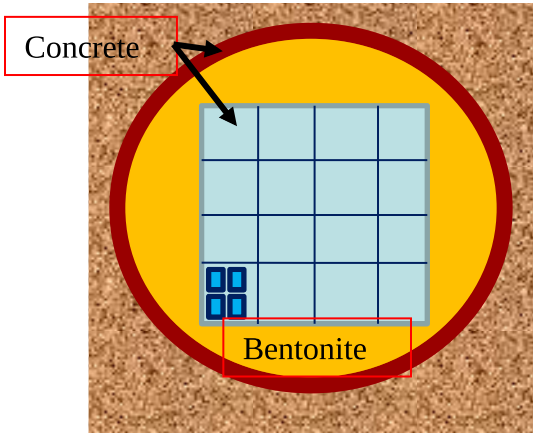
1. Background

- The long-term alteration phenomenon of bentonite using cement materials is a key issue of the waste disposal in Japan.





"HLW"



"TRU"

- Bentonite is unstable at high pH caused by cement leachates.

↳ Ophiolites have been identified as sources of high pH groundwaters.

- The reaction rates of between bentonite and high pH fluids are so slow as to be difficult to observe.

↳ Natural Analogues can be applicable in geological time scale.

1. Objectives

Natural Analogues

- NA study is to find out Natural Analogous phenomenon to understand Geochemical behavior of Bentonite Reaction, and evaluate long-term stability(longevity) of Bentonite under hyperalkaline conditions.
- NA could play a valuable role to bridge Dispparity in Realism and Timescales between Laboratory Experiments and Systems represented in Repository Performance Assessment.
- NA could contribute Modelling to make a Robust Safety Case.

Main task

- To better understand Long-term stability of Bentonite in contact with Water Analogous to low alkali cement leachates
  - Key Process
  - Reaction Pathway
  - Environment Condition
- To establish comprehensive scenario of Bentonite Reaction
- To provide Data-sets for Improvement of Performance Assessment Modelling

1. 1st phase IPNAP Plan (2007~2011)

2007	2008	2009	2010	2011	2012~

Literature research

Saile Mine (Fossil Type)

Preliminary survey

- Outline investigation of geology

- Geological survey
- Groundwater survey
- Trench survey
- Boring survey

Main survey of NA

- Chemical and mineralogical analysis
- Geological survey and fracture system evaluation
- Groundwater survey
- Trench survey

- Geochlonometry
- Chemical and mineralogical analysis
- Groundwater survey and simulation
- Trench survey

- Modeling
- Geochlonometry
- Chemical and mineralogical analysis

Bigbiga or Poonbato (Active Type)

Preliminary survey

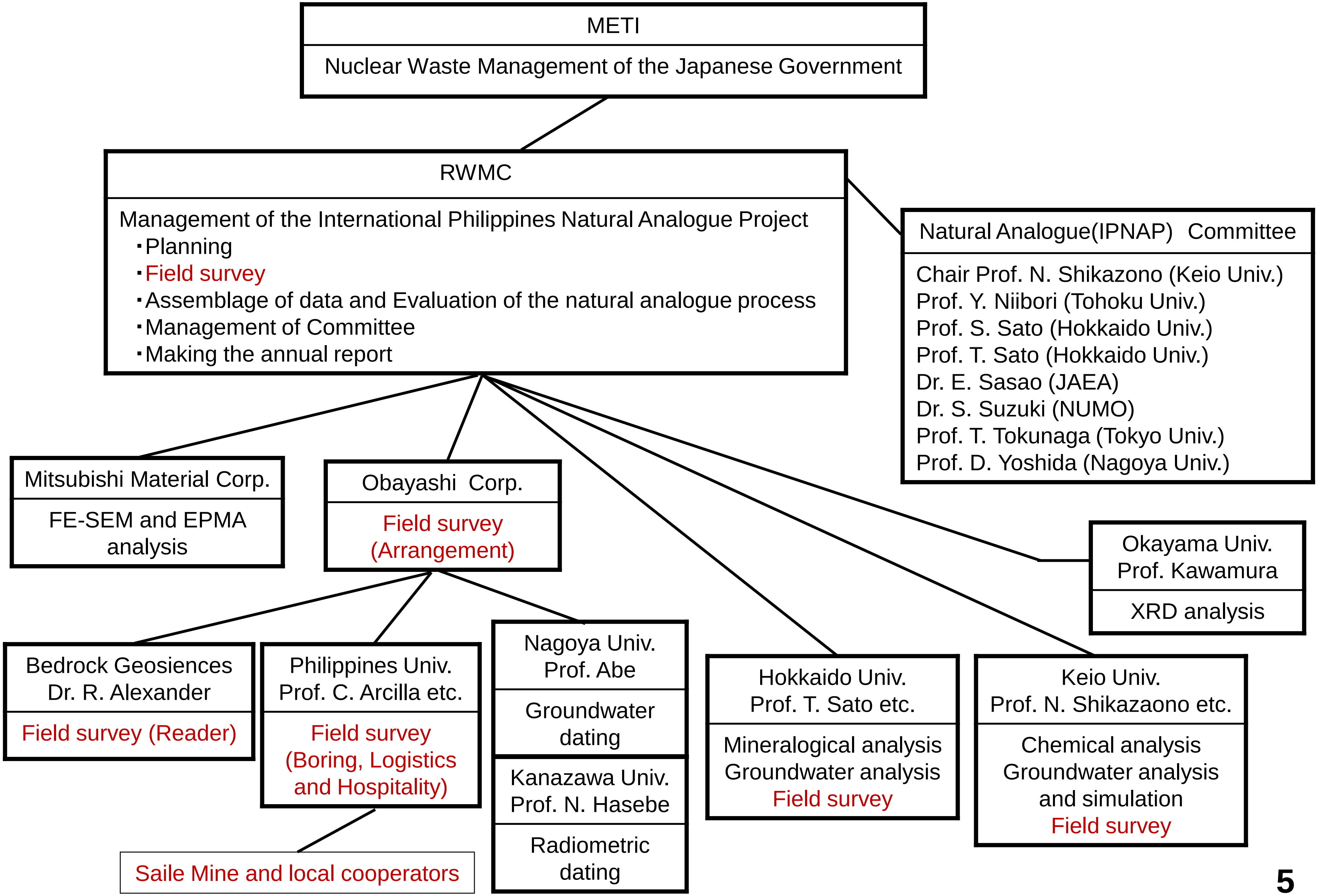
- Geological survey and fracture system evaluation
- Groundwater survey

- Geological survey
- Boring survey
- Groundwater survey
- Trench survey
- Chemical and mineralogical analysis

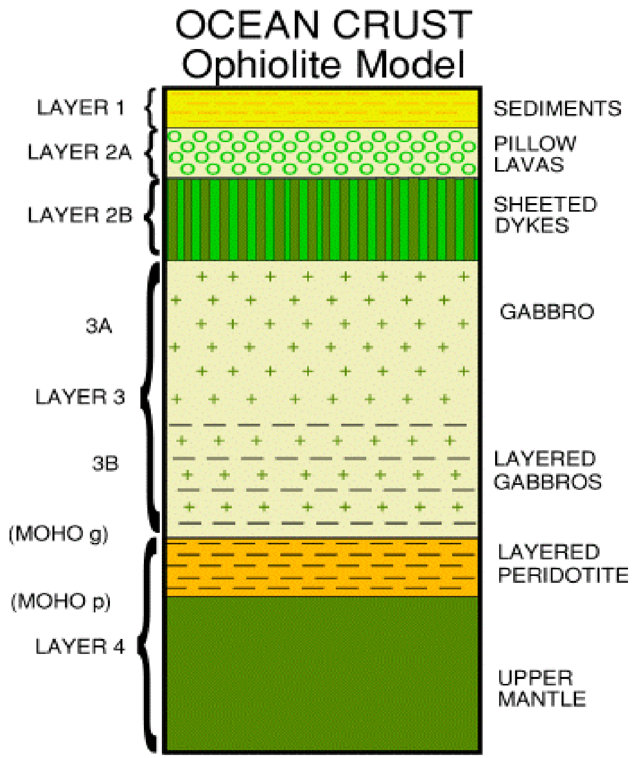
Main survey of NA

- Boring survey
- Groundwater survey
- Chemical and mineralogical analysis

1. Organization-System



2. Concept of Natural Analogue



We focus on serpentinizing "Ophiolite" now as environment which generates hyperalkaline groundwater.

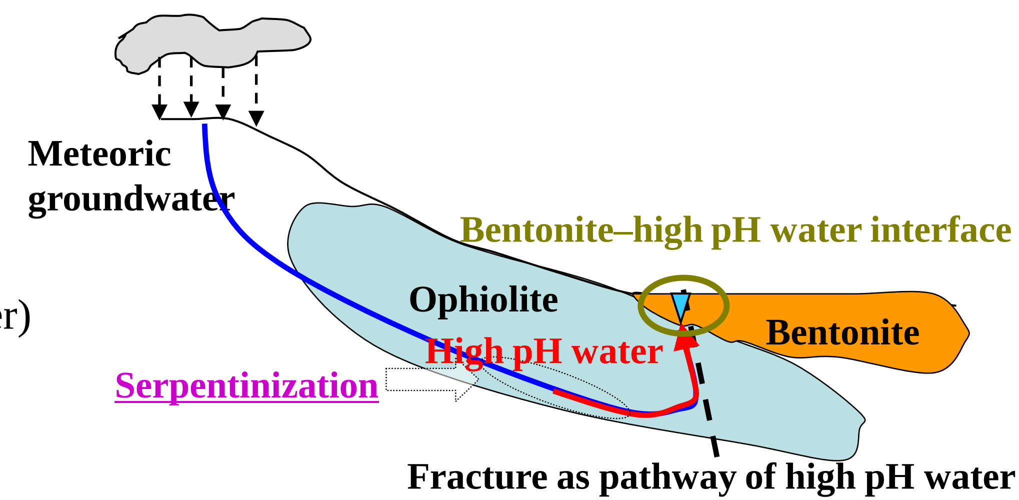
Serpentinization of Ophiolite (Ultramafic Rocks)

Water-Ultramafic Rocks Interaction

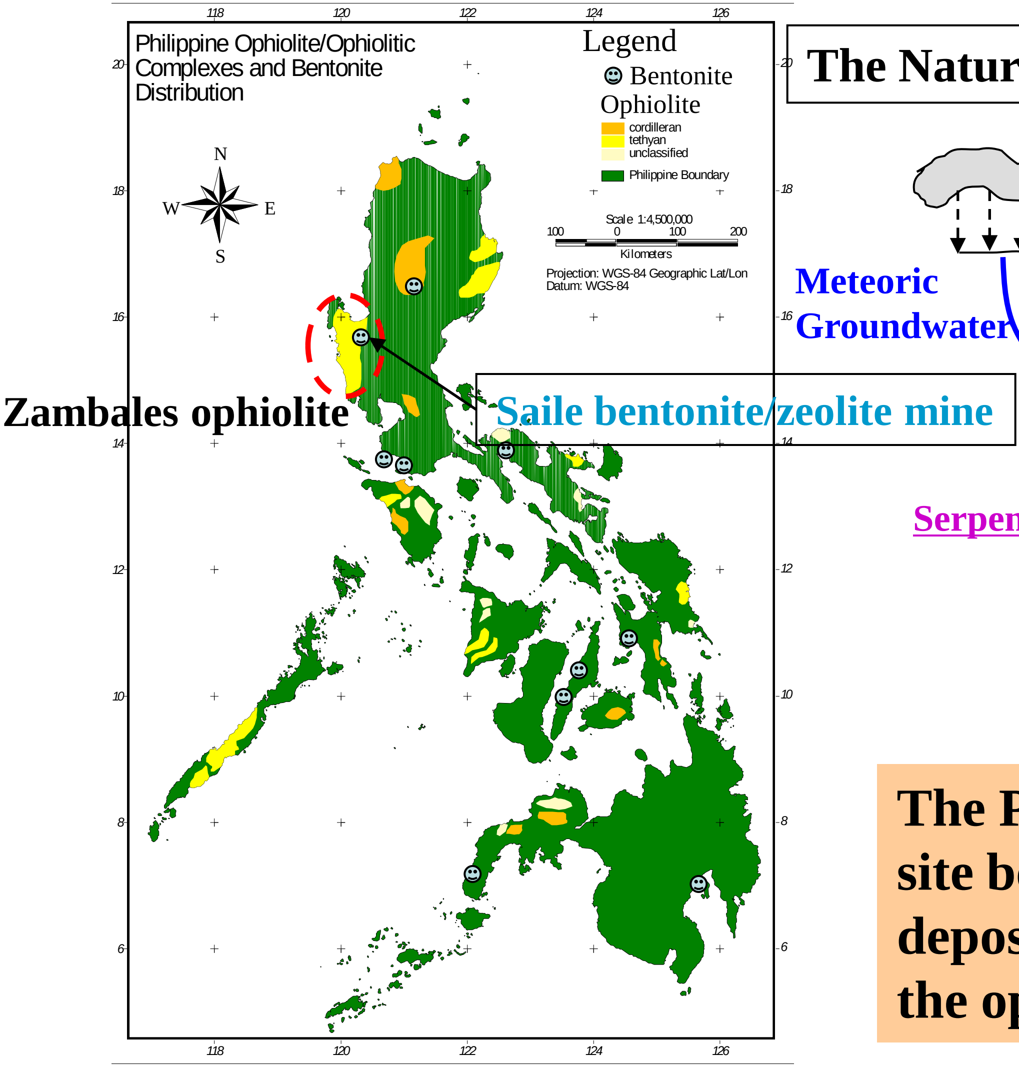
(1) Dissolution of Olivin / Pyroxenes
(2) Precipitation of Serpentine Mineral Assemblages
(3) Precipitation of Carbonates
(4) Production of OH^- (High pH condition)
(5) Generation of Gas mixtures
(6) Exothermic Reaction (Hot Spring)
(7) Reduicing Condition

Essential components for supporting concept of NA

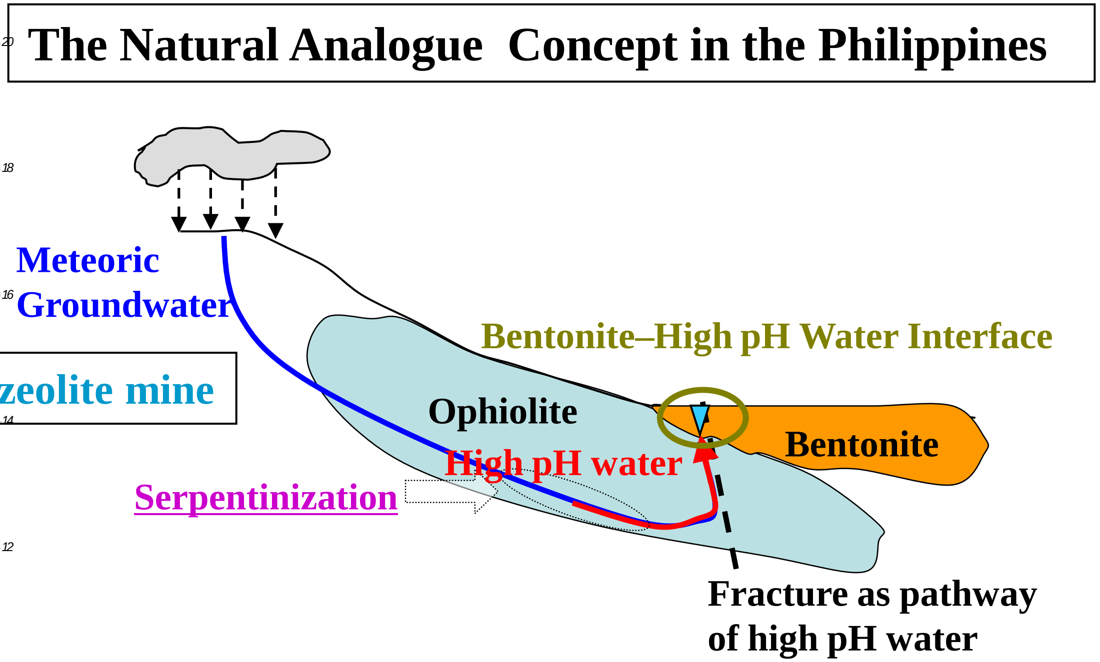
(1) Bentonite layer (Bed)
(2) High pH water (Fluid)
(Generation of hyperalkaline groundwater)
(3) Pathway of High pH water
(Bentonite – high pH water inteface)



2. Why Philippines ?

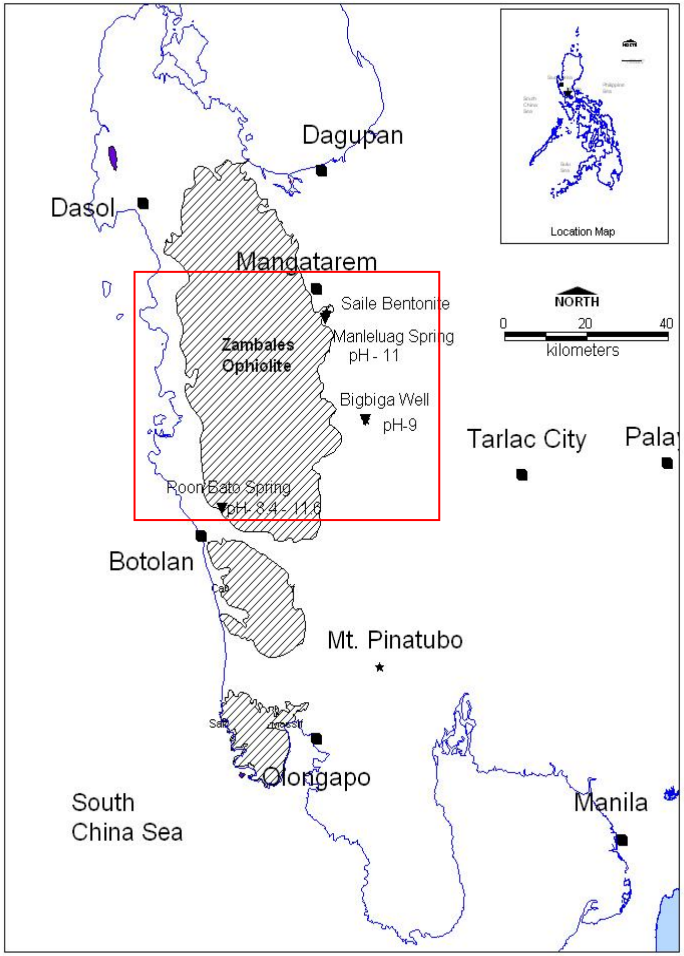


Distribution of Opiolite and Bentonite deposits in the Philippines

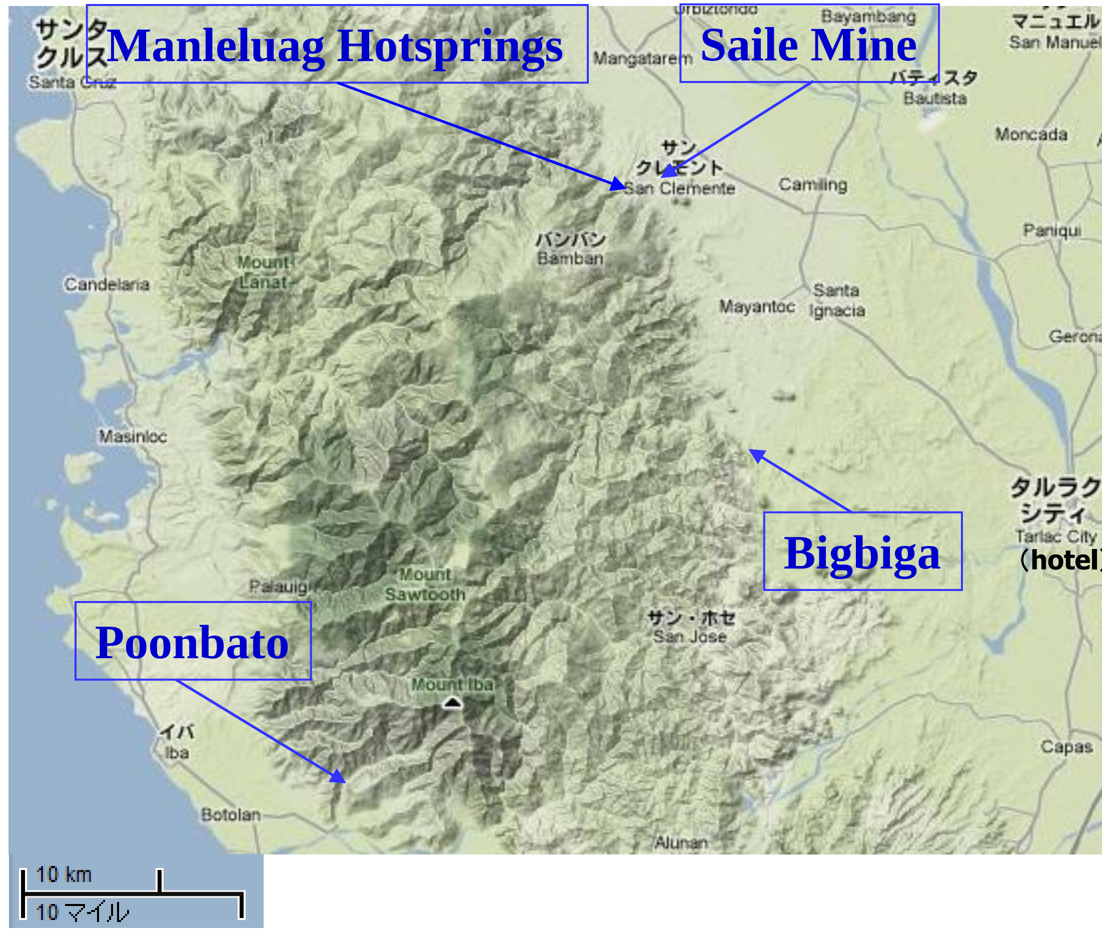


The Philippines was selected as research site because of existence of bentonite deposits near hyperalkaline springs in the ophiolite basement.

