The International Philippines Hyperalkaline Analogue Project (IPHAP)
- NA studies for bentonite reaction under hyperalkaline conditions -

The 13th NAWG Workshop

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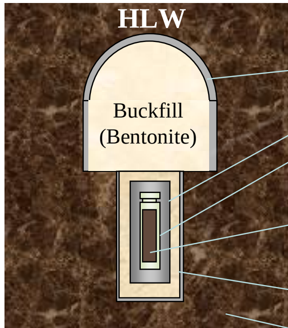
Contents

1. Background

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



Principal features of each component

Concrete support

Overpack

Canister

Waste packages, Filler(Cementitious materials)

Structural framework

Properties influenced by hyperalkaline water

Vitrified waste

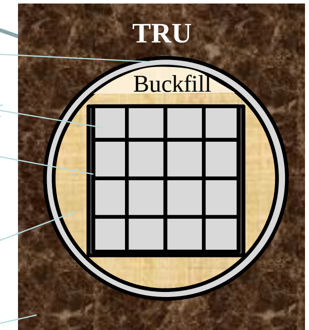
Release control of nuclides

Buckfill →(Sorption, Diffusion)

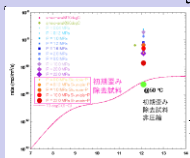
Buffer(Bentonic materials)

→Migtation control (Sorption, Diffuison, Restriction of groundwater movement)

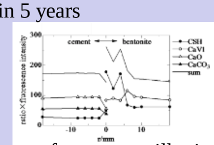
Host rock →Migtation control (Sorption, Diffuison)



Experiment and Analysis

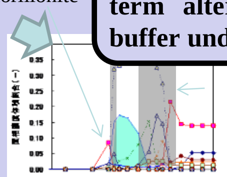


Ca-XAFS of the interface between bentonite and cement contact in 5 years



Dissolution rates of montmorillonite under conosolidation

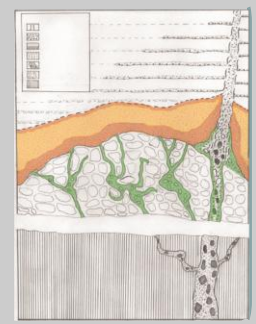
Montmorillonite



Prediction of altered bentonite after 10,000 years

Evaluation of the long-term change of barrier performance and the long-term alteration process of bentonic buffer under hyperalkaline condition.

Natural Analogue



Conceptual Model based on NA

NA can show long-term evidences over 100,000 years, which cannot be find lab test.

Thickness of altered layer
Dating

→Reaction rate / Verification of mass transport

Mineralogical process by alkaline alteration

→Input data (secondary minerals) of analysis

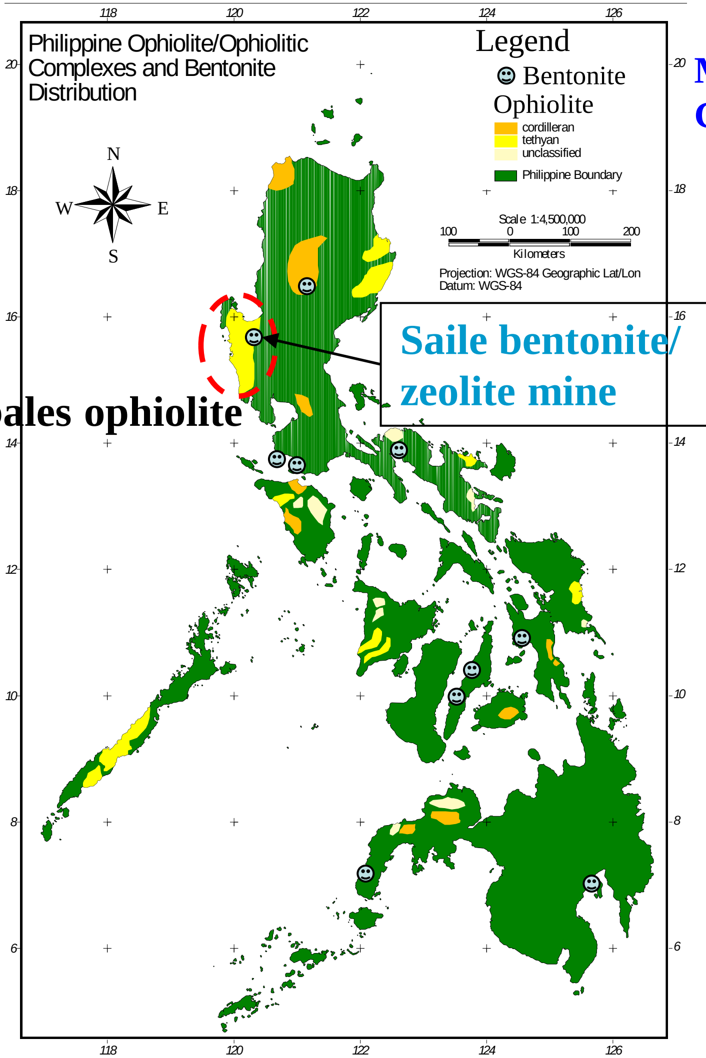
- Bentonite is unstable at high pH caused by cement leachates.

Ophiolites have been identified as sources of high pH groundwater.

