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

The 12th NAWG Workshop

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ON. 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)
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1. Background and Objectives
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3. Geology and Groundwater Chemistry in Zambales area
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6. Interaction between hyperalkaline groundwater and Smectite
7. Alteration Process of Bentonite
8. Summary and Future plan
1. Background

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

- 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 Disparity 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)

<table>
<thead>
<tr>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
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<td><strong>Literature research</strong></td>
<td><strong>Preliminary survey</strong></td>
<td><strong>Saile Mine (Fossil Type)</strong></td>
<td><strong>Main survey of NA</strong></td>
<td><strong>Bigbiga or Poonbato (Active Type)</strong></td>
<td><strong>Preliminary survey</strong></td>
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</table>

**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

**Bigbiga or Poonbato (Active Type)**
- Preliminary survey:
  - Geological survey and fracture system evaluation
  - Groundwater survey
- Main survey of NA:
  - Boring survey
  - Groundwater survey
  - Chemical and mineralogical analysis
1. Organization-System

METI
Nuclear Waste Management of the Japanese Government

RWMC
Management of the International Philippines Natural Analogue Project
- Planning
- Field survey
- Assemblage of data and Evaluation of the natural analogue process
- Management of Committee
- Making the annual report

Mitsubishi Material Corp.
FE-SEM and EPMA analysis

Obayashi Corp.
Field survey (Arrangement)

Bedrock Geosciences
Dr. R. Alexander
Field survey (Reader)

Philippines Univ.
Prof. C. Arcilla etc.
Field survey (Boring, Logistics and Hospitality)

Nagoya Univ.
Prof. Abe
Groundwater dating

Kanazawa Univ.
Prof. N. Hasebe
Radiometric dating

Hokkaido Univ.
Prof. T. Sato etc.
Mineralogical analysis
Groundwater analysis
Field survey

Keio Univ.
Prof. N. Shikazaono etc.
Chemical analysis
Groundwater analysis and simulation
Field survey

Okayama Univ.
Prof. Kawamura
XRD analysis

Natural Analogue(IPNAP) Committee
Chair Prof. N. Shikazono (Keio Univ.)
Prof. Y. Niibori (Tohoku Univ.)
Prof. S. Sato (Hokkaido Univ.)
Prof. T. Sato (Hokkaido Univ.)
Dr. E. Sasaki (JAEA)
Dr. S. Suzuki (NUMO)
Prof. T. Tokunaga (Tokyo Univ.)
Prof. D. Yoshida (Nagoya Univ.)

Saile Mine and local cooperators
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. Reducing 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 interface)
2. Why 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

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</table>

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

*Mix Proportion – Portland cement: silica fume: fly ash = 40: 20: 40
3. Geological map of Mangatarem (Manleluag Hotspring / Saile Mine)

Manleluag hot springs
pH 11
Poonbato springs
pH 11.7

Manleluag Hotspring / Saile Mine Quarry

Mangatarem Saile Mine
Bigbiga well
-pH 9-

Zambales ophiolite

Figure 5
Geologic Map of Malabobo
(Geology 215, BMG1983, 1992)
February 2008
3. Groundwater Chemistries
(Manleluag Hotspring / Saile Mine)
3. Groundwater Chemistries (Manleluag Hotspring / Saile Mine)
3. Groundwater Chemistries (Bigbiga)
3. Outcrop (Poonbato)

Hyperalkaline groundwater discharge point (pH 11.6)

Serpentinaization

Peridotite
Serpentine
Calcite

Travertine

Natural concrete
3. Groundwater Chemistries (Poonbato)
3. Origin and Residence Time of Groundwater

### Stable Isotope Ratio of Rain Water and Groundwater

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<th>Location</th>
<th>δD</th>
<th>δ(^{18})O</th>
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<td>Manleluag M3</td>
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<td>Manleluag M4</td>
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<td>Poon Bato</td>
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<td>Manleluag2(2008)</td>
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<tr>
<td>Saile4(2008)</td>
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<td>-7.83</td>
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</tbody>
</table>