3. Survey Area



Zambales Ophiolite

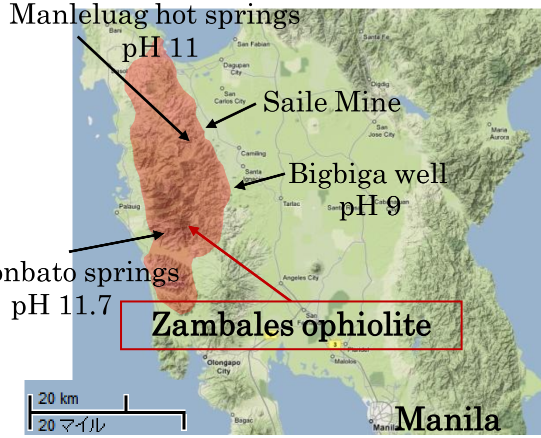


Survey site
(West central area of the island of Luzon)

3. Groundwater Chemistries of Survey Site

Site	Manleluag HSp. - M1	Manleluag HSp. - M2	Manleluag HSp. - M3	Saile Mine	Poonbato	Bigbiga Well	low alkali cement leachates (PNC 1997)*
Sample No.	MA-10-HWP-01	MA-10-HWP-02	M3-10-HWP-03	SM-10-HWP-01	PB-10-HWP-01	BB-10-HWP-06	
pH	11.08	10.75	10.83	6.73	11.69	9.09	11.09
ORP(Eh) [mV]	-713	-682	-496	65	56	252	-
Temp [℃]	34	34.1	34	27.9	27.4	30.1	60
CH_4 [ppm]	1140	470	2200	0	>5000	0 (0~560)	-
H_2 [ppm]	150	53	230	0	50~1320	0 (0~130)	-
Na^+ [ppm]	24.0	24.9	25.1	11.4	21.6	107	43
K^+ [ppm]	5.24	0.764	0.045	nd	36.4	0.215	13
Ca^{2+} [ppm]	323	68.3	95.4	84.4	182	0.599	16.8
Mg^{2+} [ppm]	2.98	0.054	0.06	44.1	0.147	0.092	-
Al [ppm]	0.463	0.242	0.336	0.02	0.103	0.012	0.3
Cl^- [ppm]	6.98	6.88	7.14	0.703	0.226	1.543	-
SO_4^{2-} [ppm]	0.502	0.413	0.330	0.081	0	1.332	-

*Mix Proportion – Portland cement: silica fume: fly ash = 40: 20: 40



Manleluag Hsp.- M1

Manleluag Hsp.- M3

The groundwater chemistry is analogous to low-alkali cement leachates.

3. Geological map of Mangatarem (Manleluag Hotspring / Saile Mine)

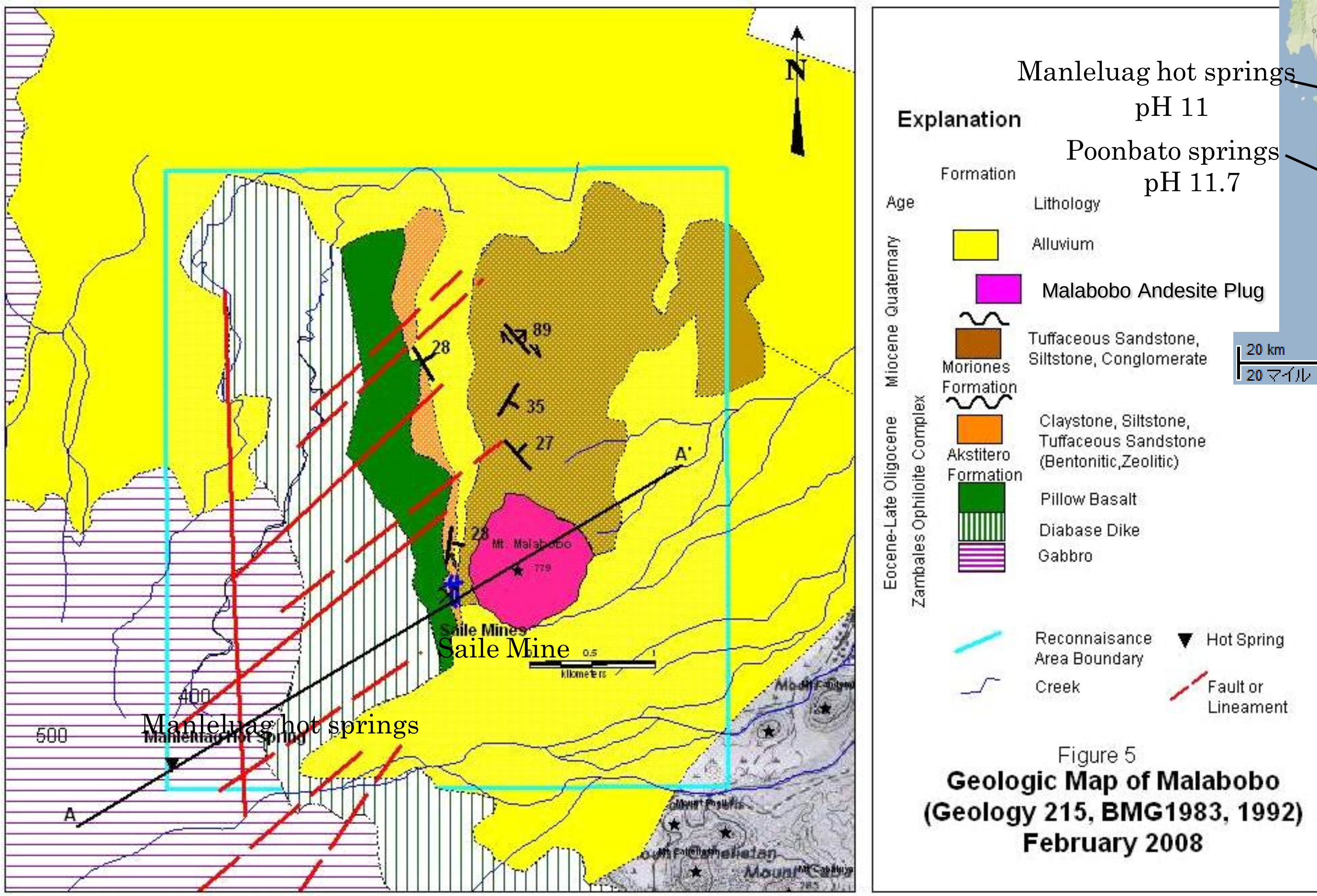
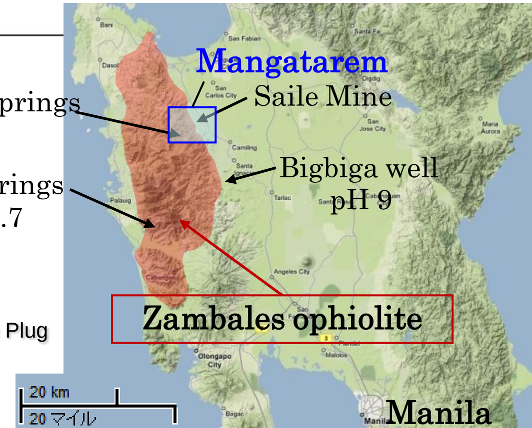
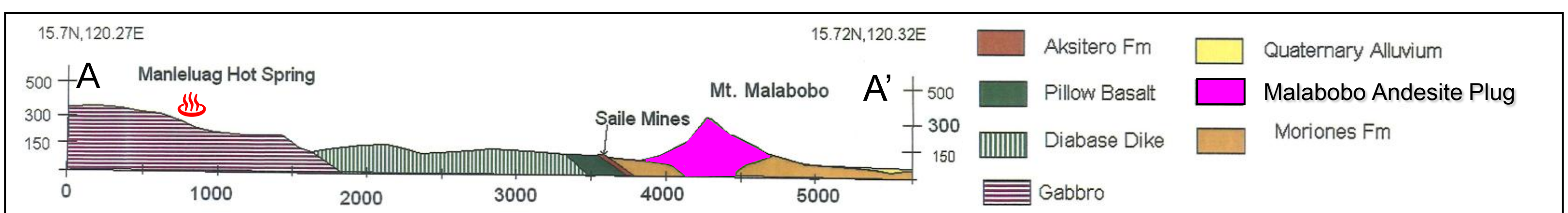


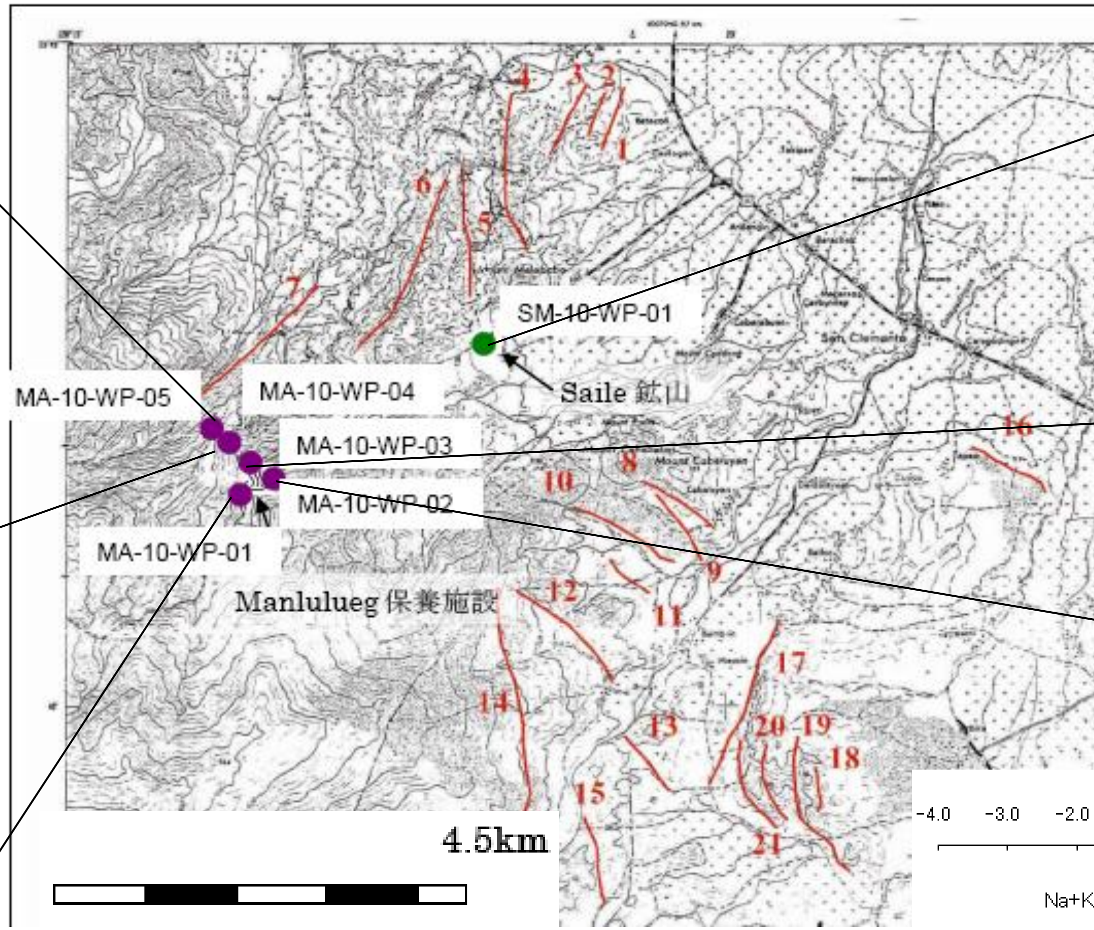
Figure 5
Geologic Map of Malabobo (Geology 215, BMG1983, 1992) February 2008



Saile Mine Quarry



3. Groundwater Chemistries
（Manleluag Hotspring / Saile Mine）



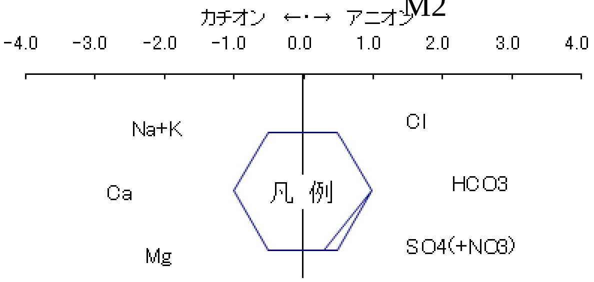

Saile Mine Well


M3

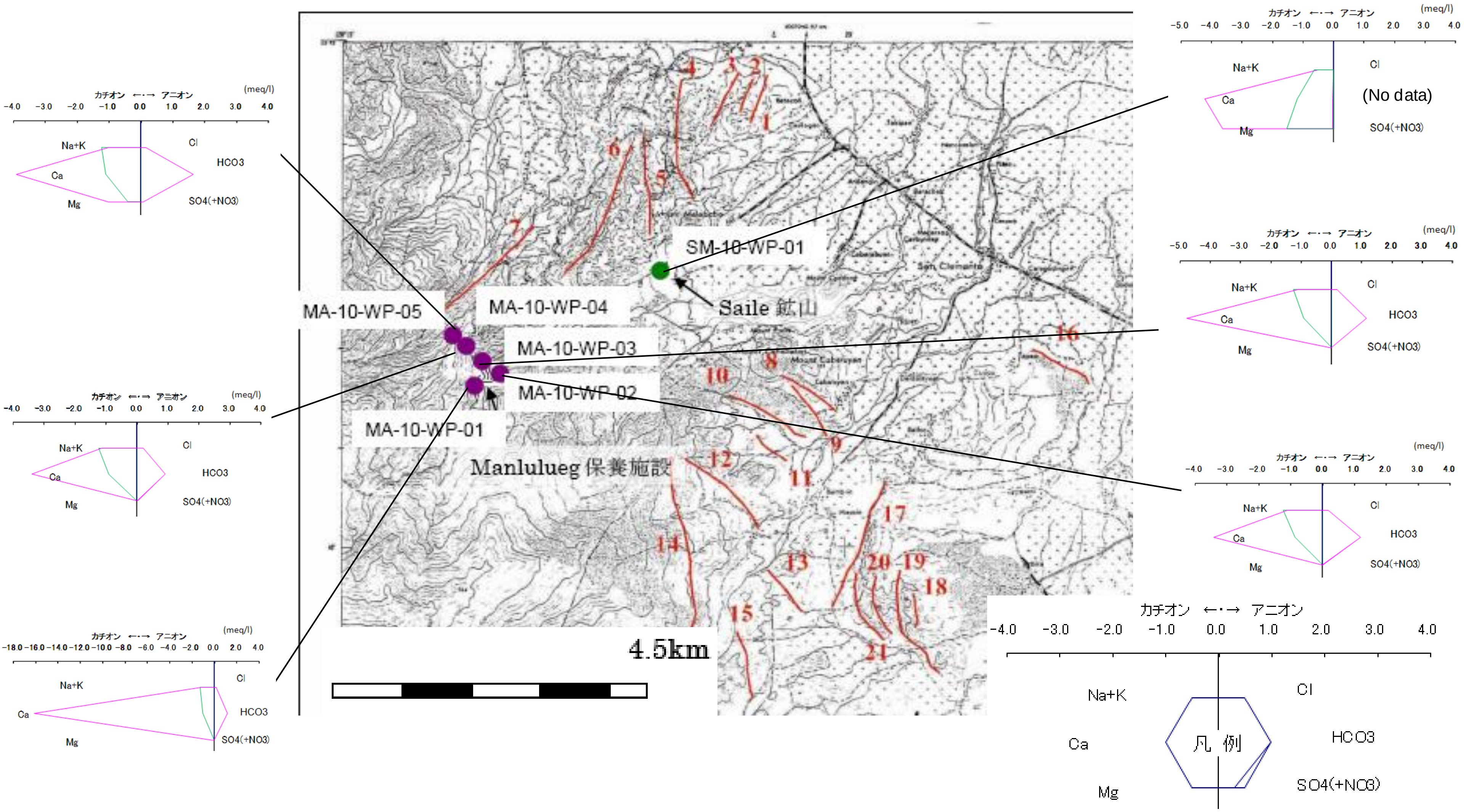

M2


M4

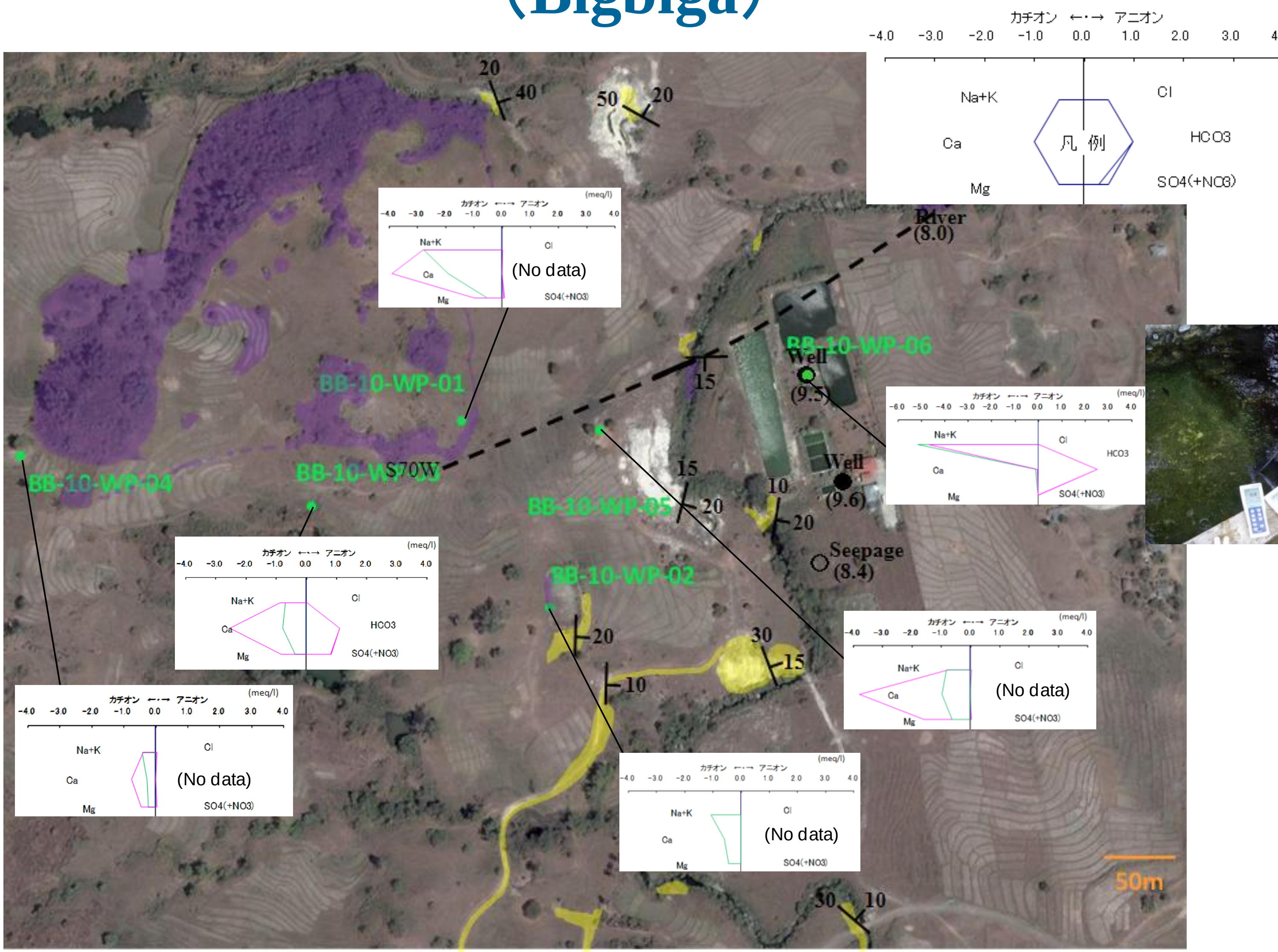

M1 (Source of Manleluag Hotsprong)