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

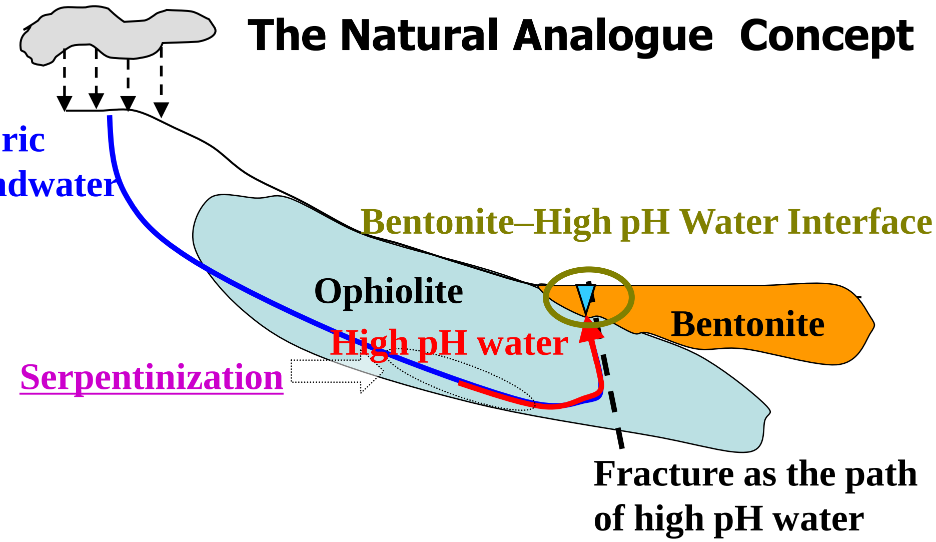
Natural Analogues can be applicable in geological time scale.

2. Reasons for selection of the Philippines as a NA site



Distribution of Opiolite and Bentonite deposits in the Philippines

The Natural Analogue Concept



Reasons for selection of the Philippines

- Distribution of many serpentinizing ophiolites
- Existence of bentonite deposits close to hyperalkaline springs in the ophiolite basement
- Resemblance to Japanese tectonics as a island-arc type

Field survey site for NA in Northwestern Luzon

3. Objectives and Work Schedule

This NA project has field survey in and around Saile mine as a site of Fossil Type NA and chemical and mineralogical analysis,

- **To better understand Long-term stability of Bentonite in contact with Hyperalkaline Groundwater**
  - **Formation of Bentonite Layer and Geological Setting**
  - **Geochemical properties of Hyperalkaline Groundwater and Environmental Conditions**
  - **Alteration(Mineralogical evolution) Process of Bentonite in contact with Hyperalkaline Groundwater**
- **To establish comprehensive scenario of Bentonite Reaction**

Work schedule for1st phase IPNAP (2007~2012)

Mangatarem -Saile mine and Manleluag hotsprings- (Fossil Type)

2007	2008	2009	2010	2011	2012
Literature research					
Preliminary survey	Preliminary survey	Main survey of NA	Main survey of NA	Main survey of NA	Main survey of NA
• Outline investigation of geology	• Geological survey • Groundwater survey • Trench survey • Boring survey	• Chemical and mineralogical analysis • Geological survey and fracture system evaluation • Groundwater survey • Trench survey	• Geochlonometry • Chemical and mineralogical analysis • Trench survey	• Geochlonometry • Chemical and mineralogical analysis • Basic Physical Property Test	• Modeling • Geochlonometry • Chemical and mineralogical analysis • Basic Physical Property Test

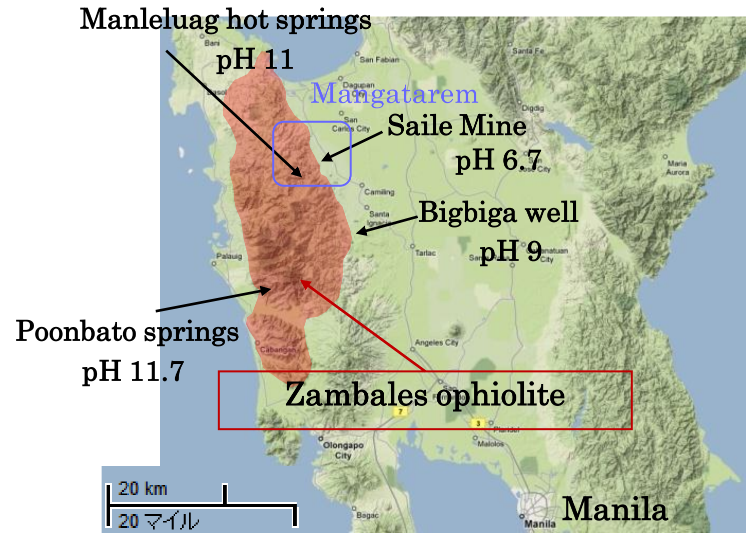
Bigbiga or Poonbato (Active Type)

2007	2008	2009	2010	2011	2012
		Preliminary survey	Preliminary survey	Preliminary survey	Preliminary survey
		• Geological survey and fracture system evaluation • Groundwater survey	• Geological survey • Boring survey • Groundwater survey • Trench survey • Chemical and mineralogical analysis	• Geological survey • Groundwater survey • Chemical and mineralogical analysis	• Geological survey • Boring survey • Groundwater survey • Chemical and mineralogical analysis