- 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

※From Abaya (2005)
3. Basic Concept of Regional Groundwater Flow System in Mangatarem

**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 tuffaceous sandstone
- **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

- **Diagram Notes**
  - General Stratigraphy
    - Quaternary
      - Alluvium
      - Andesite plug
      - Moriones Formation: Tuffaceous sandstone, Siltstone, Conglomerate
        - Aksitero Formation: Claystone, Sandstone, Tuffaceous sandstone (Bentonitic, Zeolitic)
    - Miocene
      - Zambales Ophiolite
      - pillow lava
      - Diabase dike
      - Gabbro

- **Geological Structures**
  - Manleluag hot springs (pH 11)
  - Bentonite layer (Impermeable zone)
  - Malabobo andesite plug (Quaternary)
  - Saile Mine (Open Pit)
  - Active serpentisation (Producing: high pH, reducing condition, H2/CH4 gas)
  - Neutral water
  - Dispersed balance of high pH water into deep sediment
4. Field Investigation in Saile Mine (Fossil Type)

Aerial photo around Saile Mine

Topographic map of Saile industry quarry
4. Field Evidences for Existence and Generation of Hyperalkaline Groundwater in Saile Deposits

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

Fracture filling materials (F₃)

Manganese(γ-MnOOH)

(2) Fracture filling materials (C₂)

Calcite (white)

Serpentine (green)
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

BU1

BM1

BL1

3 parts of Baseline 1

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

XRD Results (Tokyo Institute of Tech.)

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

FESEM image of smectite
5. Mineralogical characterization of Bentonite

2. Mineral Composition of Trench 6 West Wall

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

<table>
<thead>
<tr>
<th></th>
<th>Trench 5 (S・SW Wall)</th>
<th>Trench 6 (W Wall)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite Layer</td>
<td>Sm+Zeo</td>
<td>Sm</td>
</tr>
<tr>
<td></td>
<td>Sm+Zeo+Qz+Plag</td>
<td>Sm+Zeo</td>
</tr>
<tr>
<td></td>
<td>Sm+Zeo</td>
<td>Sm+Cal</td>
</tr>
<tr>
<td>Bleached Zone</td>
<td>Zeo+Sm</td>
<td>Zeo+Sm</td>
</tr>
<tr>
<td>(Alteration Halo)</td>
<td>Sm+Zeo+Sp</td>
<td>Zeo+Sm+Cal</td>
</tr>
<tr>
<td>Pillow Lava</td>
<td>Sm+Cal+Zeo+Sp</td>
<td>Sm+Zeo+Cal+Sp</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Bentonite Layer</th>
<th>Trench 5 (S-SW Wall)</th>
<th>Trench 6 (W Wall)</th>
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<td>Sm+Zeo</td>
<td>Sm</td>
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<td>Sm+Zeo+Qz+Plag</td>
<td>Sm+Zeo</td>
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<tr>
<td></td>
<td>Sm+Zeo</td>
<td>Sm+Cal</td>
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<tr>
<td>Bleached Zone (Alteration Halo)</td>
<td>Zeo+Sm</td>
<td>Zeo+Sm</td>
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<tr>
<td></td>
<td>Sm+Zeo+Sp</td>
<td>Sm+Cal+Zeo</td>
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<tr>
<td>Pillow Lava</td>
<td>Sm+Cal+Zeo+Sp</td>
<td>Sm+Zeo+Cal+Sp+Plag</td>
</tr>
</tbody>
</table>

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)

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\textbullet{}Si-rich (Core) and Fe\textbullet{}Mg rich (Rim)) of smectite(Parallel-growth)

2. Type 2; Surrounding outside of Ca-rich core with Fe \textbullet{} Mg-rich smectite showing the shape of corona (Over-growth)

3. Type 3; Fe-rich smectite occurred as interstitial filling near Ca-rich smectite
# 5. Chemical Composition of Bentonite

## Type 1

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<th>5S-08_35</th>
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### Cations based on O = 22 (apfu)