3. Groundwater Chemistries
（Manleluag Hotspring / Saile Mine）

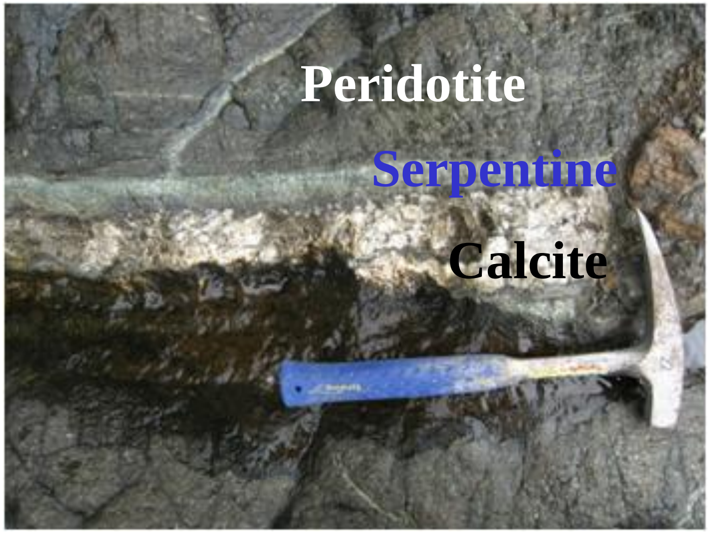


3. Groundwater Chemistries (Bigbiga)



3. Outcrop (Poonbato)

Hyperalkaline groundwater discharge point
(pH11.6)

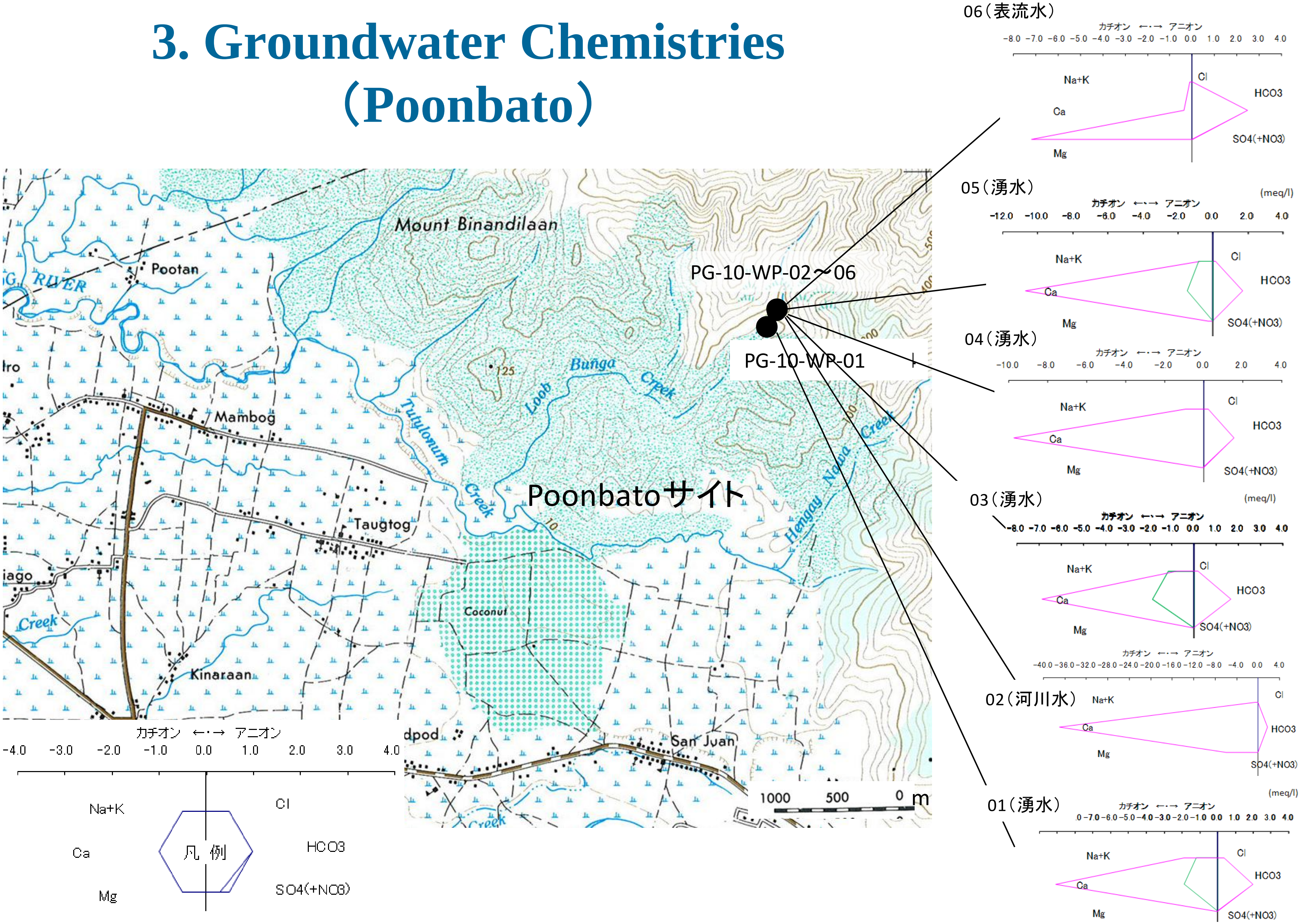


Serpentinaization

Travertine

Natural concrete

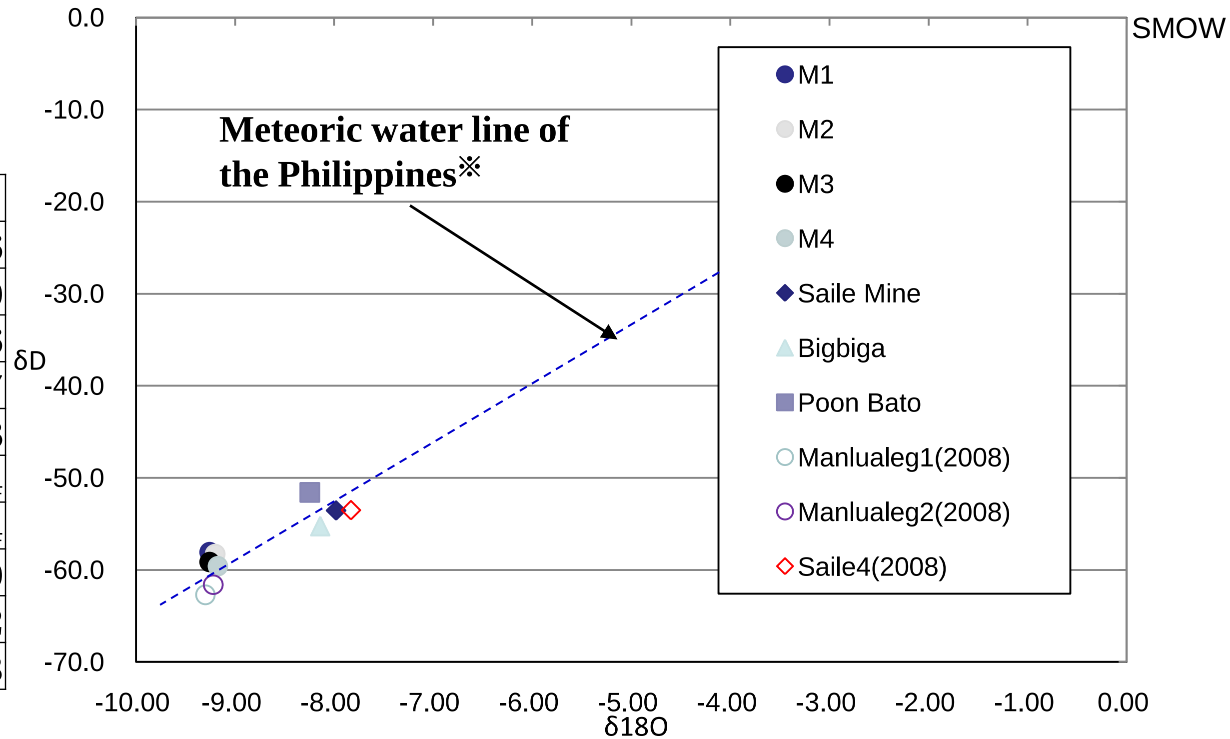
3. Groundwater Chemistries（Poonbato）



3. Origin and Residence Time of Groundwater

Stable Isotope Ratio of Rain Water and Groundwater

		δD	$\delta^{18}O$
Manleluag	M1	-58.1	-9.26
	M2	-58.3	-9.20
	M3	-59.1	-9.26
	M4	-59.6	-9.17
Saile Mine		-53.5	-7.98
Bigbiga		-55.2	-8.14
Poonbato		-51.6	-8.24
Manleluag1(2008)		-62.7	-9.30
Manleluag2(2008)		-61.6	-9.22
Saile4(2008)		-53.5	-7.83



※From Abaya (2005)

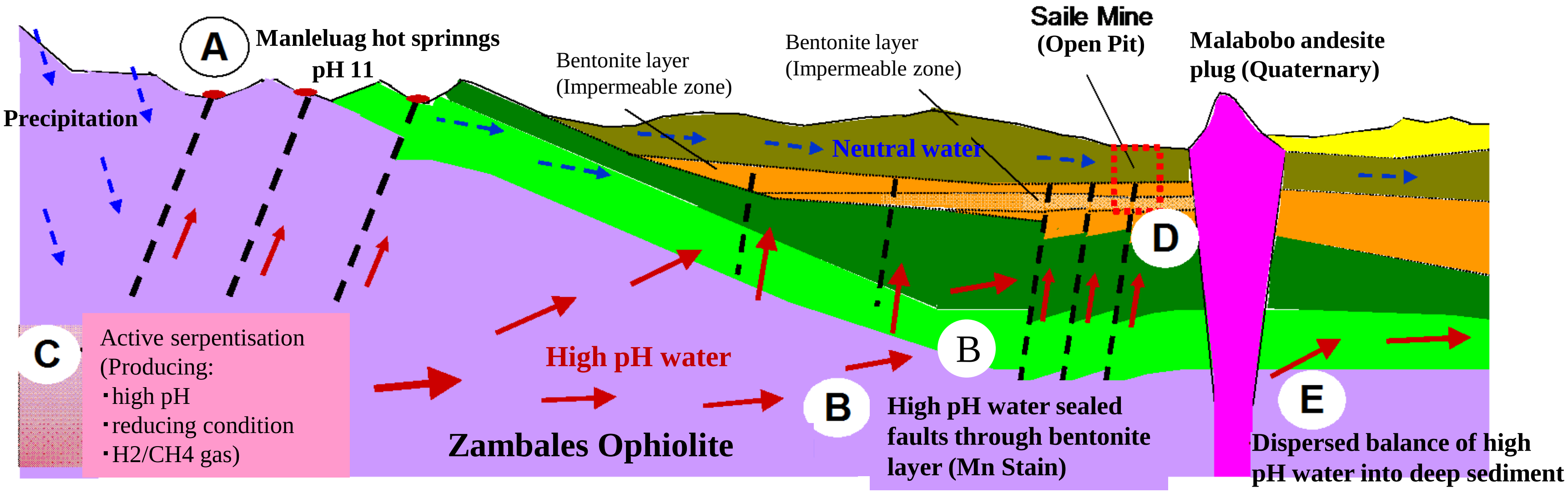
- Meteoric water origin
- Around 1000m of Recharge Elevation

Groundwater Dating by ^{14}C method

•Quantification by Tandem Accelerator Mass Spectrometry in Tono

•About 3000 years of residence time of groundwater at Bigbiga even if the oldest

3. Basic Concept of Regional Groundwater Flow System in Mangatarem



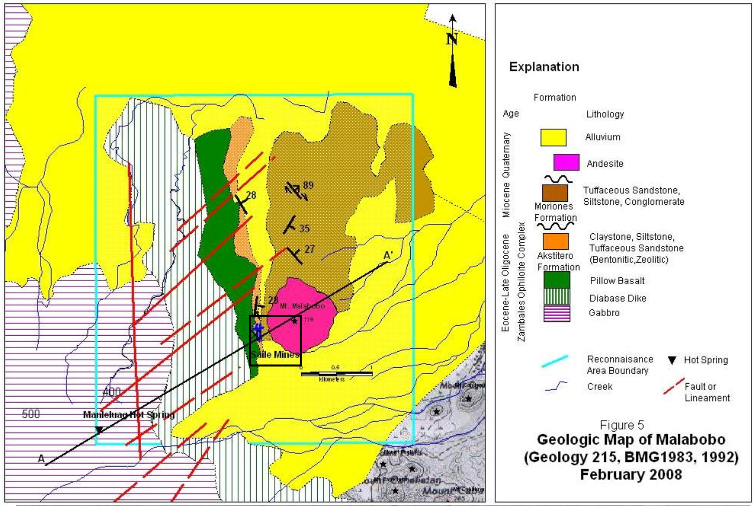
General Stratigraphy

- Quaternary
  - Alluvium
  - Andesite plug
- ~~~~~ <unconformity>
- Miocene
  - 「Moriones Formation」 Tuffaceous sandstone, Siltstone, Conglomerate
- ~~~~~ <unconformity>
- Eocene ~ Late Oligocene
  - 「Aksitero Formation」 Claystone, Sandstone, Tuffaceous sandstone (Bentonitic, Zeolitic)
  - 「Zambales Ophiolite」
    - Pillow lava
    - Diabase dike
    - Gabbro

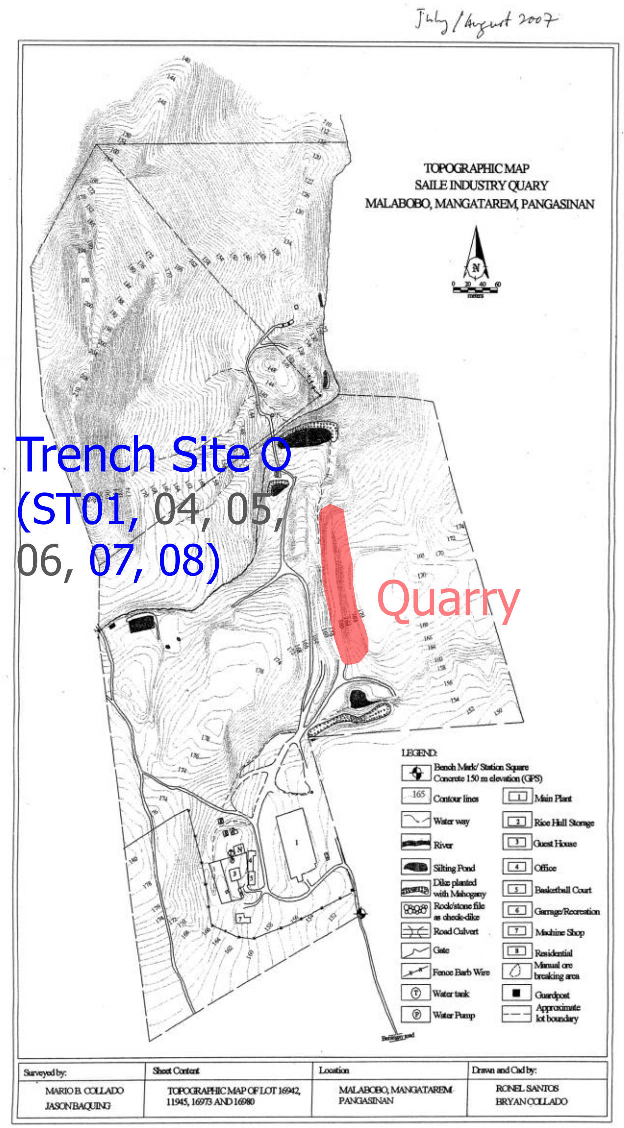
Aksitero Formation

- ▼ Occurrence(Width:30~150m, Strike: about 2000m around Saile mine)
- ▼ Lithofacies
  - ➢Medium-grained sandstone, siltstone, claystone accompanied by tuffaceous(volcanic ashes: pumice, volcanic glass) lamina
  - ➢Tuffaceous lamina and limestone accompanied by tuffaceous fine-grained turbidite layer
  - ➢Calcareous and tuffaceou sand stone
- ▼ Mineral Composition of Bentonite/Zeolite deposits (Saile Mine)
  - Main mineral: Ca-Montmorillonite
  - accessory mineral: Serpentine
    - Zeolite (Heulandite, Clinoptilolite, Mordenite)
    - Calcite
    - Manganite
    - Magnetite
    - Quartz,
    - Plagioclase
    - Xenocrysts of Chromite, Clinopyroxene

4. Field Investigation in Saile Mine (Fossil Type)



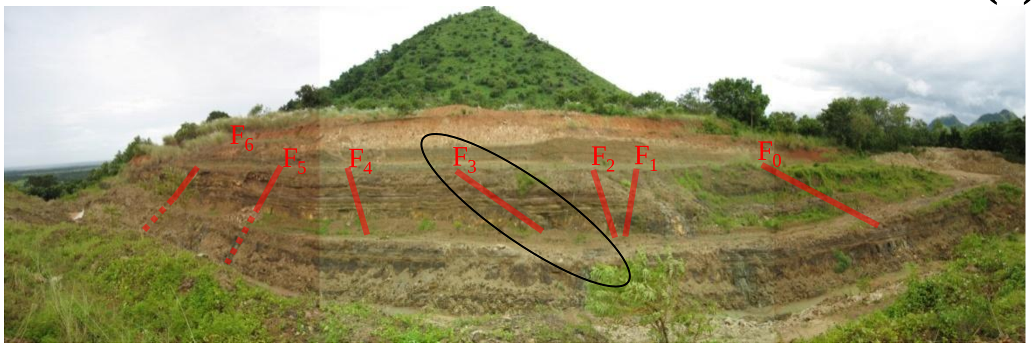
Aerial photo around Saile Mine



Topographic map of Saile industry quary

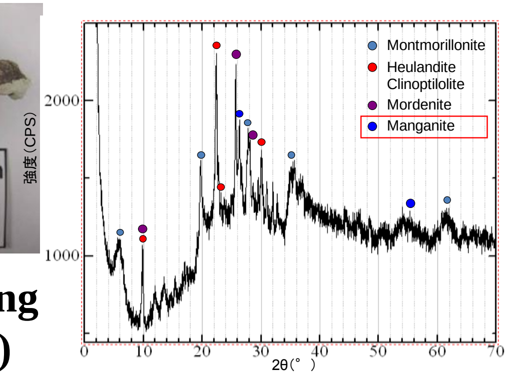
4. Field Evidences for Existence and Generation of Hyperalkaline Groundwater in Saile Deposits

(1) Mn-Staining (Mn-precipitation: Black)

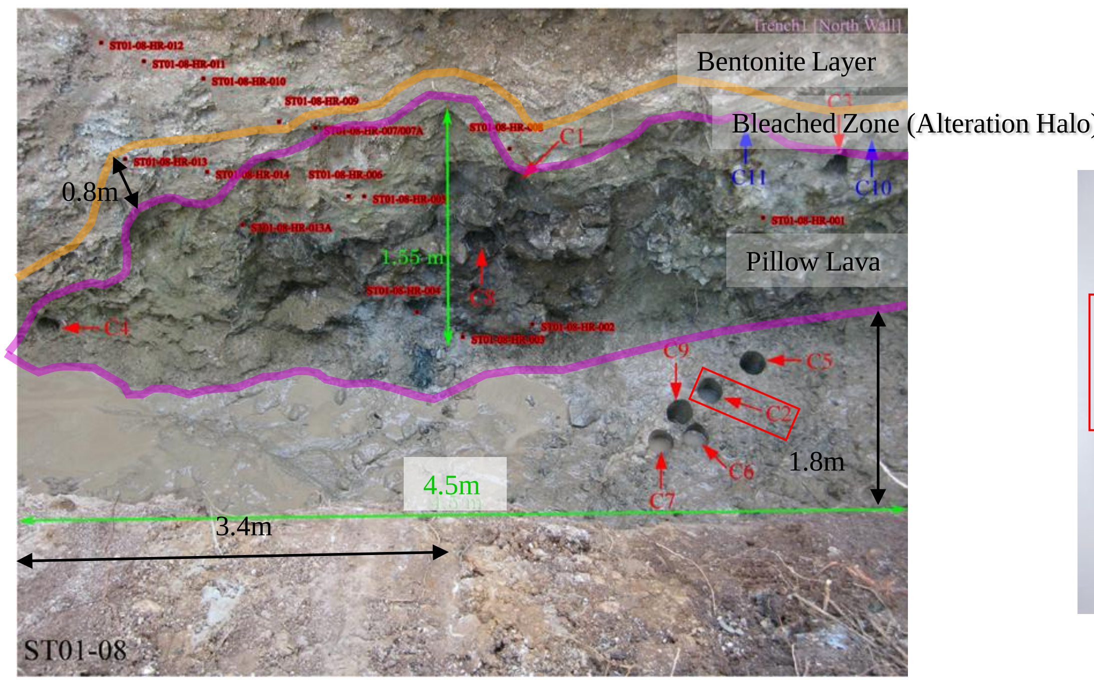


【Quarry】

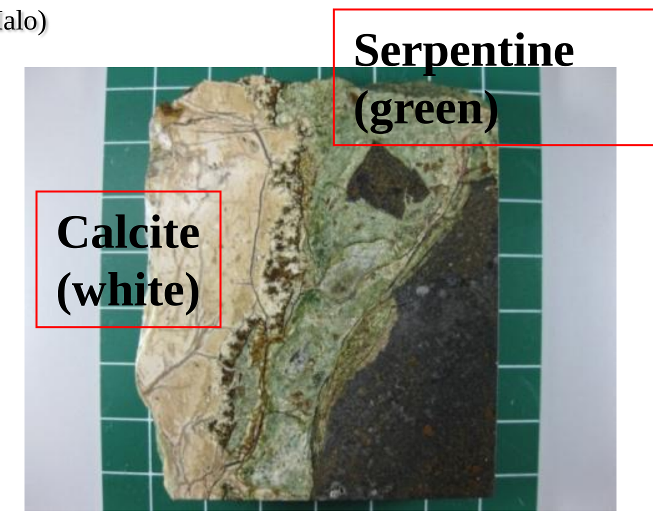
Fracture filling materials (F_3)