4. Groundwater Chemistries of Survey Sites

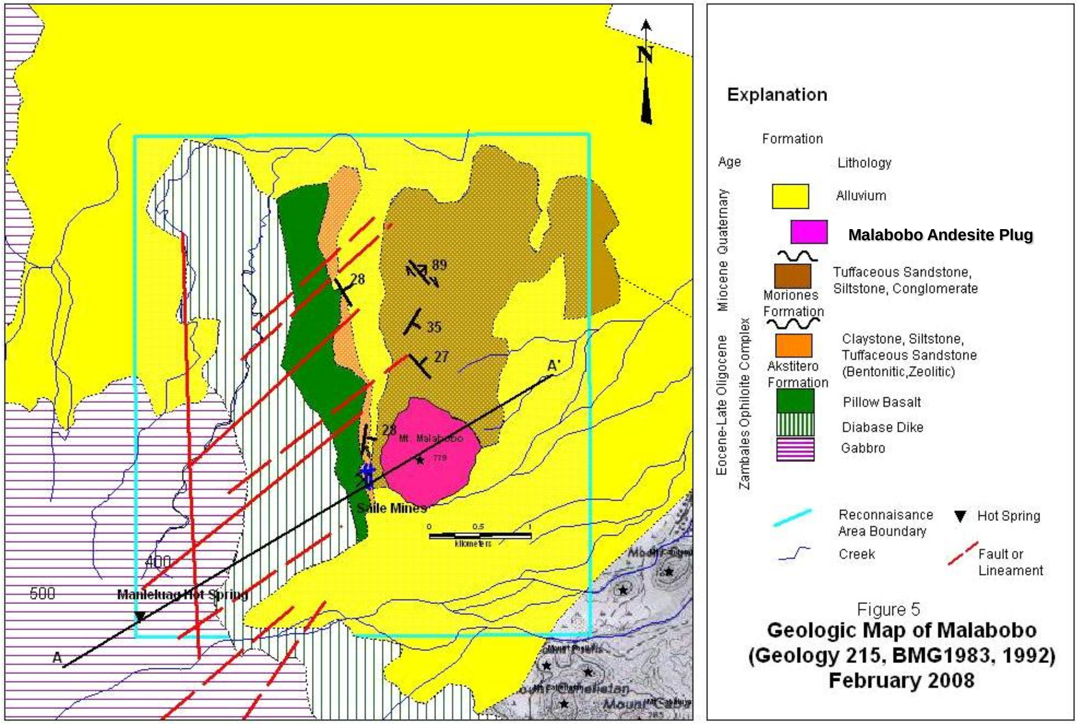
Site	Manleluag HSp. - M1	Manleluag HSp. – M4	Saile Mine Well	Poonbato Spring	Bigbiga Well	low alkali cement leachates (PNC 1997)*
Sample No.	M1-11-KWP-01	M4-11-KWP-04	SA-10-KWP-01	PB-10-KWP-01	BB-11-Well1	
pH	10.84	10.92	6.73	11.62	9.16	11.09
ORP(Eh) [mV]	-662	-698	65	27.6	-118	-
Temp [℃]	34.1	34.2	27.9	27.6	29.6	60
CH_4 [ppm]	>5000	0 (2200)	0	>5000	0 (0~560)	-
H_2 [ppm]	62	0 (230)	0	50~1320	0 (0~130)	-
Na^+ [ppm]	1.58	1.57	13.5	23.6	7.13	43
K^+ [ppm]	0.28	0.22	1.92	6.85	0.76	13
Ca^{2+} [ppm]	23.6	23.75	23.9	37.4	0.33	16.8
Mg^{2+} [ppm]	0.17	0.01	18.5	0	0	-
Si^{2+} [ppm]	11.5	12.2	24.0	1.40	36.3	
Al^{3+} [ppm]	20.3	24.8	0.02	0	1.11	0.3
Cl^- [ppm]	16.6	16.6	-	-	4.99	-
HCO_3^- [ppm]	73.5	55.6	232.8	124.1	153.8	-

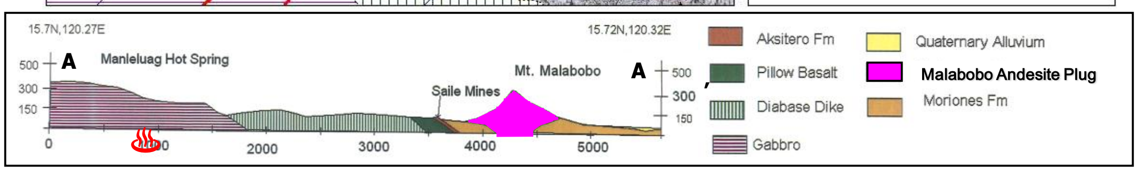
***Mix Proportion – Portland cement: silica fume: fly ash = 40: 20: 40**



- **High pH, high Ca, reducing and 30~40°C** (Groundwater is **analogous to low alkaline cement leachate.**)
- **Origin from metric water, high Ca and low Mg and effusion of H_2 and CH_4 gas** (These are the typical characteristics of hyperalkaline groundwater formed by serpentinization.)
- Degree of the reaction between water and rock: **Poonbato > Manleluag > Bigbiga > Saile mine,**
  Residence time: **Poonbato > Manleluag > Bigbiga > Saile mine**

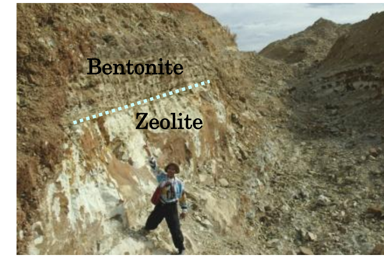
5. Geology of Survey site for NA of Fossil Type (Manleluag Hot spring / Saile Mine)





Geological map of Mangatarem (Manleluag hot spring / Saile mine)

Wellhead of Manleluag hot spring (pH11)



Alternation of a bentonite bed and zeolite bed

Outcrop identified 6 faults in Saile Mine Quarry

Aksitero Formation

▼ Origin

Pelagic-semipelagic sediments, Diagenisis

▼ Occurrence

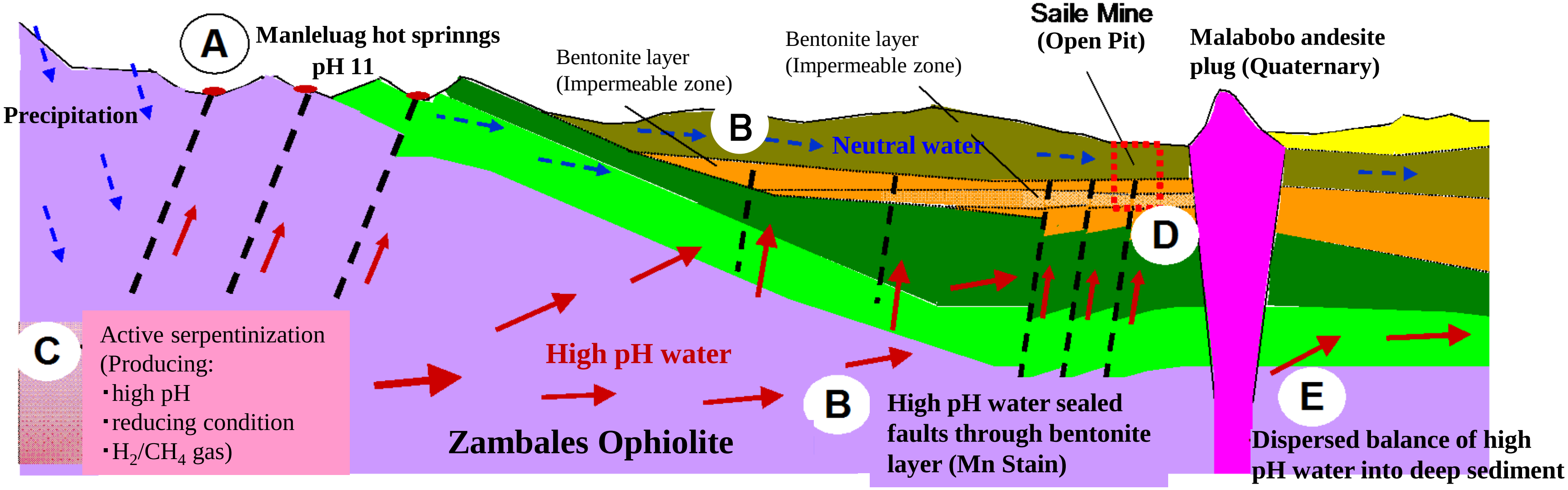
Width:30~150m, Strike: about 2000m around Saile mine