Manganite(γ-MnOOH)



【Trench 1】

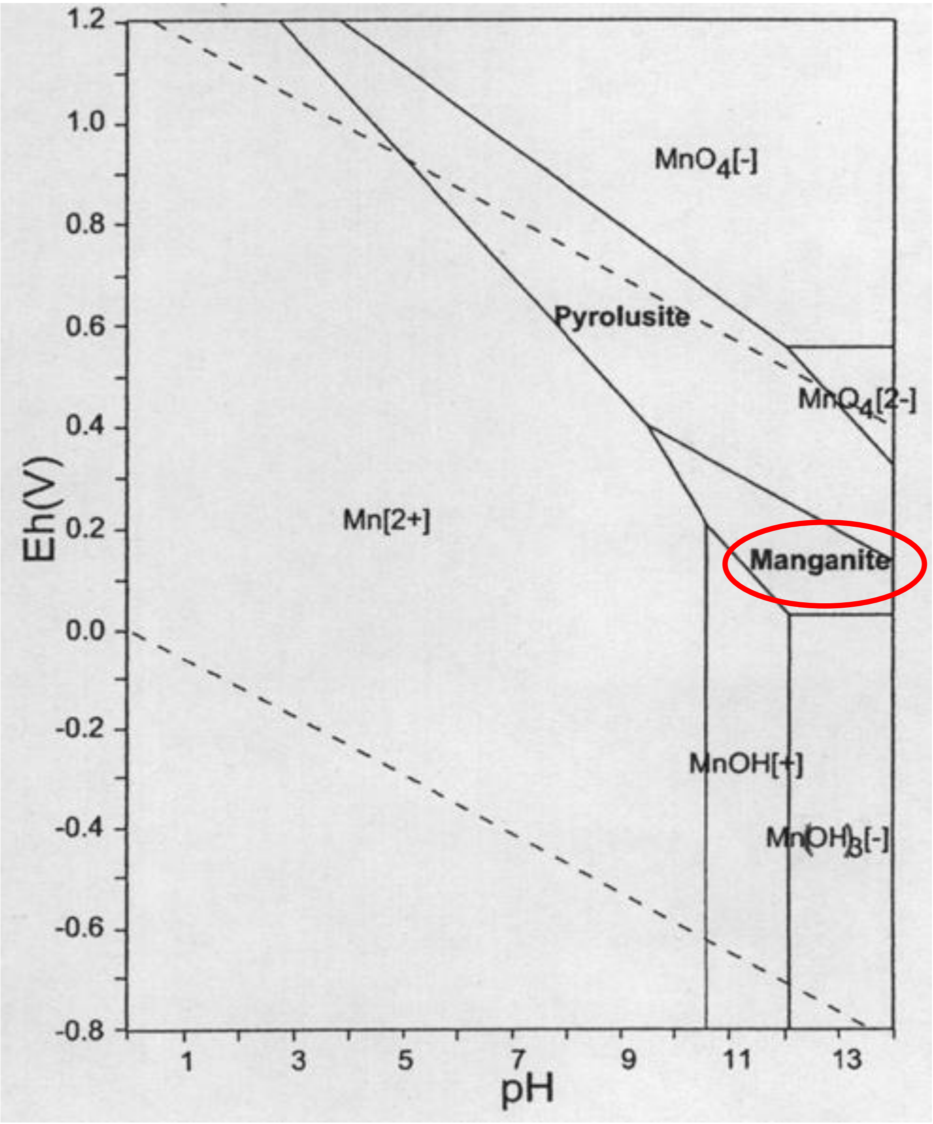


(Inner) (Outer)

(2) Fracture filling materials (C_2)

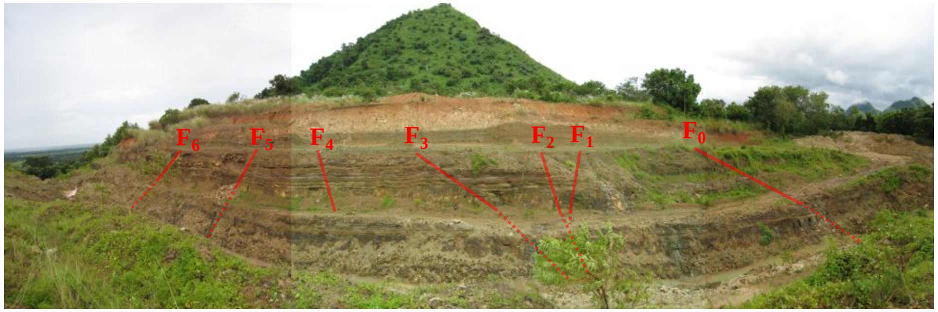
4. Phase Diagram of Mn-oxides and Mn-hydroxides

(JNC-TDB 011213g2 / GWB)

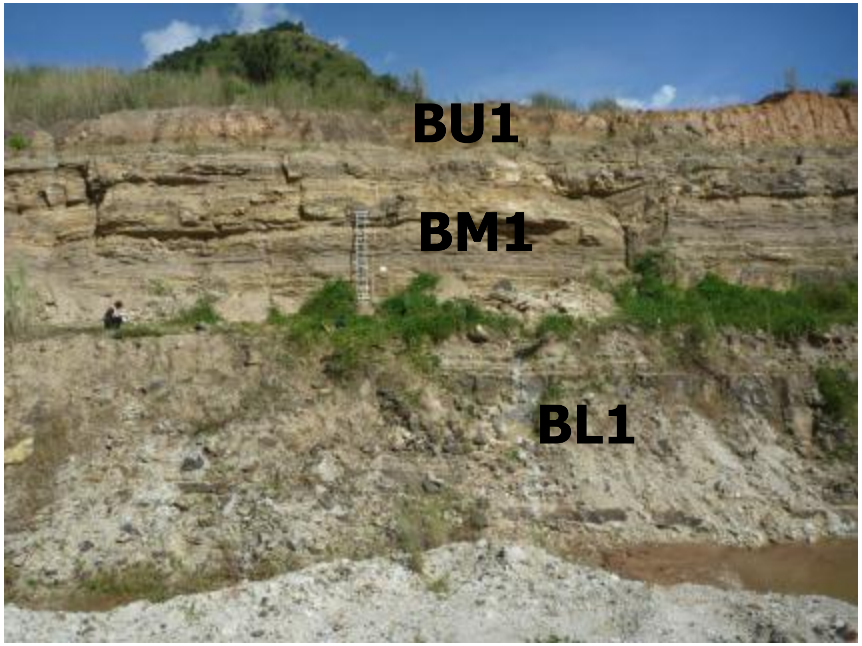


5. Formation of bentonite

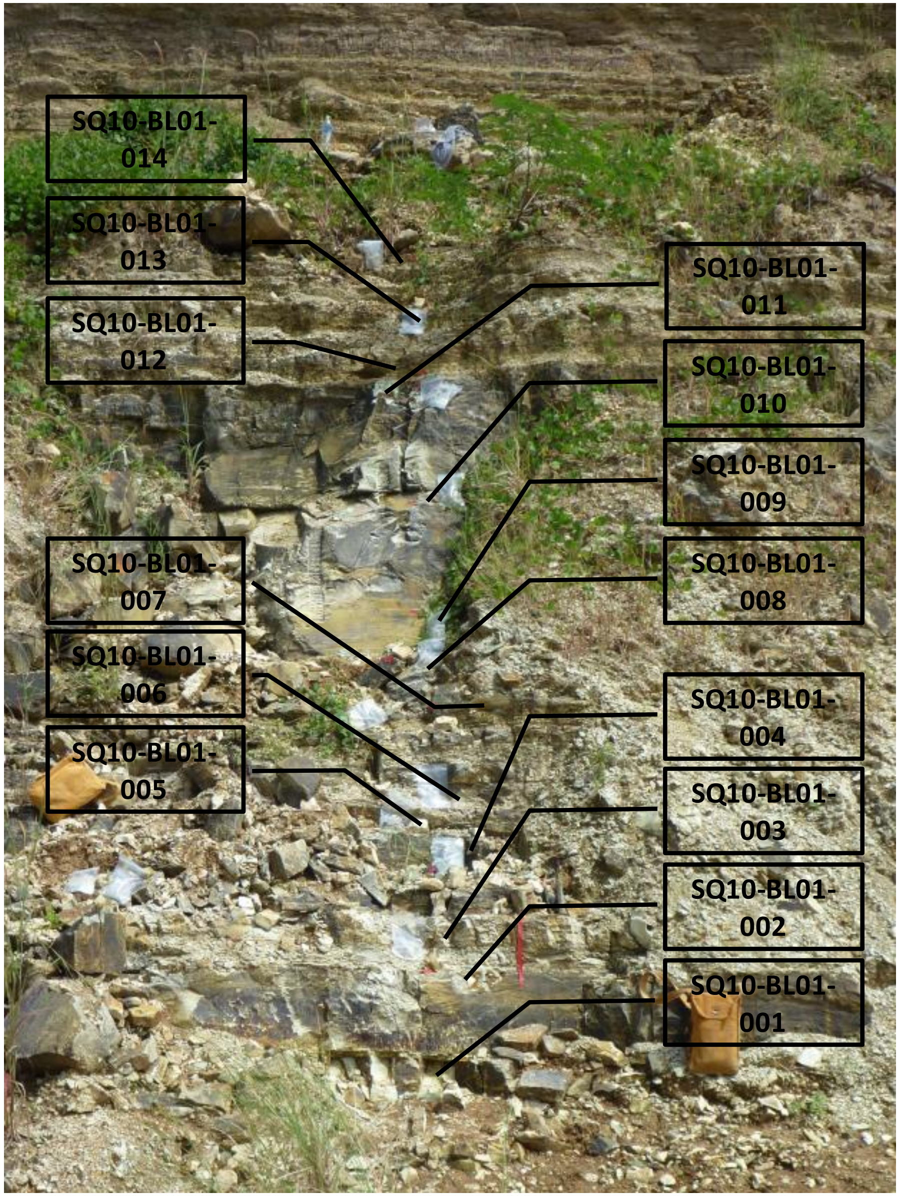
Systematic sampling of bentonite/zeolite layer – Baseline 1



Quarry



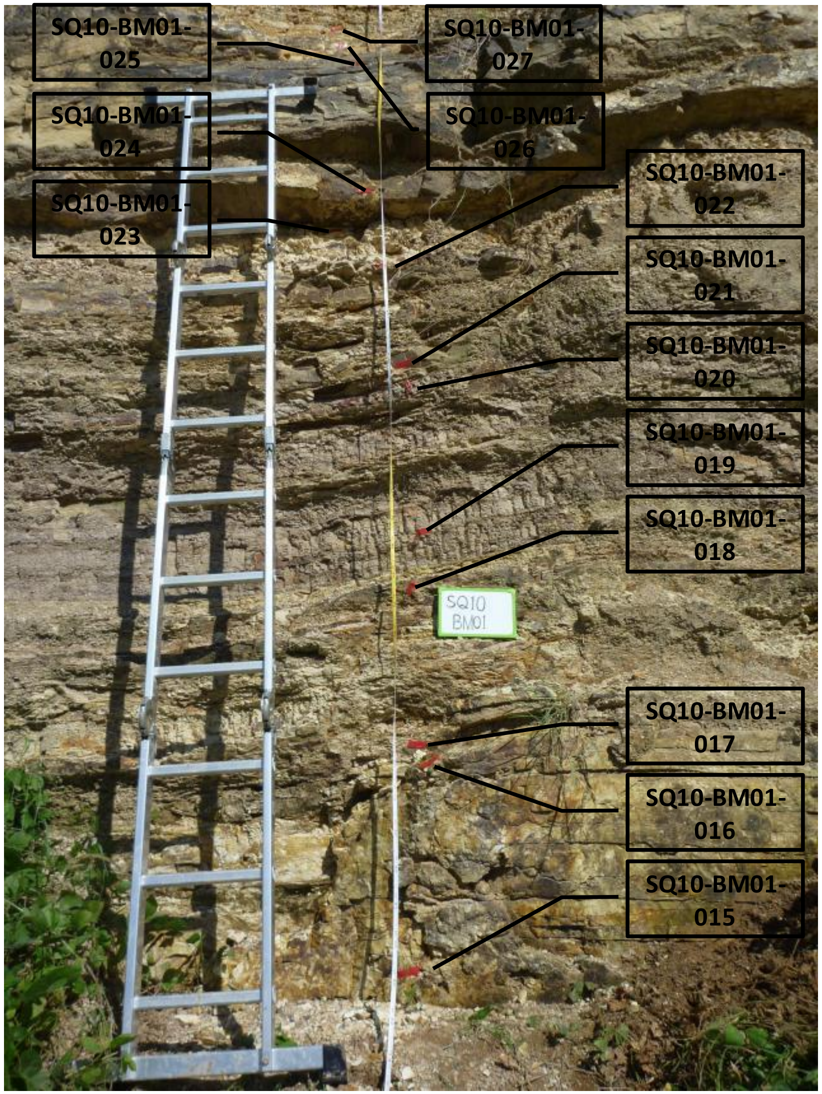
3 parts of Baseline 1



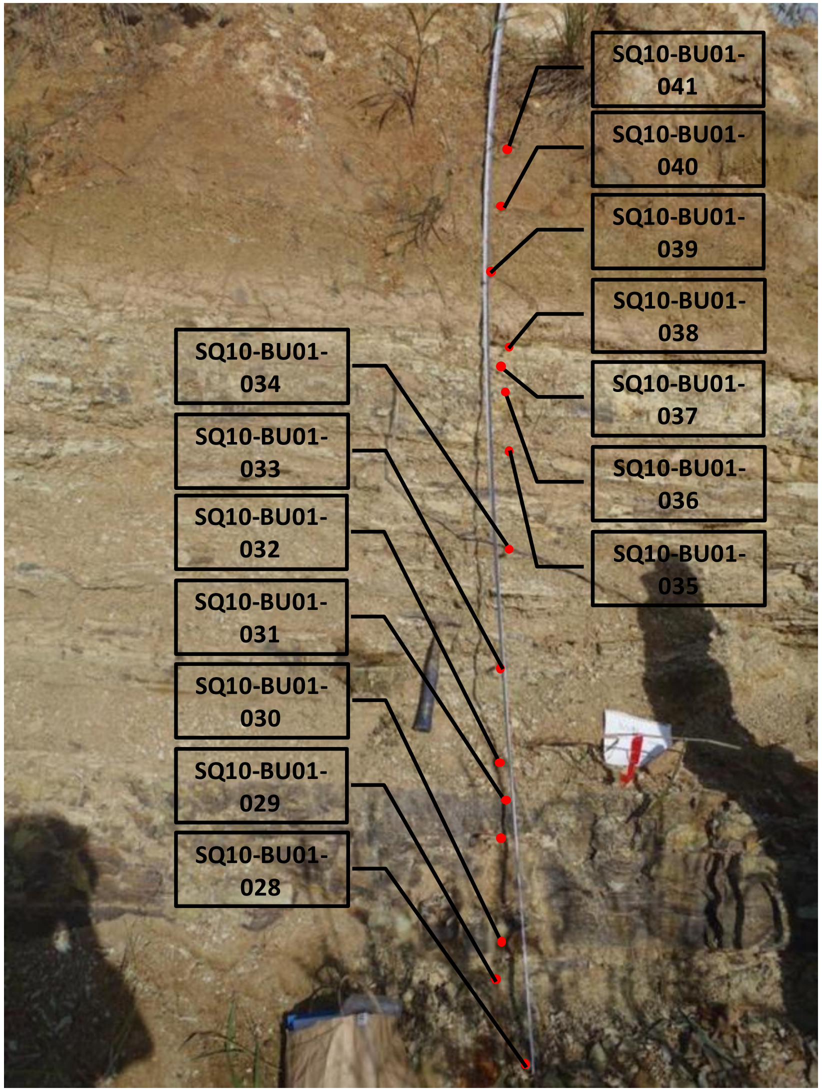
Sample location of BL1
(SQ-10-BL1-001～014)

5. Formation of bentonite

Systematic sampling of bentonite/zeolite layer – Baseline 1



Sample location of BM1
(SQ-10-BM1-015～027)

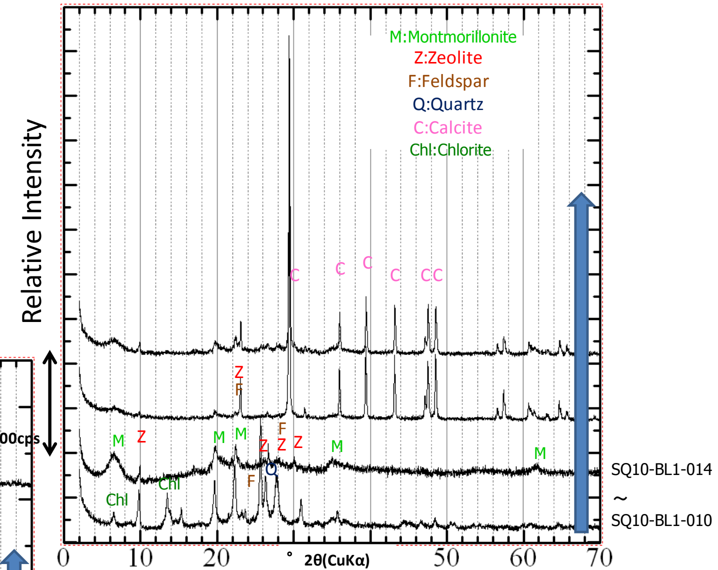


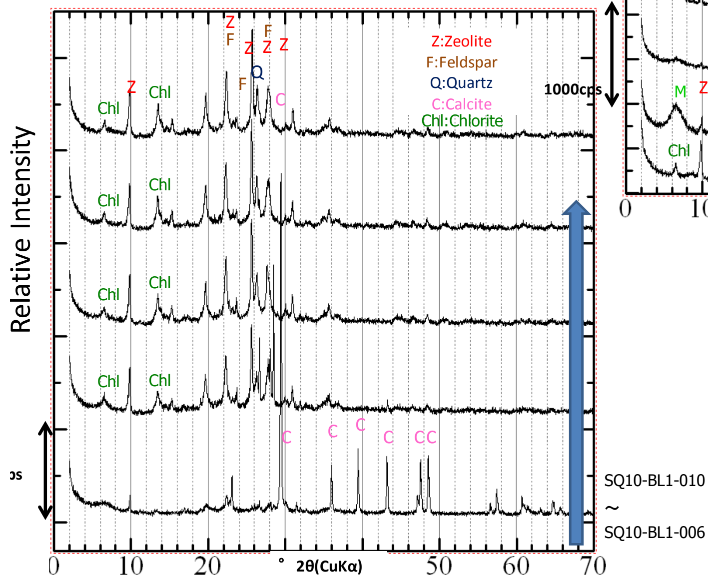
Sample location of BU1
(SQ-10-BU1-028～041)

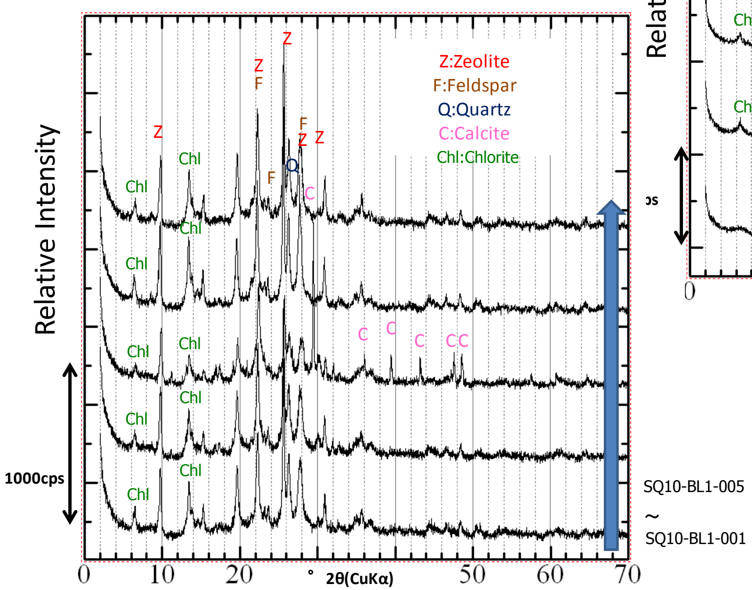
5. Formation of bentonite

XRD- Baseline 1（BL1）

- Basic composition: zeolite, plagioclase, chlorite, smectite, quartz
- Remakable peak of chlorite of bottom parts
- Dominant calcite in several parts



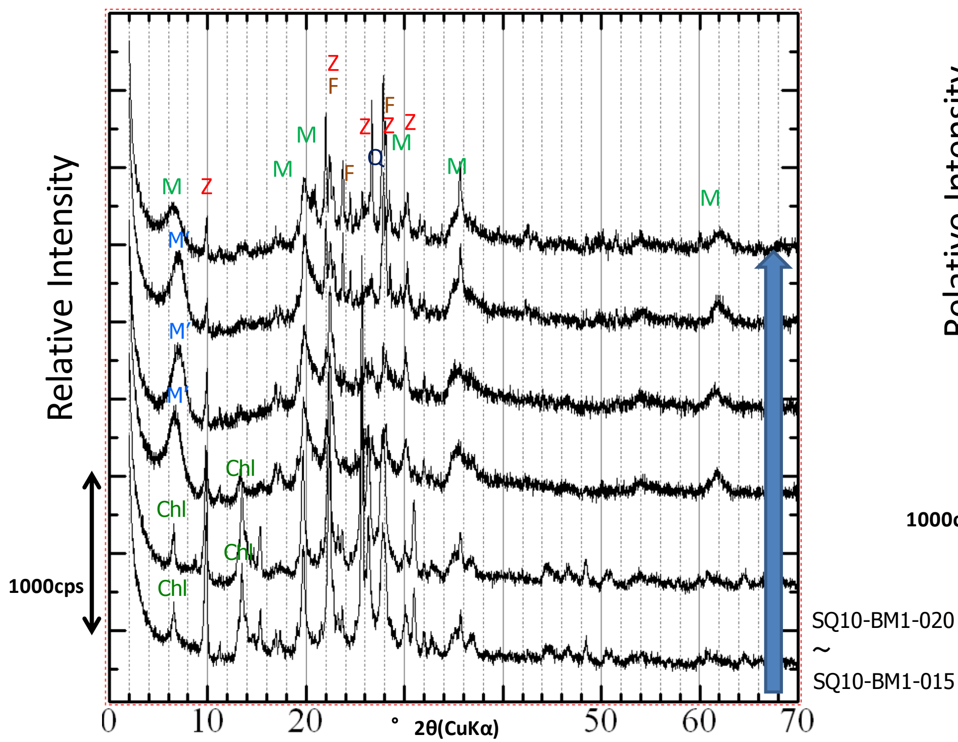


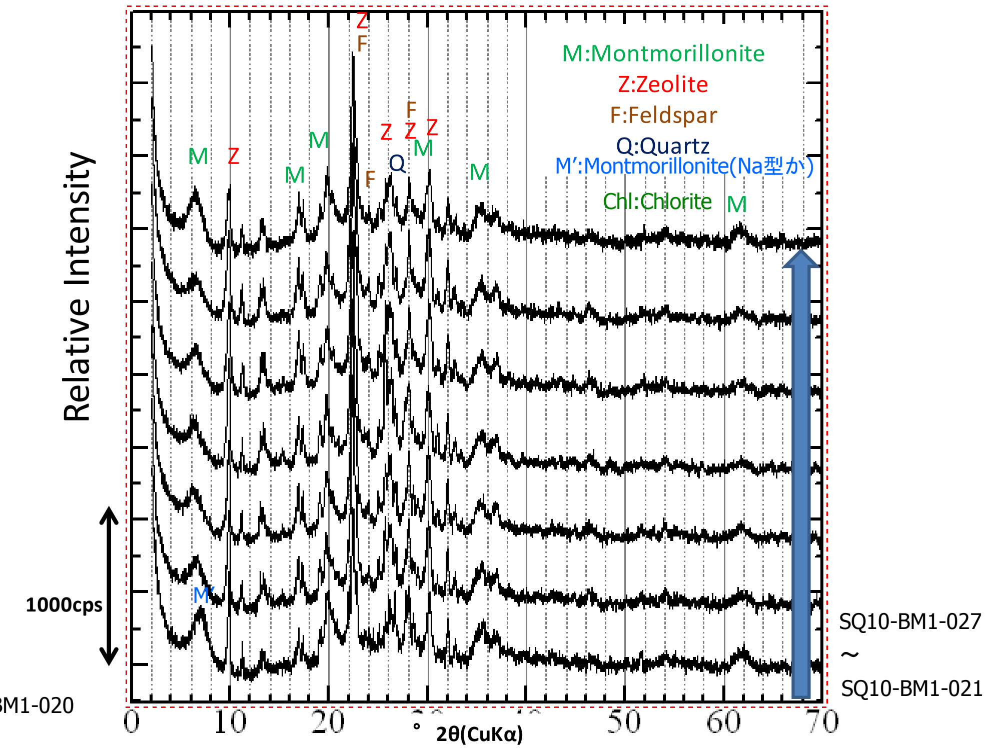


5. Formation of bentonite

XRD- Baseline 1（BM1）

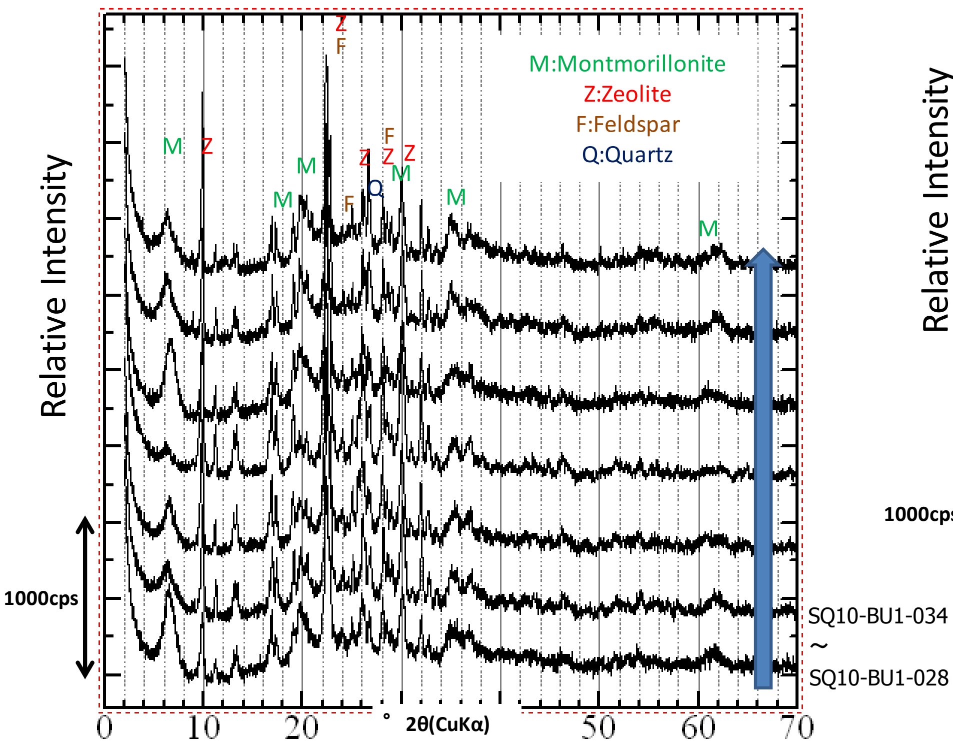
- Basic composition: zeolite, plagioclase, smectite (Disappearance of Chlorite), quartz
- Dominant zeolite in several parts
- Different peak of 001 with each horizon (Different interlayer cation of smectiite)
  →XRD under relative humidity control

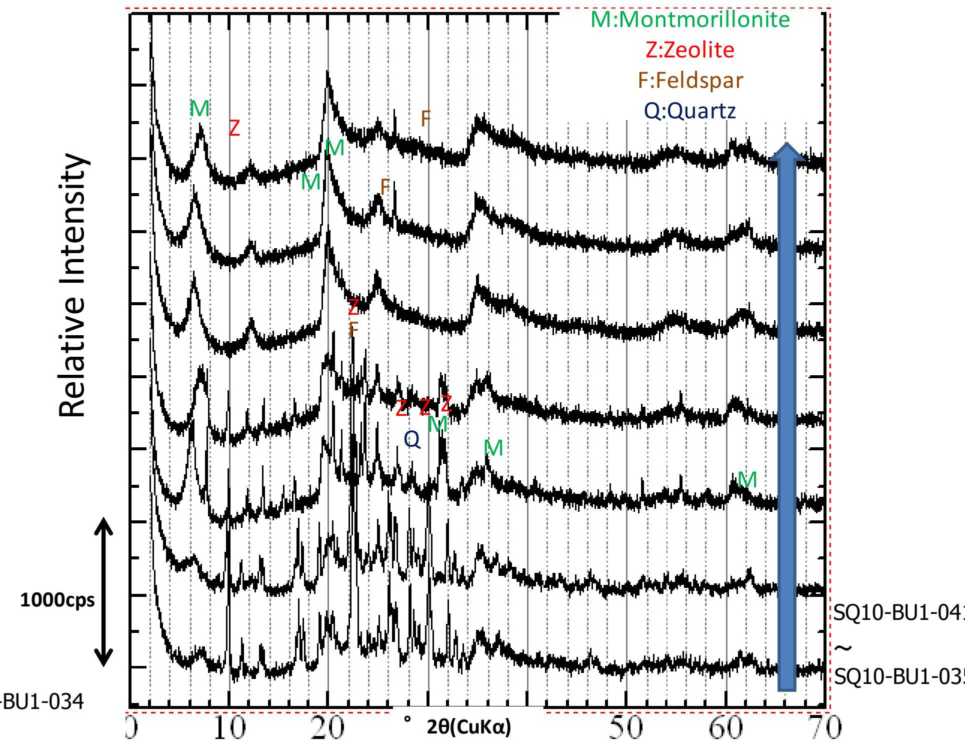




5. Formation of bentonite

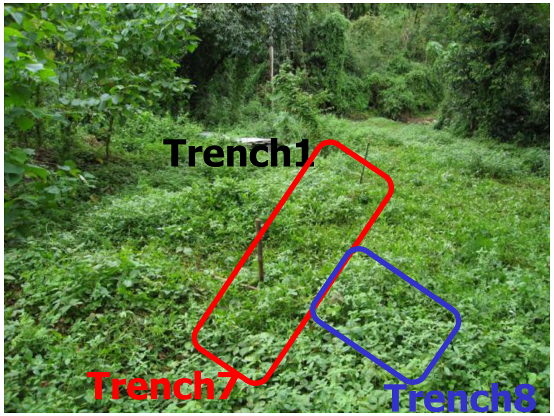
XRD- Baseline 1（BU1）





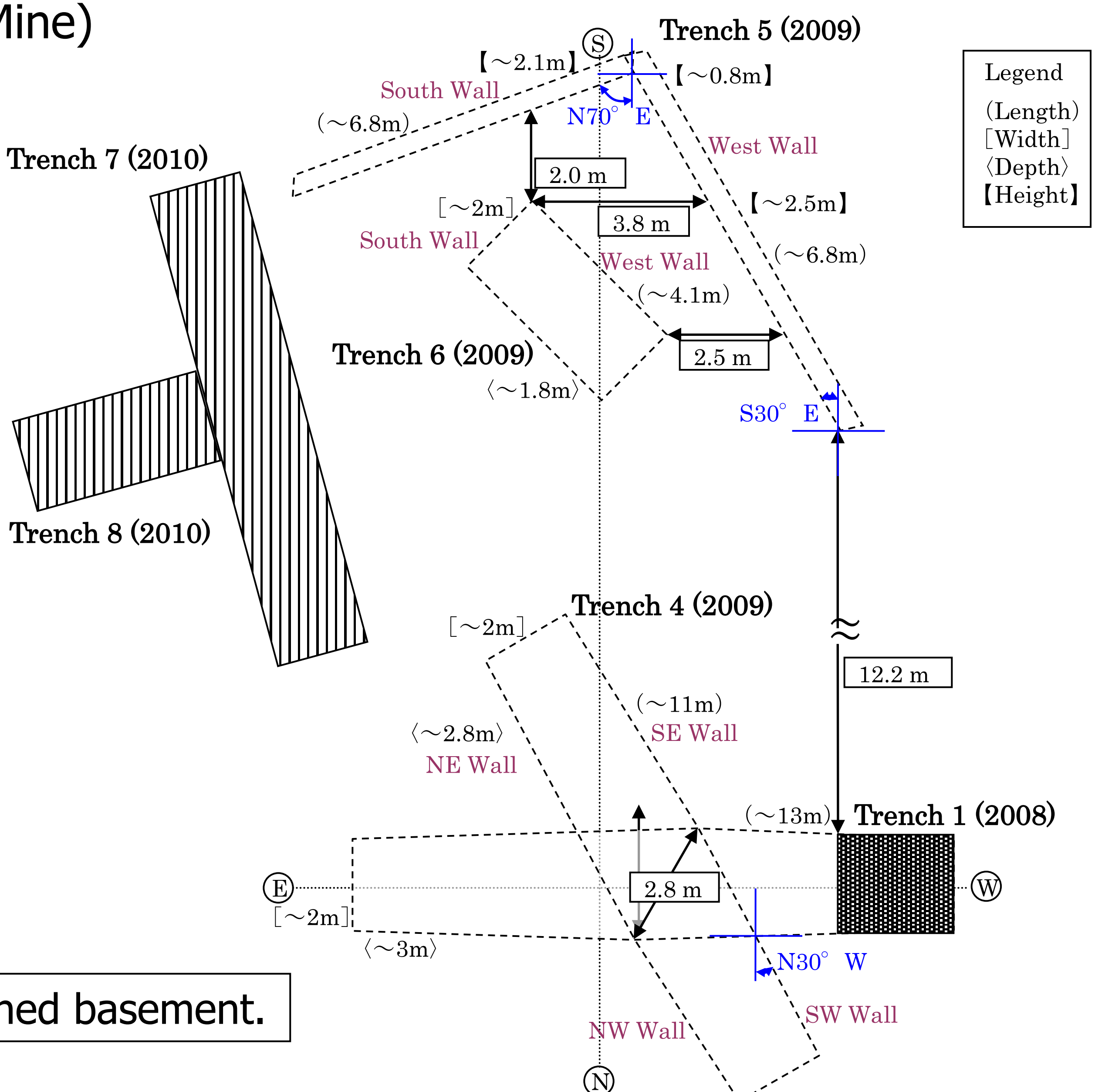
5. Trench Survey

Trench location (Saile Mine)



Before digging

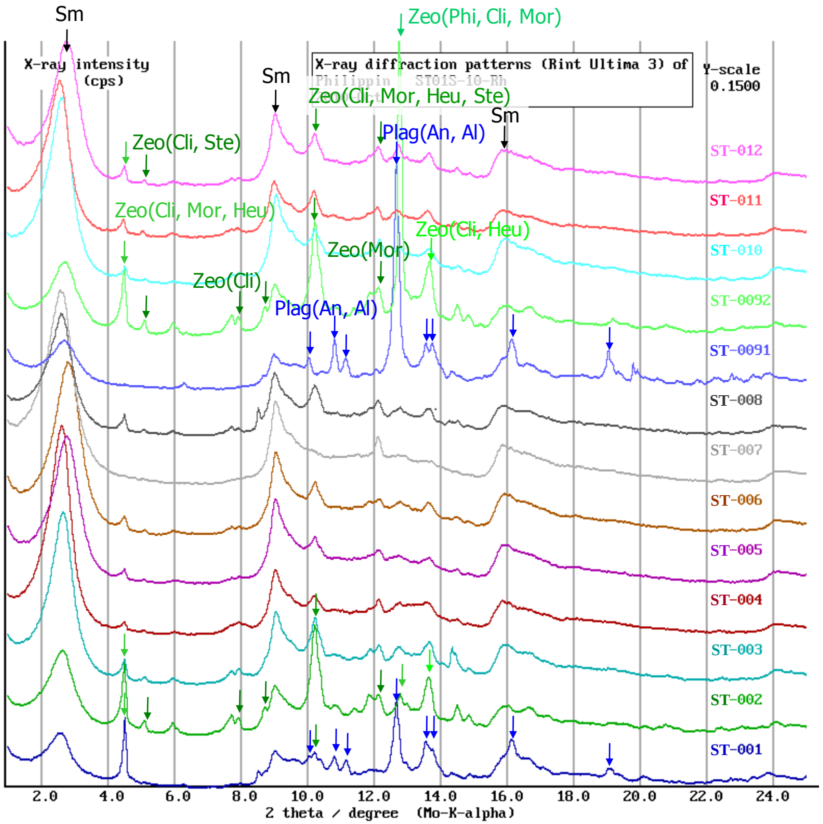
Digging of Trench 7



Trench 1, 5, 6 reached basement.

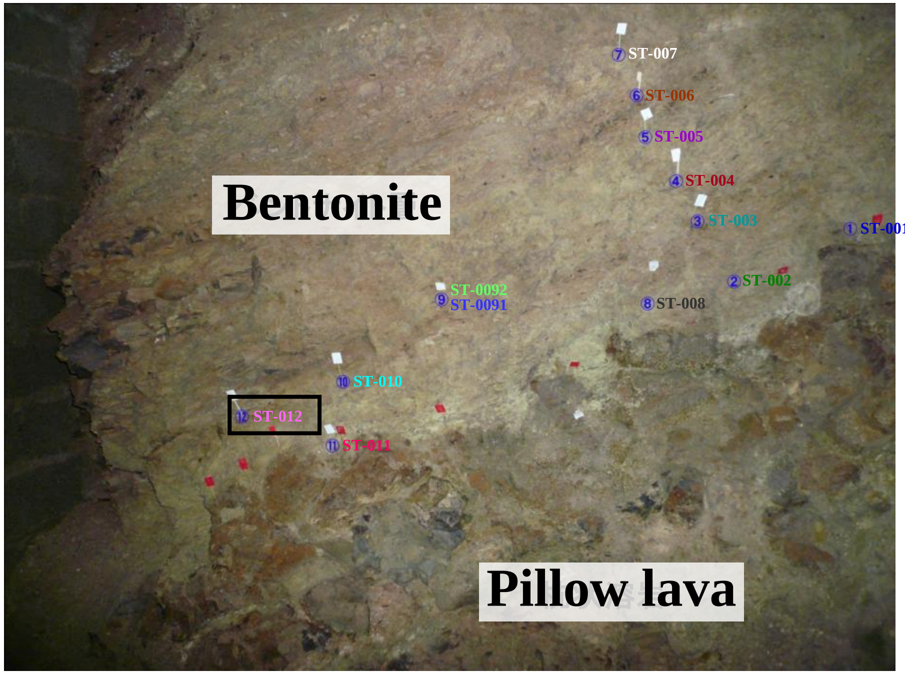
5. Mineralogical characterization of Bentonite

1. Mineral Composition of Trench 1 South Wall

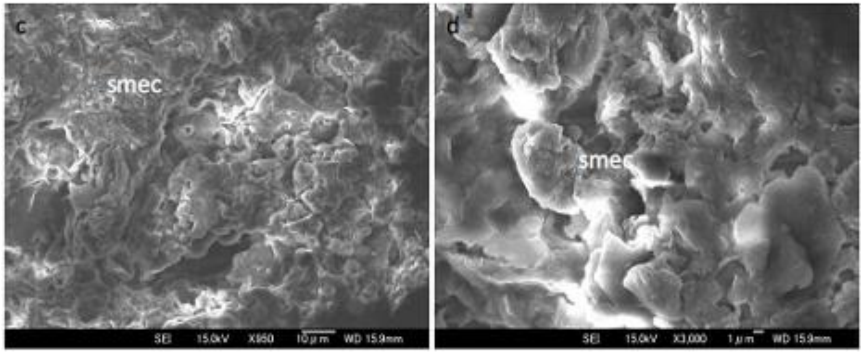


Sm:Smectite, Zeo:Zeolite (Cli: Clinoptilolite, Mor: Mordenite, Heu: Heulandite, Phi: Phillipsite, Ste: Stellerite), Qz:Quartz, Cal:Calcite, Plag:Plagioclase

XRD Results (Tokyo Institute of Tech.)