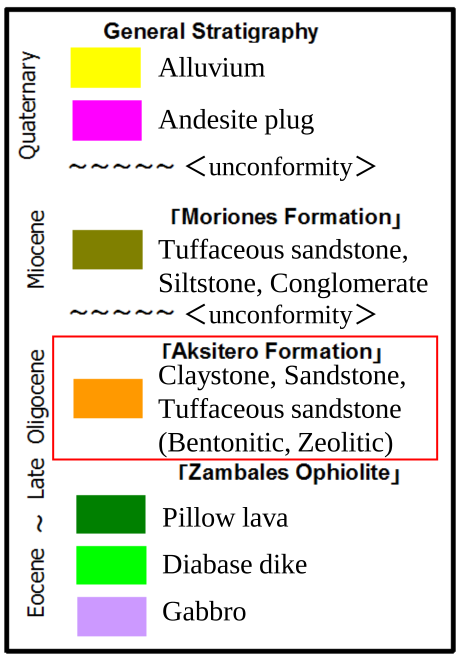
▼ Mineral Composition of Bentonite

- Main mineral: Ca-Montmorillonite

- **Saile bentonite/zeolite mine (bentonite beds alternate with zeolite beds in Aksitero Formation) is situated at the eastern edge of the Zambales ophiolite on the Northwestern Luzon. Manleluag Hot Springs (pH 11) exist about 2.5 km southwest of the quarry, situated in the gabbro of the Zambales ophiolite.**
- **The Aksitero formation, which includes bentonite layer, directly overlies on volcanic basaltic breccias and pillow lava at the top of Zambales ophiolite and is deposited horizontally.**
- **6 normal faults exist in the Saile mine quarry. The most of fault zones have been brecciated, and coated with characteristic Mn-staining on the surface as well as the concentration on Mn-material on the bedding plane concordantly.**

5. Basic Concept of Regional Groundwater Flow System in Mangatarem





Ⓐ Hyperalkaline springs in gabbro

Hyperalkaline groundwaters flow through faults in the basement rock.

Ⓑ High pH water under bentonite, neutral water above it

Bentonite layer acting as impermeable layer isolates the hyperalkaline deep groundwater from neutral shallow groundwater.

Ⓒ Active sepentinization in Ophiolite

Supply of meteoric water and serpentinization produce high pH and H_2/CH_4 gasses.

Ⓓ Contact (of Fossil Type)

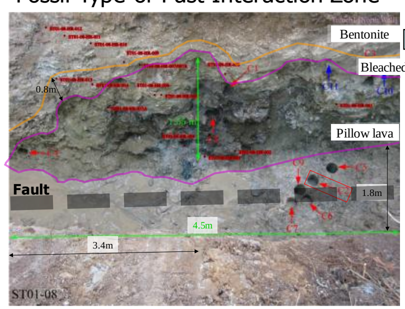
Hyperalkaline groundwaters interact with base of bentonite (in the past).

Ⓔ Dispersed release of high pH waters into deep sediment

6. Geological and Mineralogical Evidences for Existence Generation of Hyperalkaline Groundwater in Saile Deposits (Natural Analogue of Fossil Type)

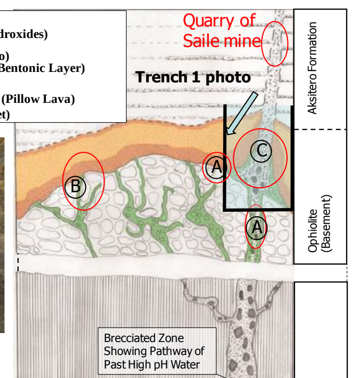
1. **Serpentine and Calcite in fracture filling materials**
   The Serpentine on the outside of the fault formed at the generation of High pH water (serpentinization). The calcite of the center of the fault precipitated by the reaction of hyperalkaline water(high Ca content) and an atmosphere, and that clogged the path.
2. **Fracture system as a hyperalkaline water flow path**
   The fault and fine fractures reach to the bentonite layer.
3. **Characteristic Minerals of alkaline alteration zone**
   K feldspar was identified at the contact interface of bentonite.
4. **Mn minerals in fracture filling materials and of the bedding plane.**
   Manganite (Mn-hidroxide：γ-MnOOH) was identified. It is stable under high pH environment.

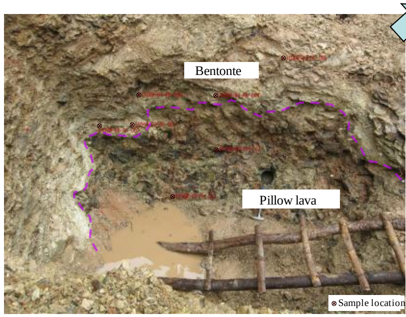
Fossil Type of Past Interaction Zone



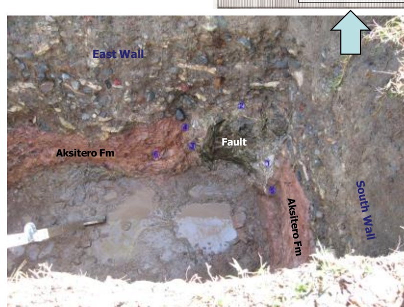
Ⓐ Saile mine Trench 1 (2008)

Fracture system of quarry





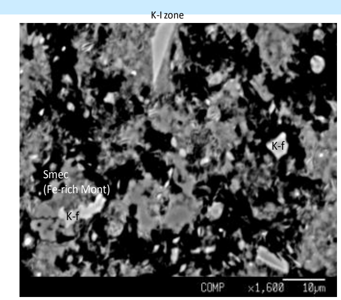
Ⓑ Saile mine Trench 6 (2009)



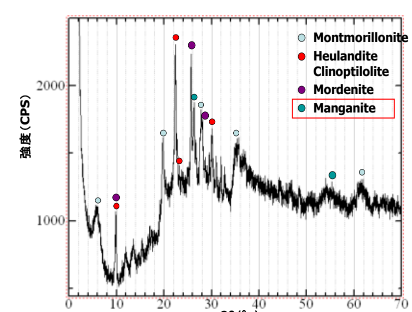
Ⓒ Bigbiga Trench BBT01 (2010)

2. Type Section of past interaction zone based on Trench Survey

1. Core of the fracture zone (Bottom of Trench-1) (White: Calcite, Green: Serpentine)



3. K-feldspar in the alkaline alteration zone of bentonite (Contact surface in Trench-5)



4. Mn-staining of the fault rock and XRD (Fault in the Quarry)

7. Mineral Assemblage and Physico-chemical Characteristics in Bleaced Zone
- Scale of the alteration -

- **Bleached zone about 20~40cm wide was observed in the bentonite layer from the (contact)surface of basaltic pillow lavas.**
- **The shape of Bleached Zone is concordant with the wavelike surface of basaltic pillow lavas. (That is mass transportation was controlled by diffusion.)**
- **The mineral assemblage, CEC and swelling power in the Bleached zone do not differ notably from those in unaltered bentonite except the part of heterogeneous calcite.**

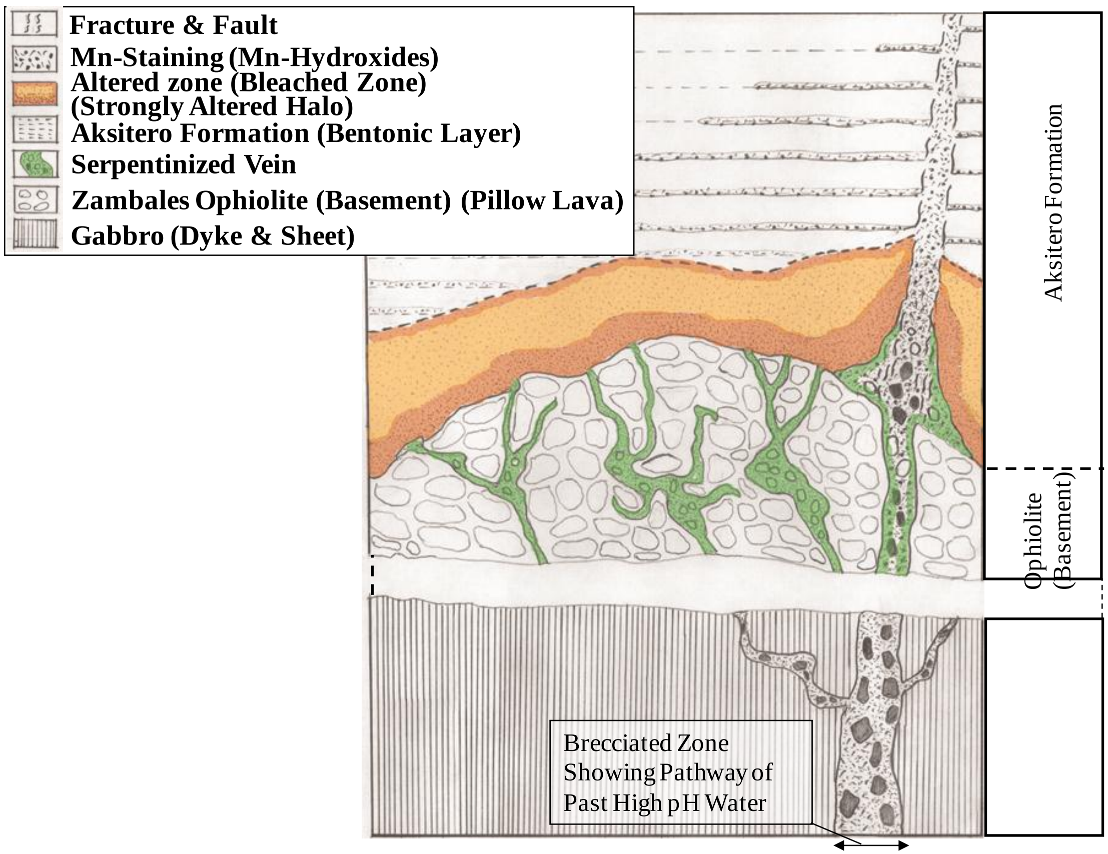


Illustration of Type Section as『Fossil Type』of Past Interaction Zone

7. Mineral Assemblage and Physico-chemical Characteristics in Bleaced Zone
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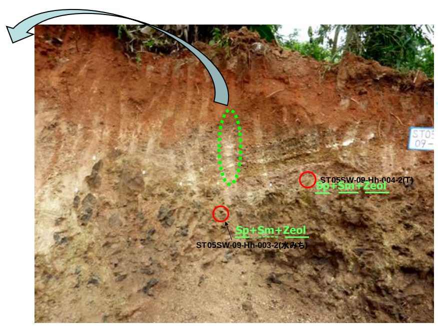
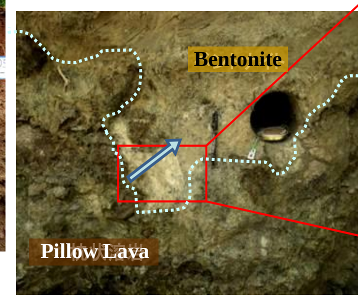
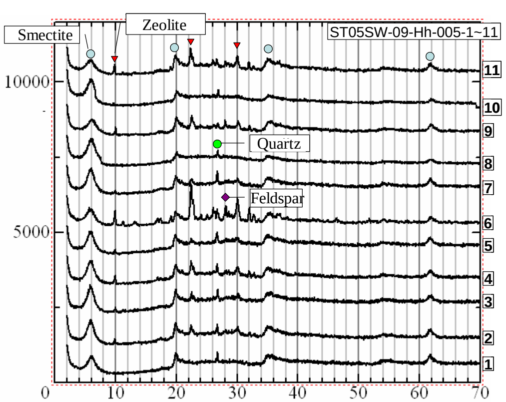