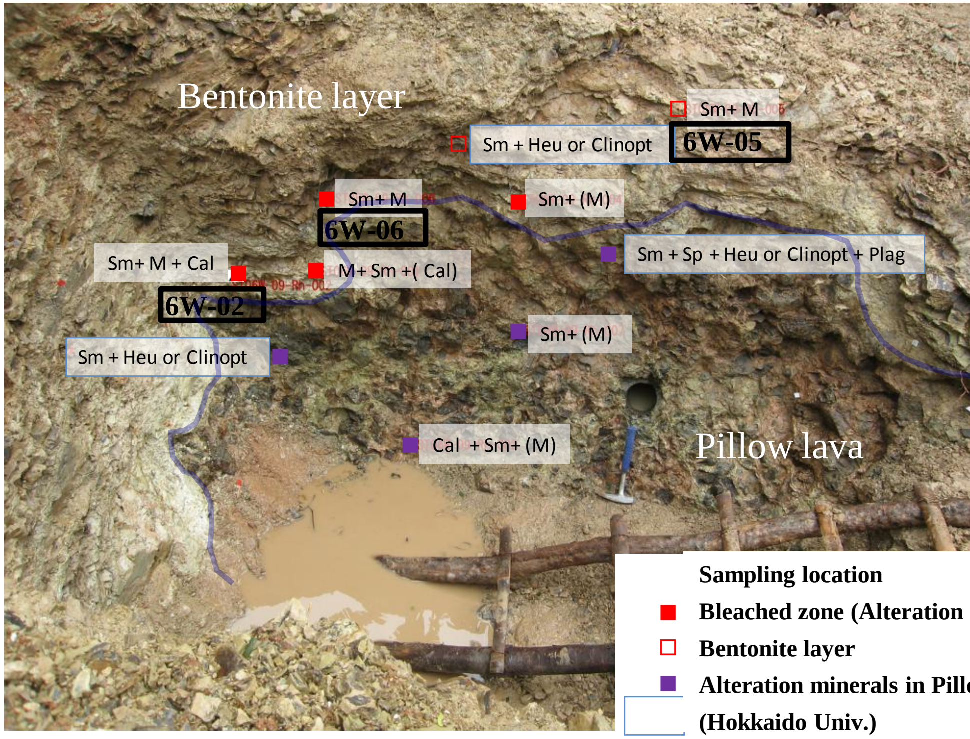
Sampling location



FESEM image of smectite

5. Mineralogical characterization of Bentonite

2. Mineral Composition of Trench 6 West Wall



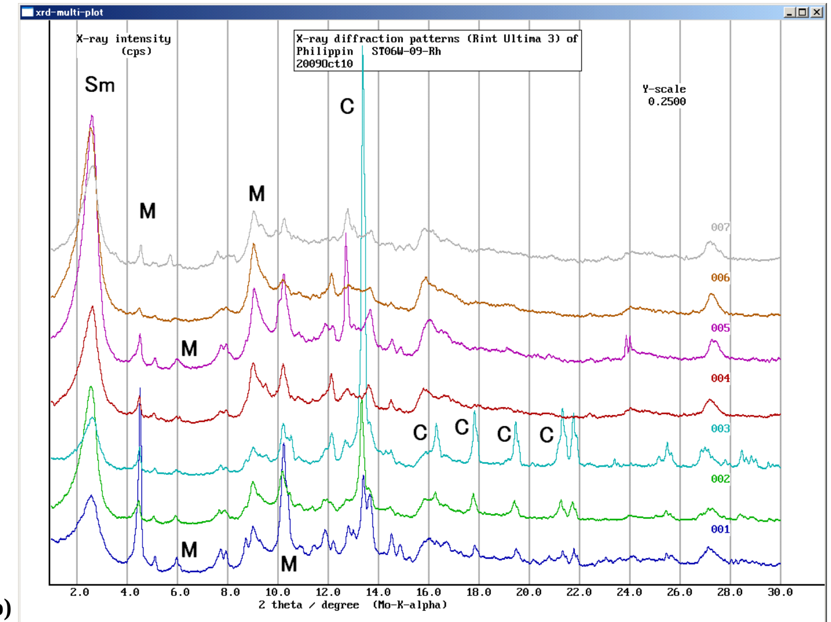
Sampling location

■ **Bleached zone (Alteration Halo)**

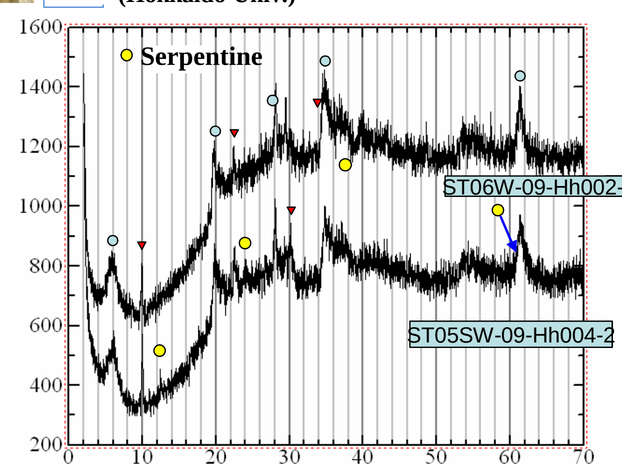
□ **Bentonite layer**

■ **Alteration minerals in Pillow lava**

(Hokkaido Univ.)



Upper left: Sampling location
Upper right: XRD Results (Tokyo Institute of Tech.)
Lower right: XRD Results (Hokkaido Univ.)

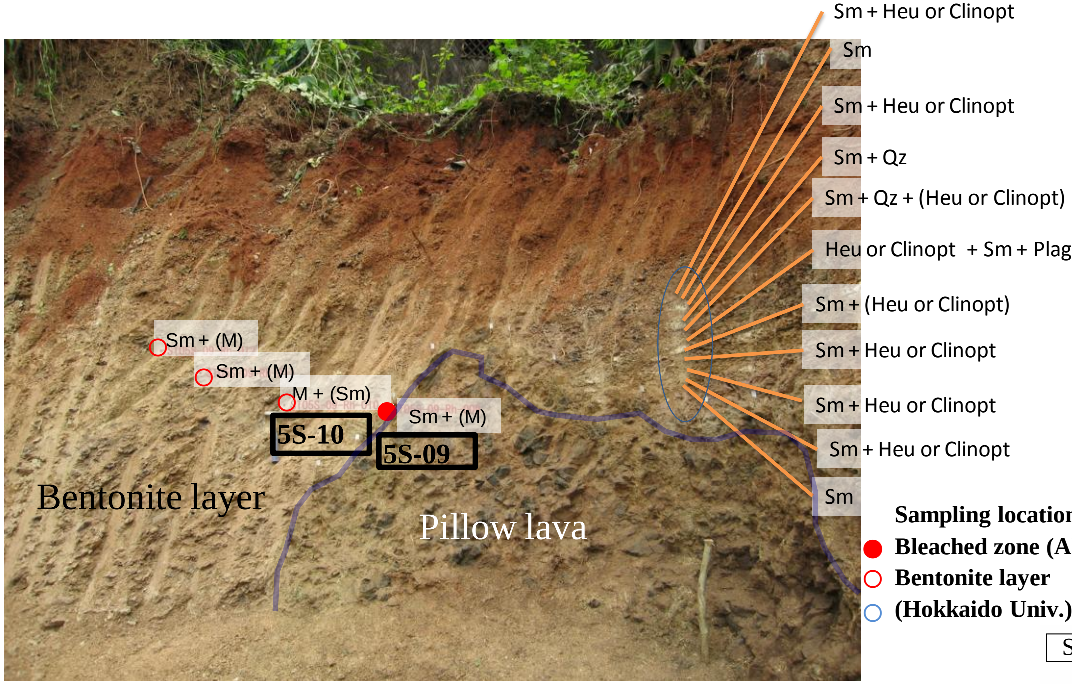


	Trench 5 (S・SW Wall)	Trench 6 (W Wall)
Bentonite Layer	Sm+Zeo Sm+Zeo+Qz+Plag Sm+Zeo	Sm Sm+Zeo Sm+Cal
Bleached Zone (Alteration Halo)	Zeo+Sm Sm+Zeo+Sp	Zeo+Sm Sm+Cal+Zeo
Pillow Lava	Sm+Cal+Zeo+Sp	Sm+Zeo+Cal+Sp +Plag

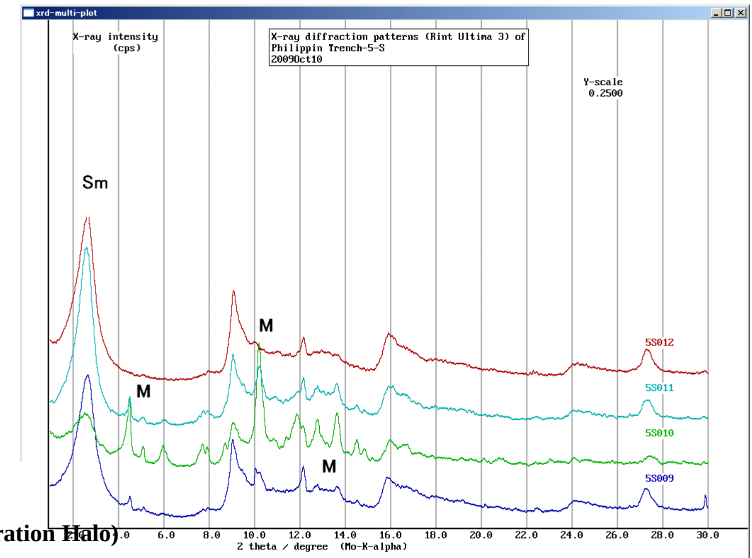
Sm: Smectite, Zeo: Zeolite) Qz: Quartz, Cal: Calcite, Sp: Serpentine, Plag: Plagioclase

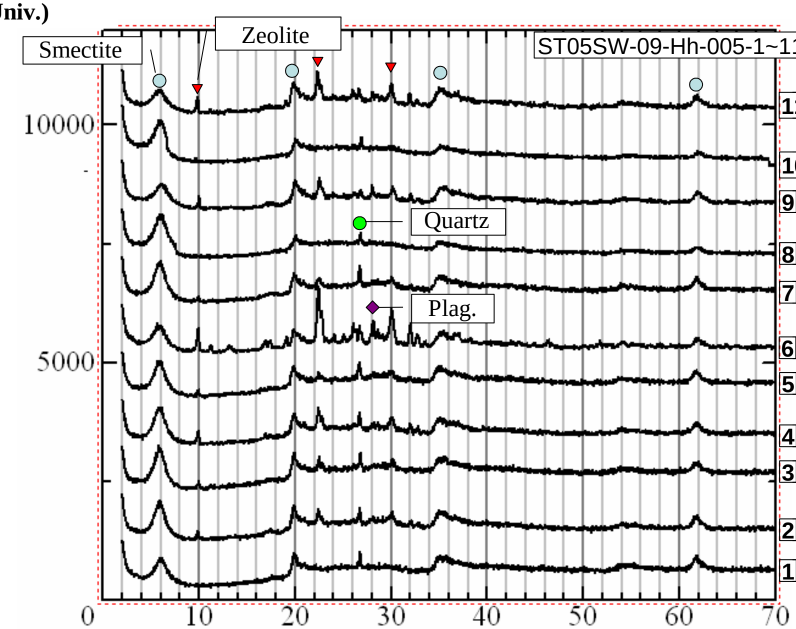
5. Mineralogical characterization of Bentonite

3. Mineral Composition of Trench 5 South Wall



Sampling location
Bleached zone (Alteration Halo)
Bentonite layer
(Hokkaido Univ.)





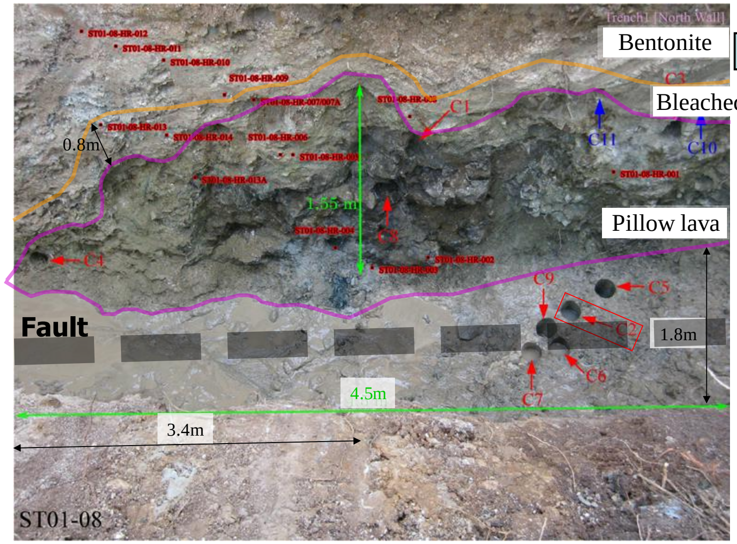
Upper left: Sampling location
Upper right：XRD Results (Tokyo Institute of Tech.)
Lower right: XRD Results (Hokkaido Univ.)

	Trench 5 (S･SW Wall)	**Trench 6 (W Wall)**
Bentonite Layer	Sm+Zeo Sm+Zeo+Qz+Plag Sm+Zeo	Sm Sm+Zeo Sm+Cal
Bleached Zone (Alteration Halo)	Zeo+Sm Sm+Zeo+Sp	Zeo+Sm Sm+Cal+Zeo
Pillow Lava	Sm+Cal+Zeo+Sp	Sm+Zeo+Cal+Sp+Plag

Sm: Smectite, Zeo: Zeolite, Qz: Quartz, Cal: Calcite, Sp: Serpentine, Plag: Plagioclase

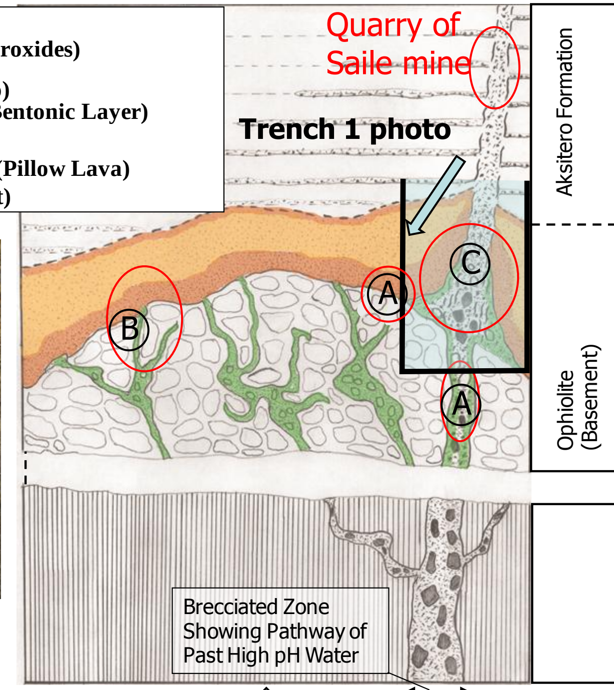
5. Conceptual Model on Pathway of the Past Hyperalkaline fluids (groundwater) formed as conduit filled with Serpentine, Mn-hydroxides, Carbonates and Ultramafic boulders (Fossil Type)

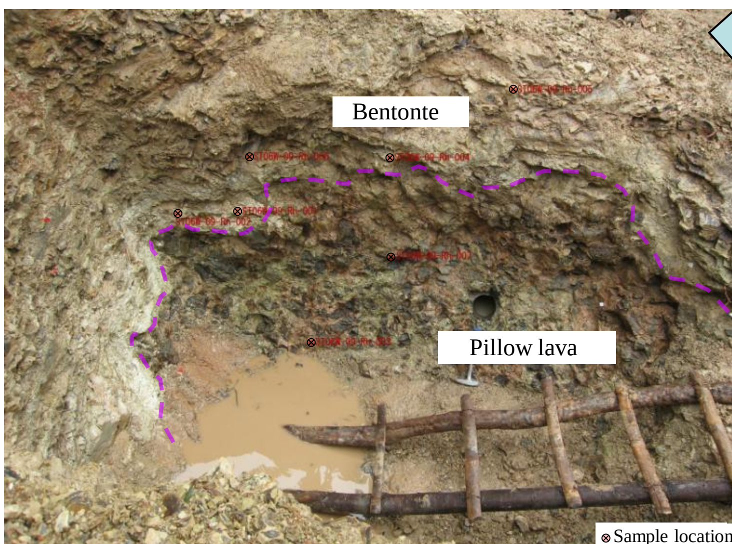
Fossil Type of Past Interaction Zone



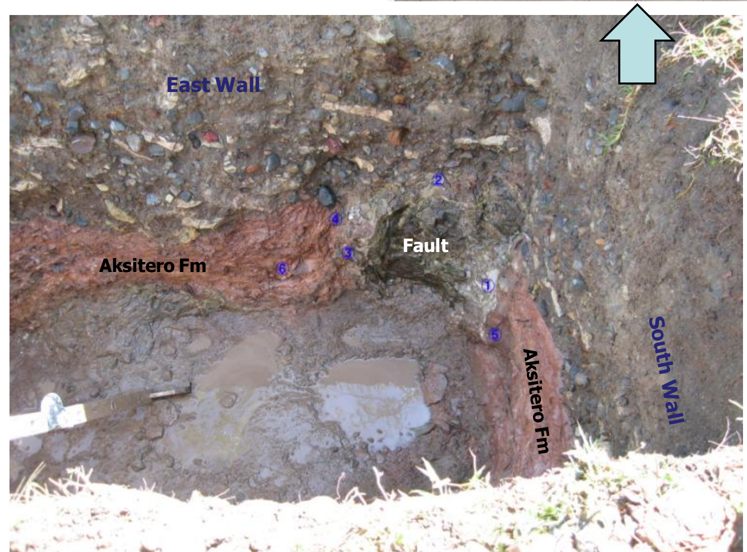
Ⓐ Saile mine Trench 1 (2008)

Fracture system of quarry





Ⓑ Saile mine Trench 6 (2009)

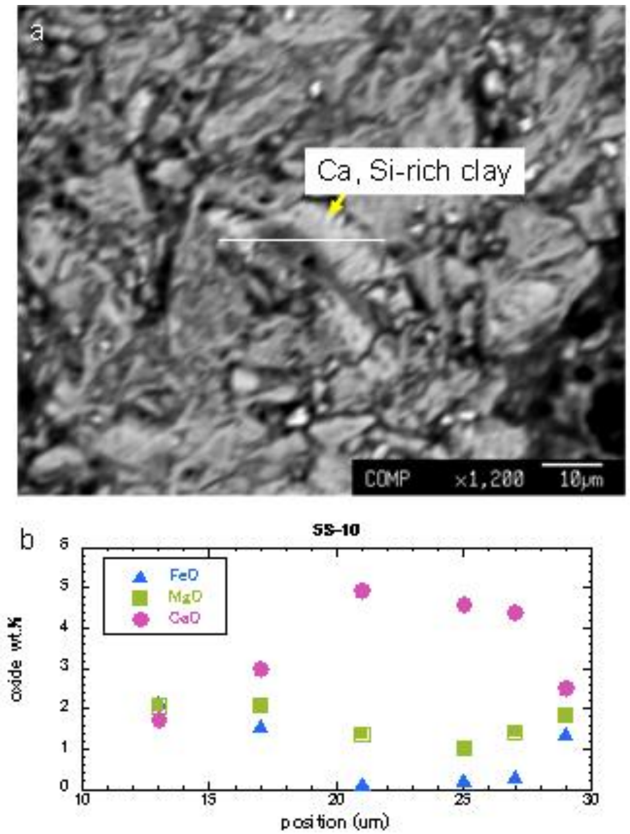


Ⓒ Bigbiga Trench BBT01 (2010)

5. Mineralogical characterization of Bentonite

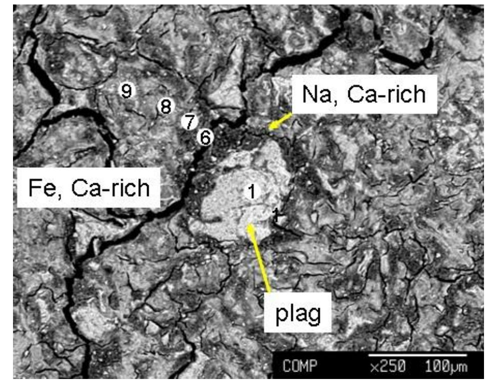
Occurrence of smectite by FE-SEM analysis

(1) Type 1; Zoning (Ca･Si-rich (Core) and Fe･Mg rich (Rim)) of smectite(Parallel-growth)



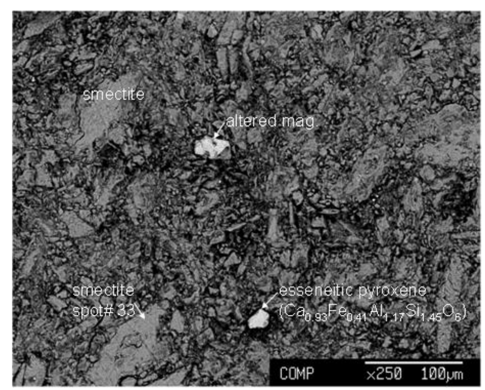
5S-10

(2) Type 2; Surrounding outside of Ca-rich core with Fe ･ Mg-rich smectite showing the shape of corona (Over-growth)



6W-05

(3) Type 3; Fe-rich smectite occurred as interstitial filling near Ca-rich smectite



5S-10

5. Chemical Composition of Bentonite

Type 1

spot#	5S-09_35	5S-09_37	5S-09_alt40	5S-09_alt42	5S-09_alt43
Oxide wt.%					
SiO2	61.79	55.91	52.07	42.97	41.87
Al2O3	16.51	13.95	16.15	12.12	10.65
TiO2	0.22	0.30	0.46	0.29	0.78
FeO	11.71	11.73	13.32	16.02	15.94
MnO	0.22	0.08	1.83	10.53	14.32
MgO	3.58	3.24	3.27	2.51	2.31
CaO	1.65	1.64	1.64	1.20	0.93
Na2O	0.06	0.16	0.10	0.04	0.23
K2O	1.66	1.48	1.49	1.06	1.17
Total	97.39	88.48	90.33	86.74	88.20
Cations based on O = 22 (apfu)					
Si	7.936	7.962	7.451	6.958	6.843
Al(4)	0.064	0.038	0.549	1.042	1.157
sumT=8					
Al(6)	2.435	2.303	2.175	1.272	0.895
Ti	0.021	0.032	0.050	0.035	0.095
Fe	1.258	1.397	1.593	2.170	2.179
Mn	0.024	0.009	0.222	1.444	1.982
Mg	0.686	0.687	0.697	0.606	0.564
sumM=4-6	4.423	4.428	4.736	5.527	5.715
XMg*	0.353	0.330	0.304	0.218	0.206
Ca	0.227	0.250	0.251	0.208	0.162
Na	0.015	0.044	0.029	0.012	0.072
K	0.273	0.269	0.272	0.219	0.245
sumIL	0.514	0.564	0.551	0.439	0.479
XCa**	0.440	0.444	0.456	0.474	0.339

NOTE *: XMg = Mg / (Mg + Fe)
**: XCa = Ca / (Ca + Na + K)

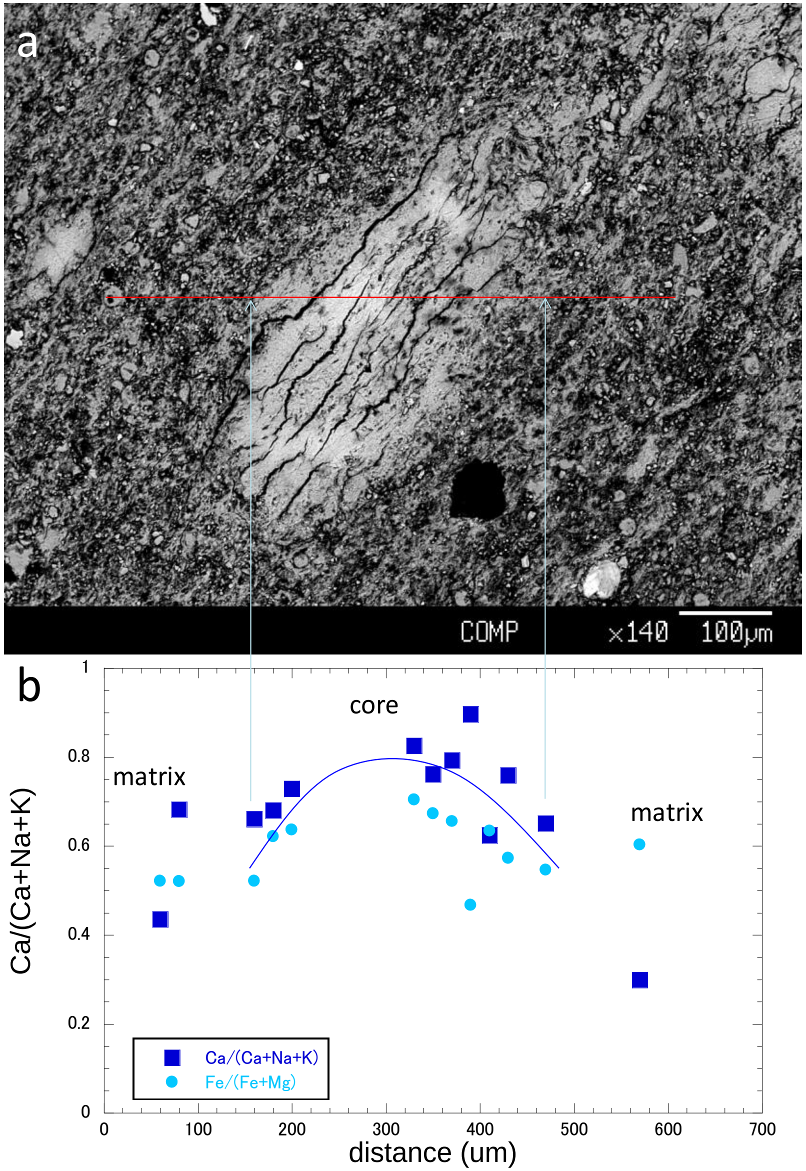
Type 2

spot#	5S-10_001	5S-10_2	5S-10_4	5S-10_ca33	5S-10_35
Oxide wt.%					
SiO2	55.71	56.23	52.04	60.26	56.87
Al2O3	22.22	22.20	22.20	27.52	24.76
TiO2	0.41	0.59	0.34	0.25	0.80
FeO	4.24	5.18	4.62	3.65	5.74
MnO	0.09	0.03	0.00	0.00	0.10
MgO	3.58	3.66	2.69	2.21	2.62
CaO	1.62	1.66	1.33	0.94	1.64
Na2O	0.07	0.10	0.11	0.06	0.09
K2O	0.69	1.08	1.24	1.09	0.44
Total	88.63	90.72	84.56	95.98	93.06
Cations based on O = 22 (apfu)					
Si	7.542	7.499	7.433	7.462	7.375
Al(4)	0.458	0.501	0.567	0.538	0.625
sumT=8					
Al(6)	3.087	2.988	3.170	3.479	3.160
Ti	0.041	0.059	0.036	0.023	0.078
Fe	0.480	0.577	0.552	0.378	0.623
Mn	0.011	0.004	0.000	0.000	0.011
Mg	0.723	0.728	0.573	0.408	0.507
sumM=4-6	4.341	4.356	4.331	4.288	4.379
XMg*	0.601	0.558	0.509	0.519	0.449
Ca	0.235	0.237	0.204	0.125	0.227
Na	0.019	0.025	0.030	0.015	0.023
K	0.119	0.183	0.226	0.172	0.072
sumIL	0.373	0.446	0.460	0.312	0.322
XCa**	0.630	0.532	0.444	0.401	0.706

NOTE *: XMg = Mg / (Mg + Fe)
**: XCa = Ca / (Ca + Na + K)

5. Zonig profile

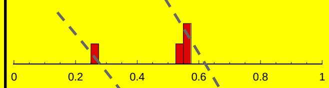
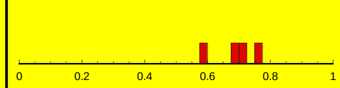
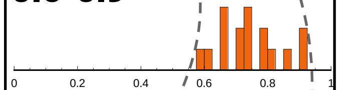
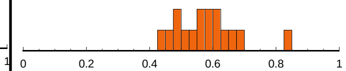
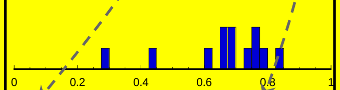
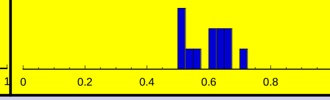
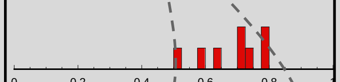
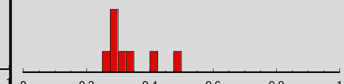
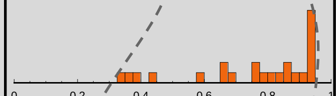
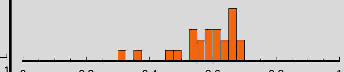
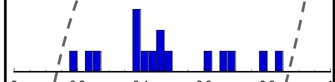
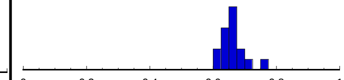
Zoning profile (Saile mine Trench 1(Bleaced))



ST-012

5. Composition change of bentonite

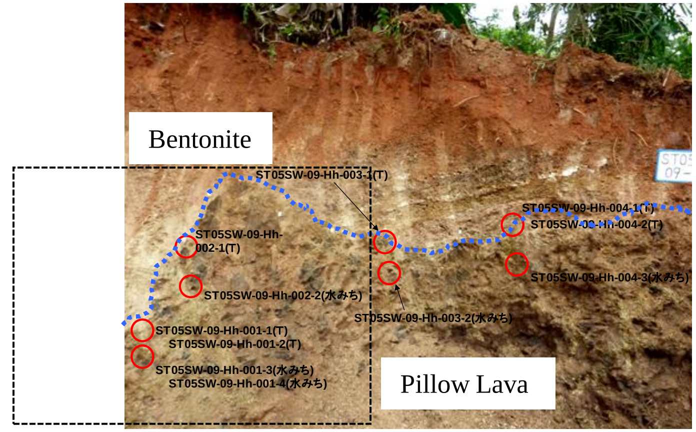
Summary of FE-SEM analysis

Sample ID	Alteration minerals	Relict minerals	Zeolite composition	Smectite XCa-composition	Smectite XFe-composition
Trench-1 (Saile Mine)					※ Yellow: Bleached Zone
ST-001	Zeolite >> Smectite	Plag, Cpx, Opx, Qz	Mordenite - Si-rich stellerite	**0.2-0.5** 	**0.6-0.8** 
ST-003	Smectite >> Zeolite	Volcanic clast			
ST-006	Smectite >> Zeolite	Plag, Qz			
ST-007	Smectite > Zeolite	Plag, Cpx, Qz	Yugawaralite	**0.6-0.9** 	**0.4-0.8** 
ST-008	Smectite >> Zeolite	Plag, Cpx, Qz			
ST-012	Smectite > Zeolite	Plag, Cpx, Qz	Clinoptilolite - Si-rich stellerite	**0.3-0.8** 	**0.5-0.7** 
Bigbiga Trench-1					※※Gray: Fractured Zone
BB-001	Zeolite >> Smectite	Plag, Cpx, Qz	Heulandite – Yugawaralite-Stellerite	**0.5-0.8** 	**0.3-0.5** 
BB-002	Zeolite >> Smectite	Plag, Cpx, Qz, Calc, Ba-phase	Yougawaralite - Stellerite	**0.3-0.9** 	**0.3-0.7** 
BB-004	Smectite > Zeolite	Plag, Cpx, Qz, Calc (Mn-rich), Apa,	Mordenite - Stellerite	**0.2-0.8** 	**0.6-0.8** 
BB-006	Smectite > Zeolite	Plag, Cpx, Qz, Calc, Apa, Mn-oxide	Stellerite		

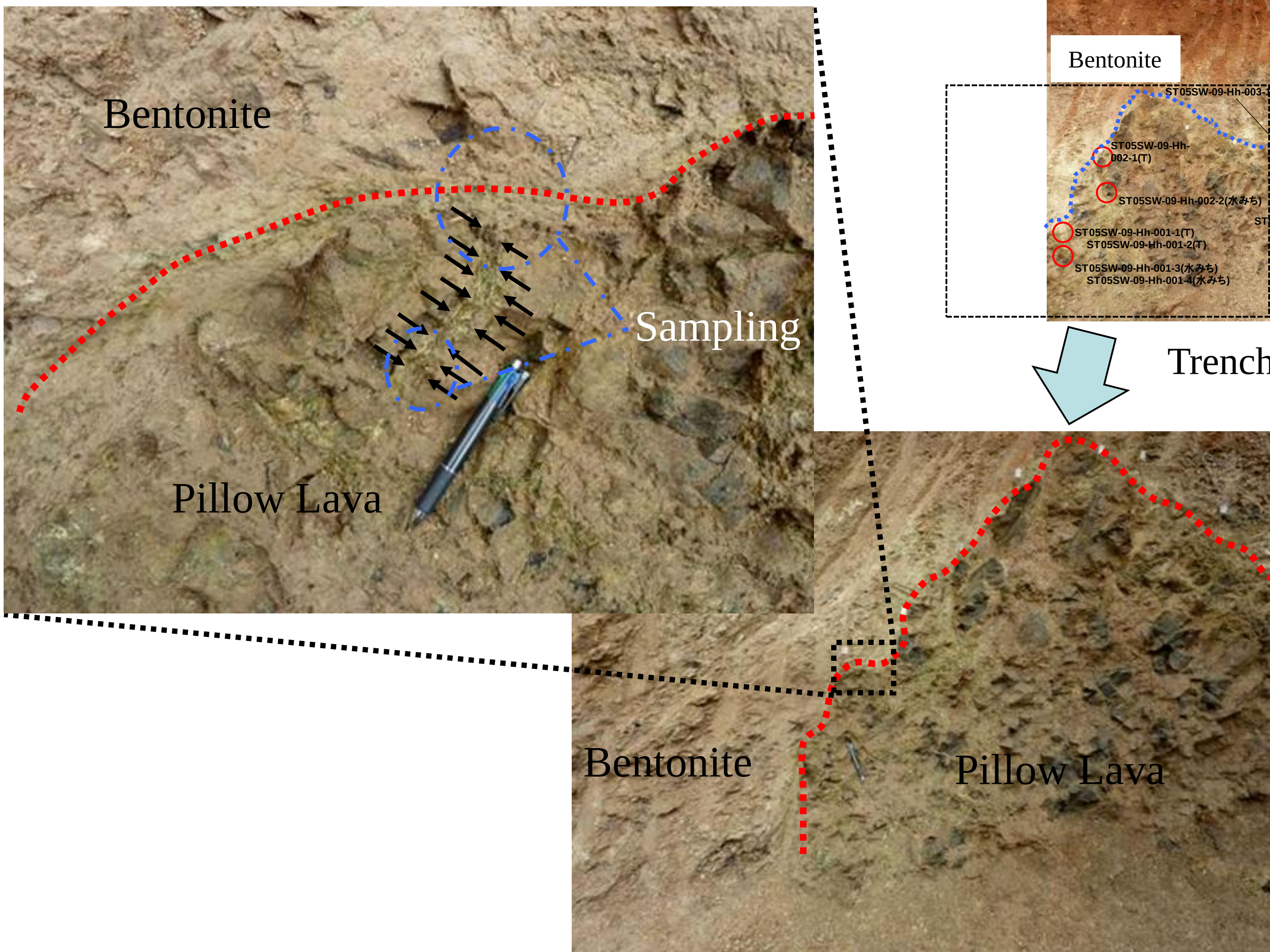
6. Interaction between smectite and hyperalkaline groundwater

Lithology of Alteration Zone between Pillow lava and Bentonite layer

(1) Sampling (Trench 5) (Hokkaido Univ.)



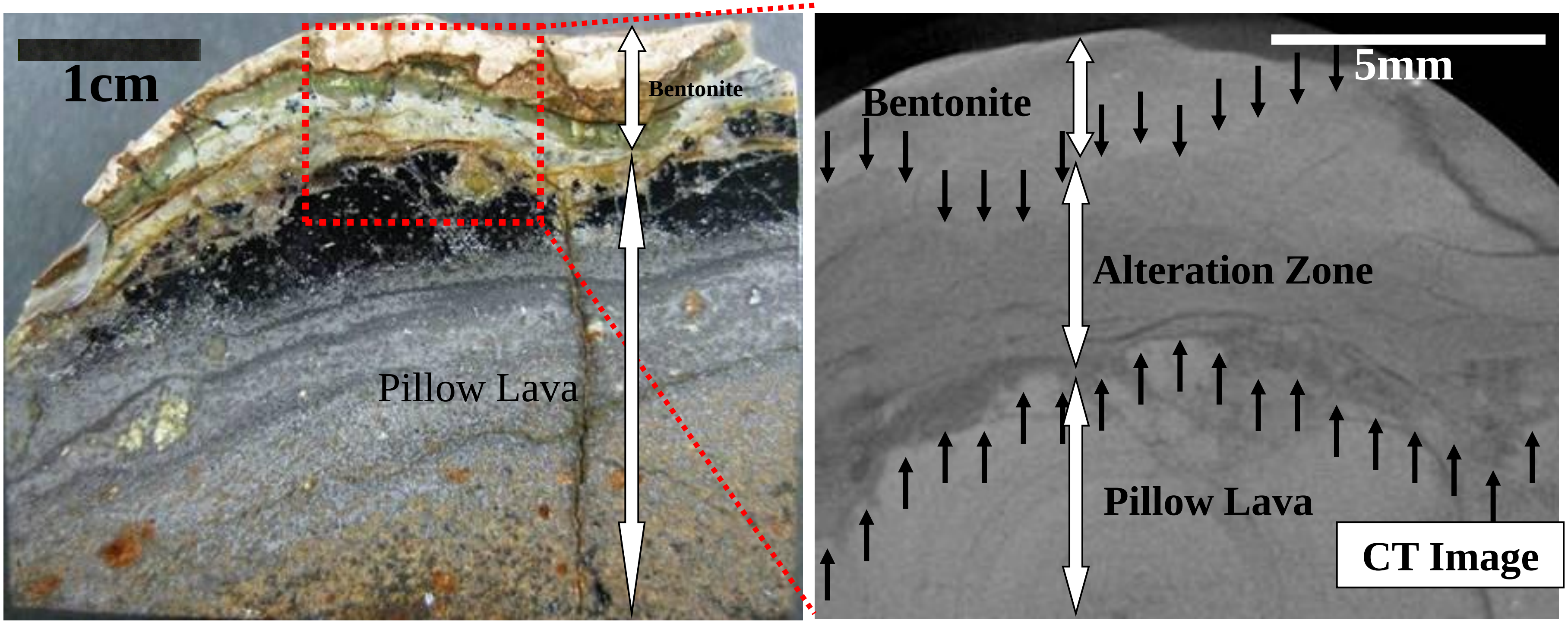
Trench 5 SW Wall



6. Interaction between smectite and hyperalkaline groundwater

Detailed Structure of Alteration Zone

(2) Alteration of bentonite in mm scale (Hokkaido Univ.)

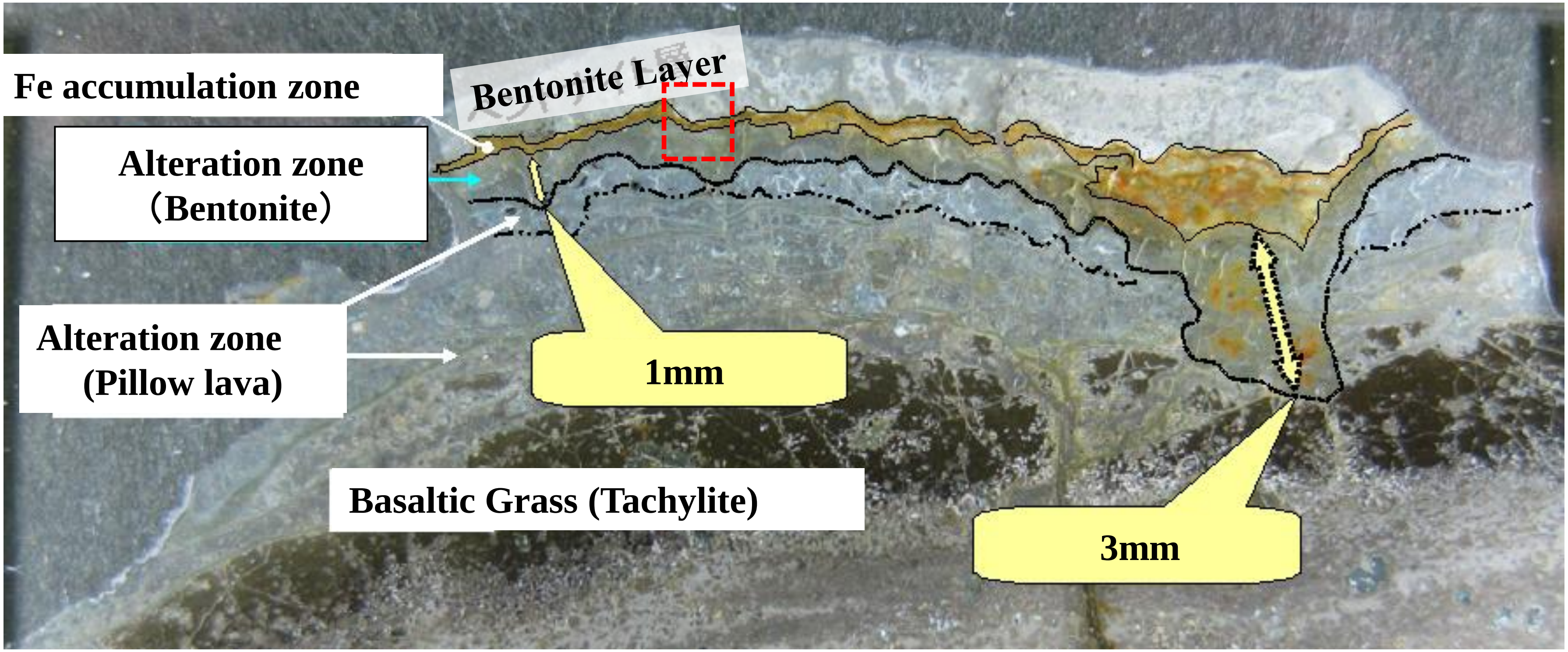


The density of alteration zone differs from bentonite and pillow lava.

6. Interaction between smectite and hyperalkaline groundwater

Detailed Structure of Alteration Zone

(3) Alteration of bentonite in mm scale (Hokkaido Univ.)