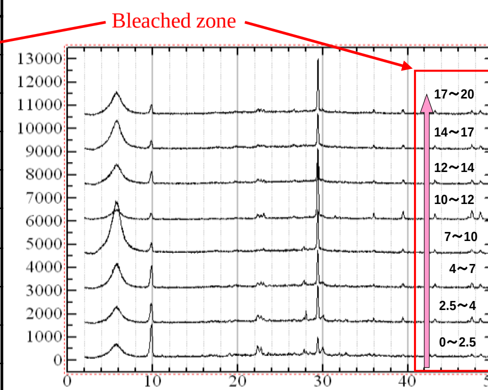


Sampling in bentonite every 2cm from the boundary between bentonite and basaltic pillow lava



XRD from the boundary to unaltered zone in Trench-5

Sample	Swelling power [ml/2g]
20	6.5
30	7.0
40	6.0
50	6.7
60	7.1
70	5.8
80	6.2
90	6.6
100	6.3
110	6.7
120	6.9
130	6.3

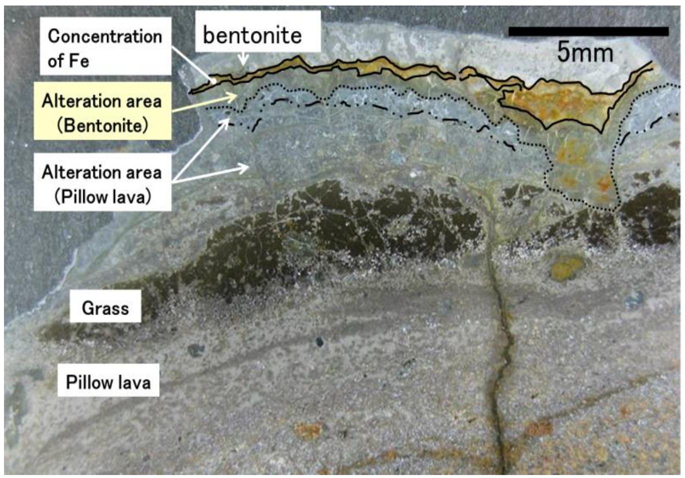


Sample	Ca	K	Mg	Na
0~2.5	102	1.158974	4.691358	1.398261
2.5~4	292	0.77641	3.786008	1.266087
4~7	274	0.506667	4.197531	1.034783
7~10	290	0.683077	4.279835	1.08
10~12	297	0.522051	2.633745	1.043478
12~14	307	0.46359	3.81893	1.106087
14~17	306	0.613333	4.592593	1.045217
17~20	290	0.688205	4.888889	1.078261

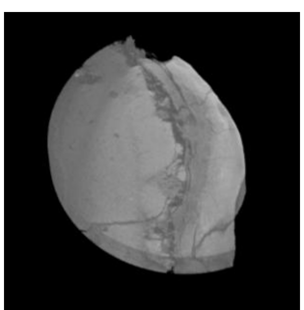
Swelling power, XRD and CEC of bleached zone in Trench-1

8. Chemical and Mineralogical Behavior of Alkaline Alteration Zone adjacent to the Interface

- **The alkaline alteration zone had formed by interaction with hyperalkaline groundwater was found in the contact interface between bentonite and basaltic pollow lava, but the width is a maximum of 5 mm.**
- **The concentarton band of Fe, which is high density by clogging nontronite and goethite, was found in the front of the alkaline alteration zone.**



Alkaline alteration zone in the interface between bentonite and pollow lava



Change of the threshold

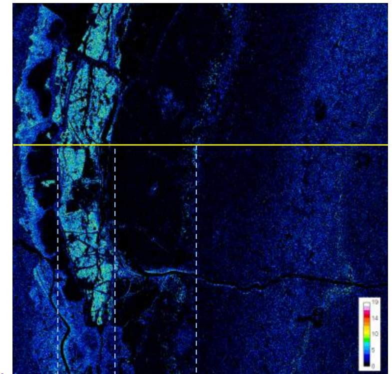
Pillow lava ⟷ Bentonite

X-ray CT of the interaface

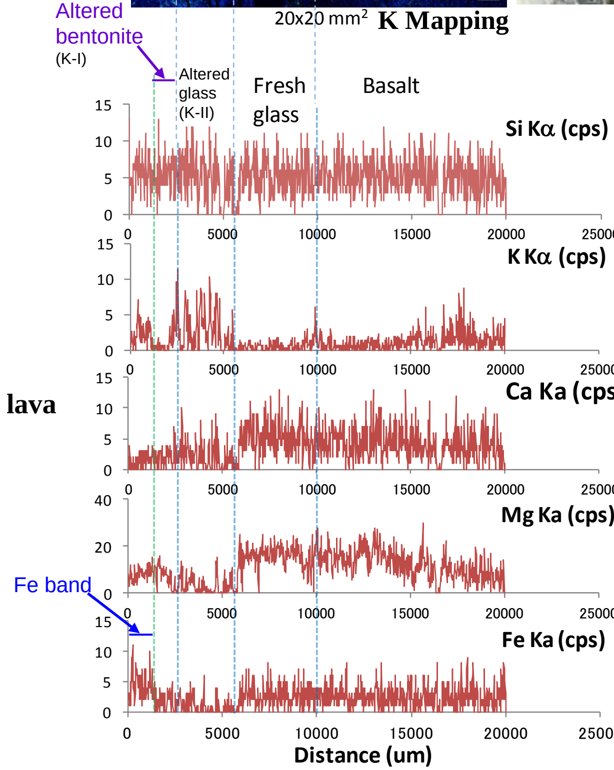
Pillow lava ⟷ Bentonite

High density part

The Sample was taken in the place where a vein of serpentine in the pillow lava has reached bentonite layer.



20x20 mm^2 **K Mapping**



Line profile in the interface

K element

- Altered basaltic glass became K high concentration because of selective leaching from basaltic glass.
- Subsequently, some of K element moved into the alteration bentonite.
- That K element might be provided for precipitation of K-feldspar.

Fe element

- Fe leached from basaltic glass formed Fe band of high density as precipitation of nontronite and goethite,
- And besides, Fe might be provided for formation of Fe-smectite.

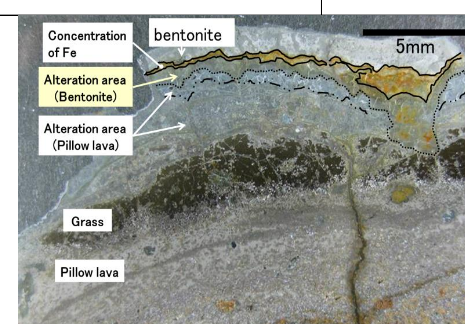
9. Mineral Assemblage of Alkaline Alteration Zone

Columnar Section \ Minerals		Characteristic minerals																Remarks
		Smectite				Zeolites				Feldspar		Silica Minerals		Opaque Minerals				
		Ca-Sm	Fe-Sm	Fe-Sap	Nont.	Heu.	Clino.	Mor.		K-Feld.	Plag.	Crystal	Amorph	Goethite	Hem-Ilm	[Fe-Mn-Ca Phase]		
Unaltered Bentonite		○				○	○	◌			<Relict> ○	○						•Bleached Zone of 30cm wide from the interface(PL) •Same distance from upper boundary of pillow lava
Iron Concentration Zone (Fe-Band)			○※ (Dioctahedral)	<Nodulated> ○ (Trioctahedral) Mg→Fe^{2+}	○ (Dioctahedral) Al→Fe^{2+} [Oxidation]	<Rectangular> ○	◌			<Irregular> ○			<halo> ○	<Annular／Ringlike> ○		<Filmlike> ○		•Fe-Mn phase •Clogging (Nont. + Goethite: 1~5mm wide, High density, High pH) •Fe-Mn Goethite
Altered Bentonite (K-I)	K-lower Zone		○※※ (Dioctahedral) Fe^{2+}(Octahedral layer)	◌	○ [Reduction]						<Relict> ○		○	○		◌		•K-Low Zone → Fe-Rich •Plag.(Relict)→Sm, Low density
	K-rich Zone		<Pillowlike> ○ (Dioctahedral) Fe^{2+}(Octahedral layer)		◌	○	◌			<Microscopic> ○	<Relict> ○		◌	◌				•Highest Fe Sm
Altered Basaltic Glass (K-II)		○				○	◌				○							
Basaltic Glass		Tachylite																Alteration minerals Mafic→Serpentine, Iddingsite, Saponite, Chlorite
Pillow Lava		Olivine Basalt																Felsic→Smectite, Zeolites (Calcite)

Boundary between bentonite and pillow lava

※ $Ca_{0.28}Na_{0.01}(Fe^{2+}{}_{1.09}Al_{0.66}Mg_{0.46}Ti_{0.07}Mn_{0.02})Si_4O_{10}(OH)_2$ [(060): 0.149~0.150 nm, Lattice spacing : 1.0~1.1 nm]

※※ $Ca_{0.11}Na_{0.05}K_{0.01}(Fe^{2+}{}_{1.2}Al_{0.62}Mg_{0.51})Si_4O_{10}(OH)_2$ [(060): 0.151 nm, Lattice spacing : 1.0 nm]



9. Mineralogical Evolution under Hyperalkaline groundwater

- The alkaline alteration zone of the contact interface between bentonite and pillow lavas formed by cation substitution reaction in main dissolved components of hyperaalkaline water, dissolution-precipitation reaction and reduction-oxidation reaction, and constitutes of Fe-type Smectite(Fe-Smectite, Fe-Saponite), Notronite(, Goethite), K-Fldspar, Ca-Zeolites(Heulandite, Clinoptilolite) and Slica Minerals.
- Nontronite and Goethite, which is a paragenetic mineral of Nontronite, formed the high-density Fe band. That played as a role of preventing from mass tranfer due to Clogging. In consequence, The alkaline alteration zone was limited to about 5mm wide.

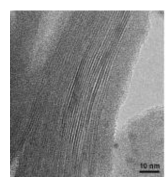
High pH Fluids
Reducing Conditions
(Major Dissolved Ions)
Si^{4+}, Al^{3+}
Fe^{2+}, Fe^{3+}
Ca^{2+}, Mg^{2+}
Na^{+}, K^{+}
OH^{-} (Cl^{-})
Temp.

① Cation Substitution dominant Process

→ Ca-Montmorillonite 1 | Ca-Montmorillonite 2 | Ca-Montmorillonite 3

Ca-Montmorillonite 2 → [Al･Mg→Fe^{2+}] → **Fe**-Saponite (Tri-Octahedral)

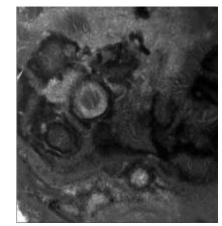
Ca-Montmorillonite 1 → [Mg･Al→Fe^{2+}] → **Fe**-Montmorillonite (Di-Octahedral)



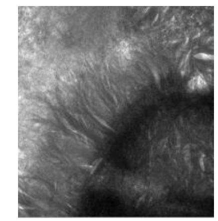
Di-octahedral type Smectite (Fe band)

③ Oxidation Process

Ca-Montmorillonite 3 → [Al･Si→Fe^{3+}] → Nontronite (Di-Octahedral) + Goethite



Nontronite(Fe-band)