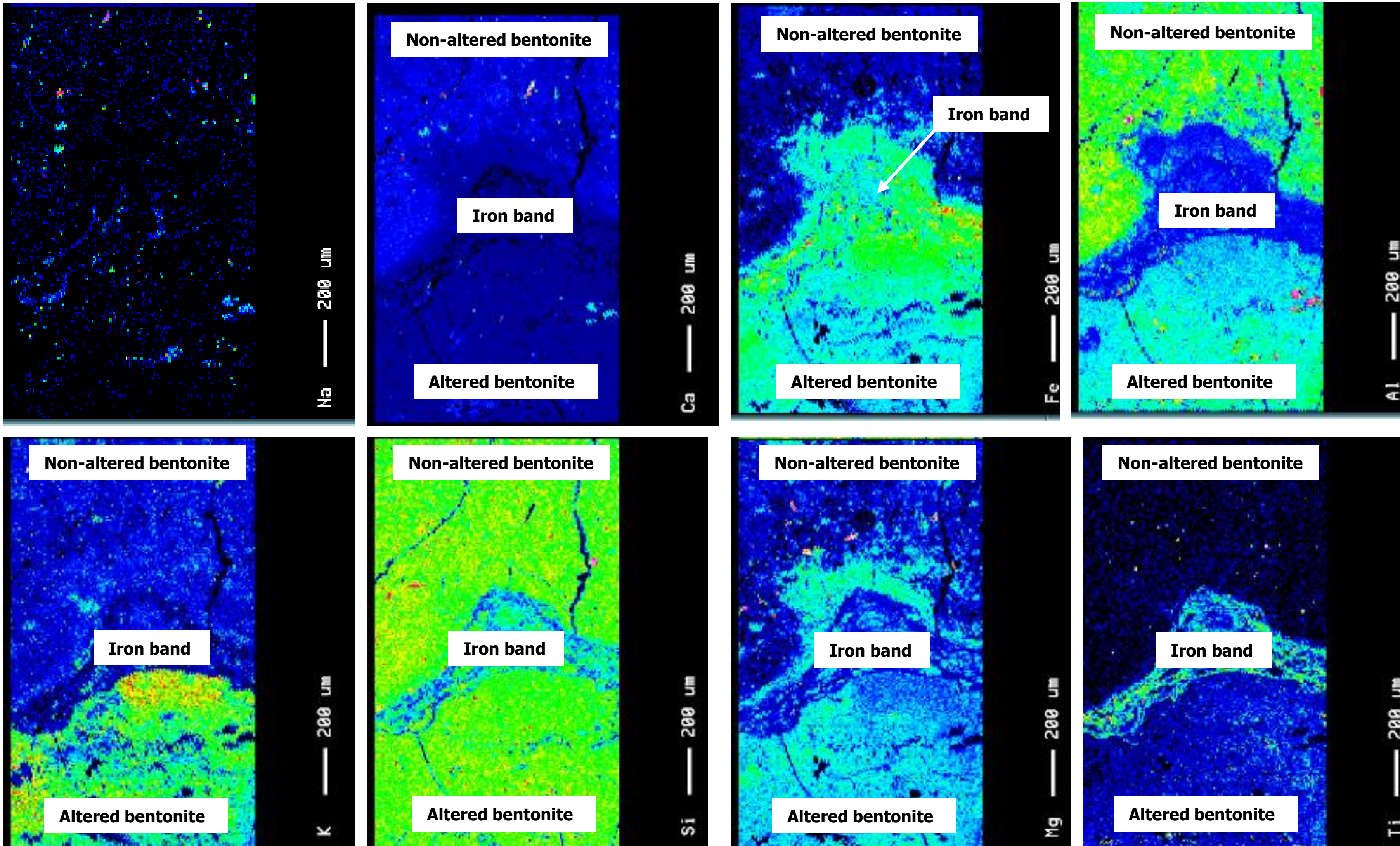


- Alteration zone between bentonite and pillow lava has been identified near the contact.
- Fe accumulation zone can be seen at the front of alteration zone.
- Width of alteration zone of bentonite is 1 - 3mm.

6. Interaction between smectite and hyperalkaline groundwater

EPMA Mapping

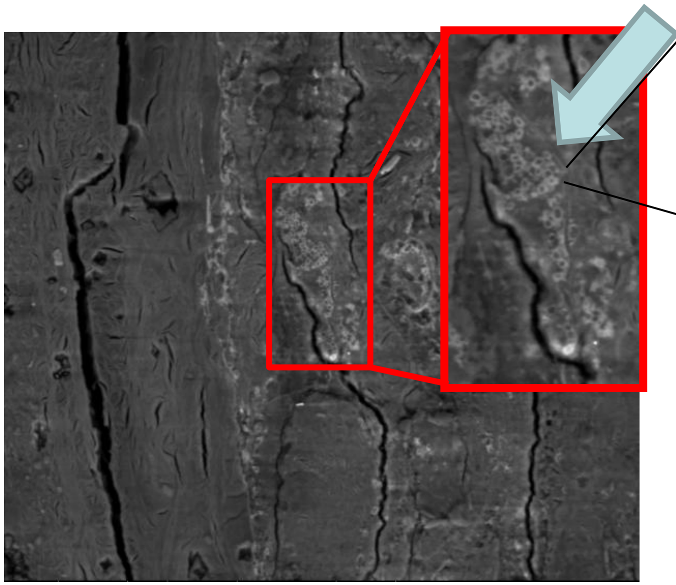
(Domain encircled by the red dotted line of the pre-slide)

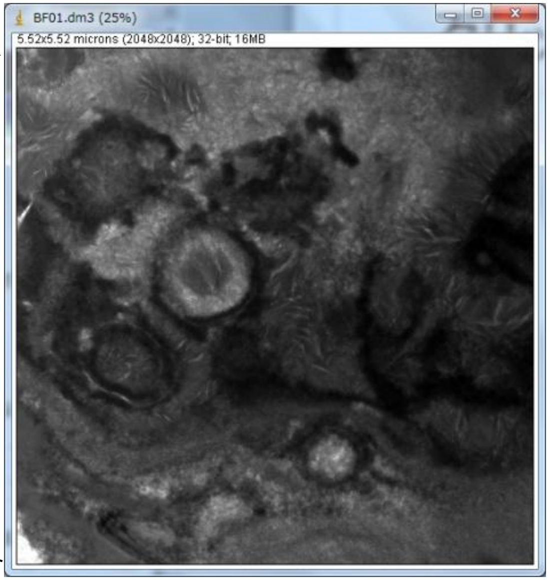


6. Mineralogical characterization of iron accumulation band in altered bentonte

SEM observation of iron band

Grain structure





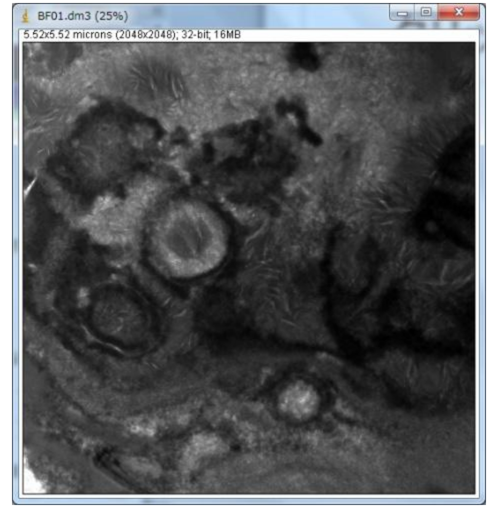
Grain structure

×4

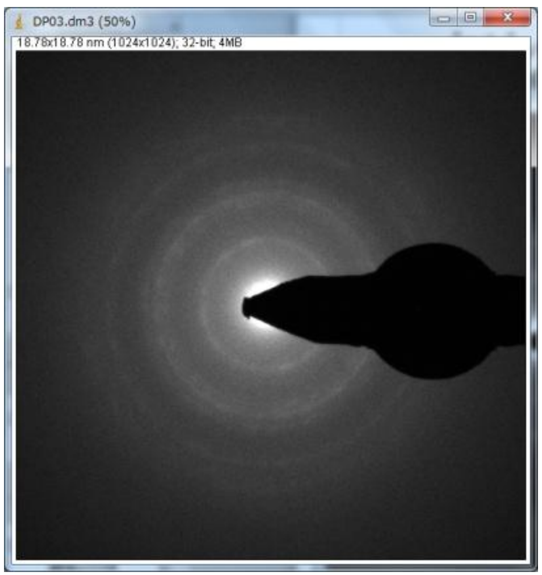
Feather structure

6. Mineralogical characterization of iron accumulation band in altered bentonite

Electron diffraction analysis



Bright part : Fe and Ti rich



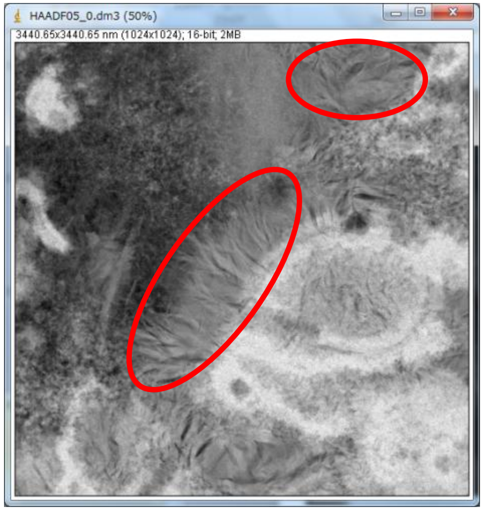
Electron diffraction pattern of Grain point

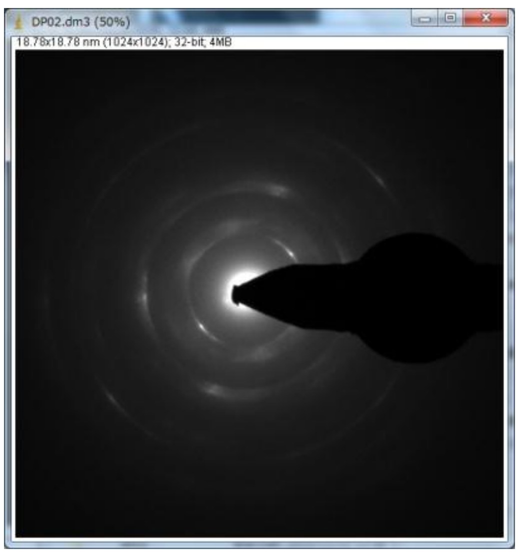
		nm
4.735	2.367	0.42
7.58	3.79	0.26
8.277	4.139	0.24
11.636	5.818	0.171

Correspondence with XRD pattern of **Goethite**

6. Nontronitization of Ca-Smectite

Electron diffraction analysis





Electron diffraction pattern of Feather stracture

		nm
4.442	2.221	0.45
6.13	3.06	0.33
7.819	3.909	0.26
8.993	4.496	0.22
13.343	6.671	0.149

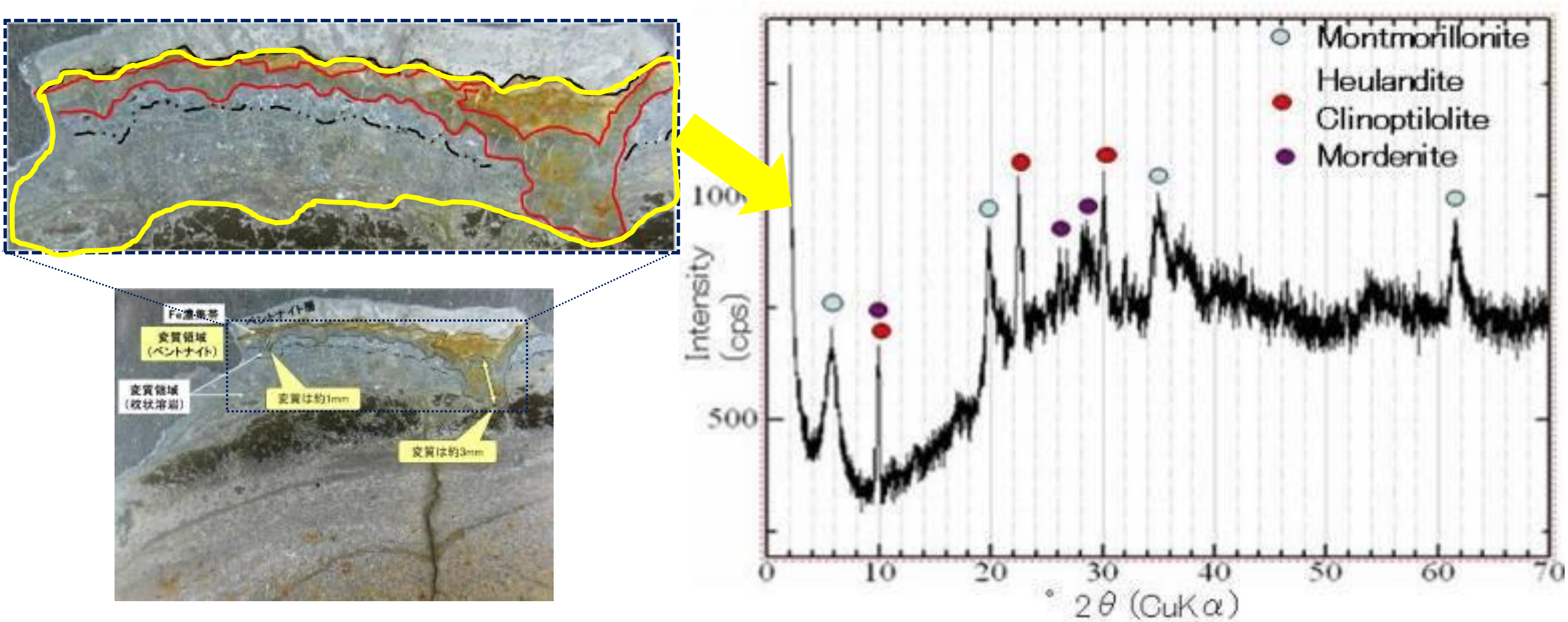
Correspondence with XRD pattern of smectite

Nontronite from point analysis of Fe accumulation band by EPMA

Element	8	9
Na	0.0082	-
Ca	0.4699	0.4617
Fe	2.5484	2.319
Mg	1.1065	1.3742
K	0.0584	0.1315
Mn	0.1498	0.1072
Al	1.0322	1.1721
Ti	0.0084	0.0149
Si	9.0636	8.9421

6. Interaction between smectite and hyperalkaline groundwater

XRD(Yellow line)



6. Interaction between smectite and hyperalkaline groundwater

Comparison with the precedence research on alteration bentonite

	Mo	Na-Cp	Ca-Cp	K-Cp	Ca-H	K-H
SiO_2	61.30	69.52	66.78	66.25	61.28	61.75
Al_2O_3	14.25	13.18	13.27	12.70	14.95	16.46
FeO	2.90	0.00	0.17	0.11	0.27	0.09
MgO	0.80	0.00	0.27	0.19	0.41	0.02
CaO	3.64	0.13	2.81	0.14	3.93	0.19
Na_2O	1.54	7.07	2.81	0.75	1.84	0.14
K_2O	2.80	0.61	1.16	9.94	1.00	10.50

Wt%

(Ogiwara 1996)

	Phillipine
SiO_2	42.98
Al_2O_3	9.72
FeO	16.10
MgO	3.90
CaO	2.67
Na_2O	0.05
K_2O	2.14

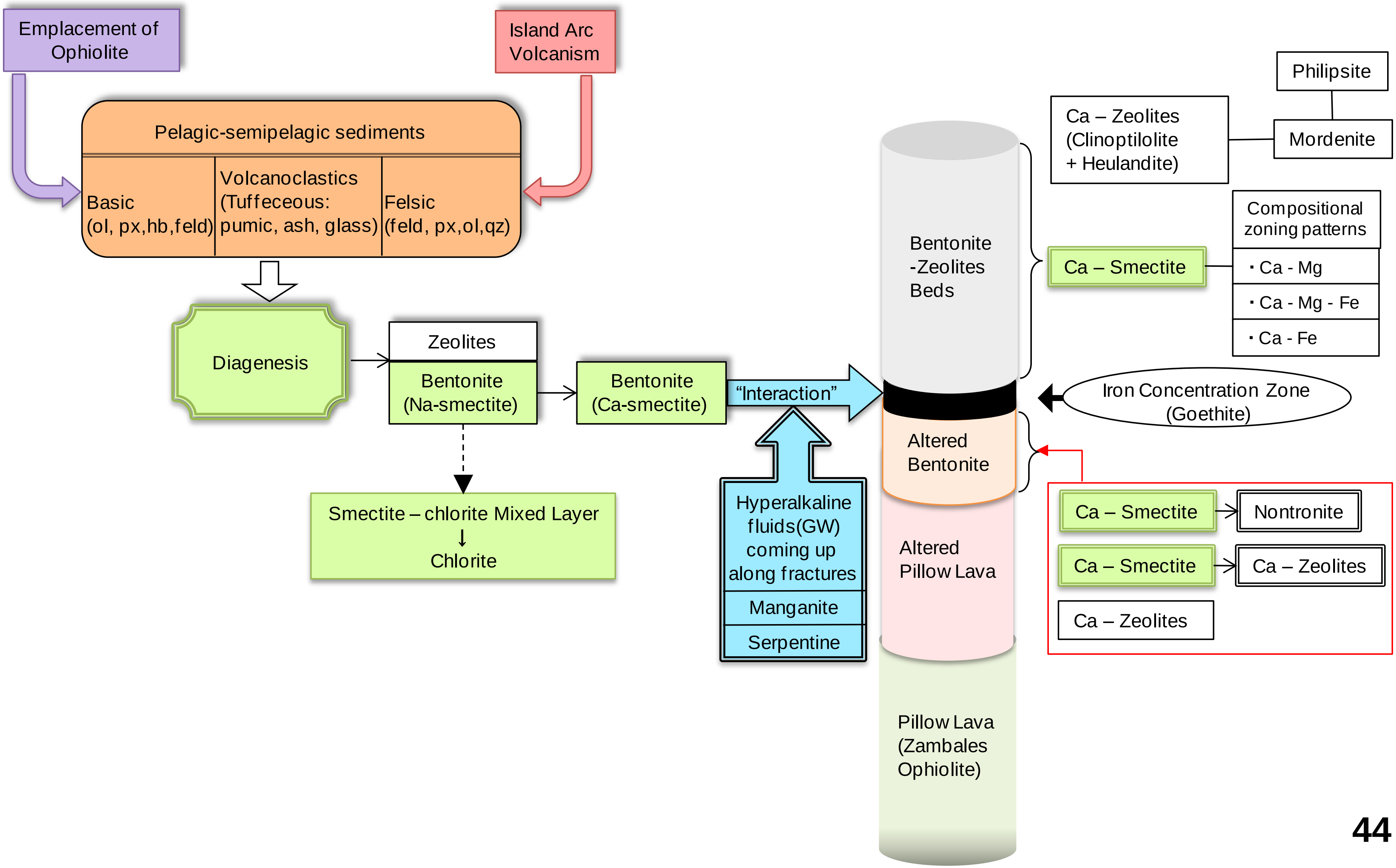
Wt%

Mo: Mordenite
Na-Cp: Na-Clinoptilolite
Ca-Cp: Ca-Clinoptilolite
K-Cp: K-Clinoptilolite
Ca-H: Ca-Heulandite
K-H: K-Heulandite

- XRD suggests that alteration bentonite is likely to Clinoptilolite or Heulandite.
- Boles (1972) defined zeolites of Si/Al>4 and Si/Al<4 are Clinoptilolite and Heulandite, respectively.
- It was reported that Clinoptilolite was generally formed result from reaction between Heulandite and Ca rich water.

↳ But, the kind of zeolite cannot have been identified yet only with such evidence.

7. Alteration Process of Bentonite in the Phillipines NA site



8. Summary and Future plan

Summary

- Some clear evidences of contact with a bentonite and hyperalkaline groundwater in the past were found out in the Philippines. (Fossil Type of Natural Analogue)
- XRD does not show the alkaline alteration of bentonite in the bleached zone. That is the bentonite maintains enough smectite.
- The characteristic occurrences of the smectite observed by FESEM are characterized by 3 types.
- From the basalt glass (Tachylite) where is a outermost part of pillow lava, Fe^{2+} oxideized and Si, Al, Na and Ca were selectively leached, cosequently the alteration zone of about 5mm was formed.
- The alteration zone of bentonite consists of smectite and Ca-Zeolite (Heulandite, Clinoptilolite, Mordenite) .
- The Fe-accumulated band consisted of mainly Goethite is located between bleached zone and unaltered bentonite bed. The width of this zone is about 1~3 mm. It is only observed notronite to occur adjacent to this zone.

Future plan

- The presence of phases formed by typical hyperalkaline alteration of smectites was not found, but this has to be investigated further.
- It is necessary to obtain chronological data to make clear the time-scales of Bentonite Reaction, and to establish scenario for Bentonite alteration in high pH conditions.
- This program should be focused on studying not only “Fossil site (Saile mine)” but also “Active site (Bigbiga)” with ongoing reaction between Bentontie and Hyperalkaline groundwater.