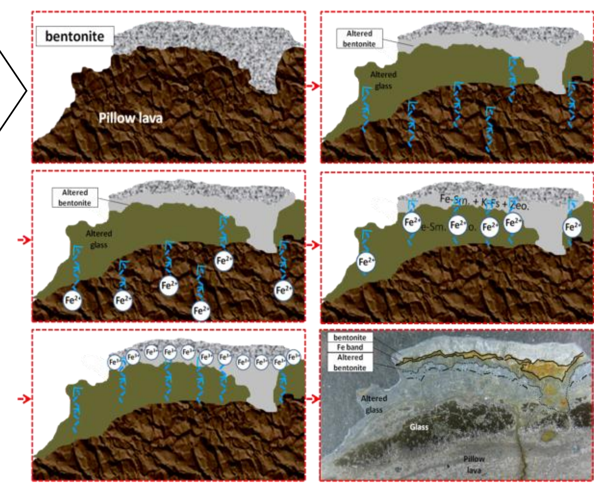
Goethite(Fe-band)

② Dissolution-Precipitation (Growth) dominant Process

→ Ca-Montmorillonite 4

[Si / Al, Na + K, Ca, High pH]

(Ca･Na)-Zeolites + K-Feldspar ± Silica Mineral



Fe concentration band formation process

10. Evaluation of reaction time with a hyperalkaline groundwater -Age Determination-

- **Time scale of the interaction between bentonite and hyperalkaline groundwater was evaluated based on the dating of fracture filling materials, because the sample was the evidence of hyperalkaline water flow**

Sample; Cores of fracture filling materials taken from the botom at Trench-1

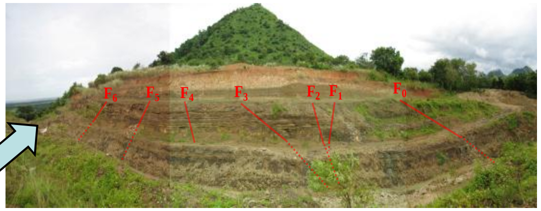
① Thermoluminescent method of Calcite(Carbonate Mineral): End time of the interaction
→Hyperalkaline water path closed by the fomation of carbonate minerals alter the reaction with air(CO_2).

②K-Ar dating of Serpentine: Beginning Time of the interaction
→Hyperalkaline water was generated by serpentinization.

Age of Calcite by Thermoluminescence: 30~100 Ka(Kilo age)

Age of serpentine by K-Ar dating was 95 Ma(Mega age). But, that might show the age of source rock of Ophiolite. The difficulty of separation of serpentine from fracture minerals causes the error.

- **Synthetic estimation of reaction time based on stratigraphic succession, sedimentation age by nannofossil and relation of fracture systems in sedimentary layers**



  - **Moriones Fm age from nannofossil: 23Ma**
  - **Aksitero Fm from nannofossil: 29Ma**
  - **<u>The fracture systems on the quarry have never cut Moriones Fm.</u>**

If the generation time of fracture systems assume the age that hyperalkaline water flowed and contacted bentonite layer, it is possible to react for very long time (at least 23Ma~100Ka).

11. Summary

Many Evidences with respect to the scale of the alteration and the mineralogical evolution in bentonite under the long-term hyperalkaline condition were found out at Saile mine (Natural Analogue site of "Fossil Type") in the Philippines.

1. As what analogue should it be used ?

- **It can be a clear evidence of the contact with groundwater over pH11 at the site of Fossil Type that K-feldspar was identified as an alkaline alteration mineral. From this evidence, this NA is applicable as low-alkaline cement or Region III leachate of OPC controled by the dissolution reaction of C-S-H.**
- **And, this NA may also be able to be considered as Region II leachate of OPC kept in equilibriumu to portlandite(Ca(OH)2) leached from OPC. But, since Region II leachate is about pH12.5, an evaluation under Region II need not only NA but also geochmical modeling.**
- **Fe element was a key parameter of the reactions of alkaline alteration between bentonite and pillow lava. If it is regarded as the influence of Fe to bentonite under alkaline condition, this NA is useful for an understand of the interaction between bentnite and overpack.**

11. Summary

2. How should the NA be used?

•Understanding of Alteration Process

- ➢ **The information of the minelarogical evolution controled by the mass balance is useful to understand long-term behavior of bentonite contact with high pH water.**

•Improvement of Performance Assessment Model

- ➢ **The NA of Fossil Type can give mineral assemblage in the bentonite after it reacted hyperalkaline water and then long time passed. From the reason, the NA can use to check the repuroducibility of geochemical modelling based on theory of chemical equilibrium and to optimize prameter, e.g. secondary minerals, and boundary condition for that modelling.**

•Supporting Evidence

- ➢ **The inhibition of the alkaline alteration by clogging is supporting evidence that bentonite keep its favorable properties for a long time under the hypealkaline environment.**

11. Summary

3. Evaluation of long-term stability of bentonite from the NA

① Range and Degree of Bleaced Zone

- The width of bleaced zone in bentonite layer is about 20~40cm. The shape suggests that mass transportation was controlled by diffusion.
- The mineral assemblage, CEC and swelling in the Bleached zone do not differ notably from those in unaltered bentonite except the part of heterogeneous calcite.

② Scale of alkaline alteration and mass transfer

- The alkaline alteration zone had formed by interaction with hyperalkaline groundwater was found in the contact interface, but the width is a maximum of 5 mm. And it constitutes of Fe-type Smectite(Fe-Montmorillonite, Fe-Saponite), Notronite(, Goethite), K-Fldspar, Ca-Zeolites and Slica Minerals.
- The Fe-accumulated band consisted of Nontronite and Goethite was formed in the front of the alkaline alteration zone. The clogging by these minerals prevented mass transfer, and restricted alteration.

③ Fact of the field in a macroscopic viewpoint

- In spite of having been in contact with hyperalkaline water flowing out actively now still on the basement rock with many faults, bentonite deposit has been maintained for a long period beyond the evaluation time of waste diposal.

Because of these facts, the long-term stability of bentonite under highpealkaline condition(pH11) will probably be enough maintained.

2007

2008

2009

Thank you for your kind attention.

2010

2011

2012