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<td>0.667</td>
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<td>K</td>
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<td>0.399</td>
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**NOTE**: XMg = Mg / (Mg + Fe)

****: XCa = Ca / (Ca + Na + K)

## Type 2

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<th>5S-10_001</th>
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<th>5S-10_4</th>
<th>5S-10_ca33</th>
<th>5S-10_35</th>
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### Cations based on O = 22 (apfu)

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<th>5S-10_2</th>
<th>5S-10_4</th>
<th>5S-10_ca33</th>
<th>5S-10_35</th>
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<tbody>
<tr>
<td>Si</td>
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<td>7.499</td>
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<td>Fe</td>
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<td>Mn</td>
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<td>0.000</td>
<td>0.000</td>
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<td>Mg</td>
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<td>0.558</td>
<td>0.509</td>
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<tr>
<td>Ca</td>
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<td>0.237</td>
<td>0.204</td>
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<tr>
<td>Na</td>
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<td>K</td>
<td>0.119</td>
<td>0.183</td>
<td>0.226</td>
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<td>0.532</td>
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<td>0.706</td>
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</table>

**NOTE**: XMg = Mg / (Mg + Fe)

**: XCa = Ca / (Ca + Na + K)
5. Zonig profile

Zoning profile (Saile mine Trench 1 (Bleaced))

![Zonig profile diagram](image-url)
### 5. Composition change of bentonite

#### Summary of FE-SEM analysis

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Alteration minerals</th>
<th>Relict minerals</th>
<th>Zeolite composition</th>
<th>Smectite XCa-composition</th>
<th>Smectite XFe-composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-001</td>
<td>Zeolite &gt;&gt; Smectite</td>
<td>Plag, Cpx, Opx, Qz</td>
<td>Mordenite - Si-rich stellerite</td>
<td>0.2-0.5</td>
<td>0.6-0.8</td>
</tr>
<tr>
<td>ST-003</td>
<td>Smectite &gt;&gt; Zeolite</td>
<td>Volcanic clast</td>
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<td></td>
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</tr>
<tr>
<td>ST-006</td>
<td>Smectite &gt;&gt; Zeolite</td>
<td>Plag, Qz</td>
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<td></td>
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<td>ST-007</td>
<td>Smectite &gt; Zeolite</td>
<td>Plag, Cpx, Qz</td>
<td>Yugawaralite</td>
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<tr>
<td>ST-008</td>
<td>Smectite &gt;&gt; Zeolite</td>
<td>Plag, Cpx, Qz</td>
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<td>ST-012</td>
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<td>Plag, Cpx, Qz</td>
<td>Clinoptilolite - Si-rich stellerite</td>
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</table>

#### Bigbiga Trench-1

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Alteration minerals</th>
<th>Relict minerals</th>
<th>Zeolite composition</th>
<th>Smectite XCa-composition</th>
<th>Smectite XFe-composition</th>
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</thead>
<tbody>
<tr>
<td>BB-001</td>
<td>Zeolite &gt;&gt; Smectite</td>
<td>Plag, Cpx, Qz</td>
<td>Heulandite – Yugawaralite-Stellerite</td>
<td>0.5-0.8</td>
<td>0.3-0.5</td>
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<tr>
<td>BB-002</td>
<td>Zeolite &gt;&gt; Smectite</td>
<td>Plag, Cpx, Qz, Calc, Ba-phase</td>
<td>Yugawaralite - Stellerite</td>
<td>0.3-0.9</td>
<td>0.3-0.7</td>
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<tr>
<td>BB-004</td>
<td>Smectite &gt; Zeolite</td>
<td>Plag, Cpx, Qz, Calc (Mn-rich), Apa,</td>
<td>Mordenite - Stellerite</td>
<td>0.2-0.8</td>
<td>0.6-0.8</td>
</tr>
<tr>
<td>BB-006</td>
<td>Smectite &gt; Zeolite</td>
<td>Plag, Cpx, Qz, Calc, Apa, Mn-oxide</td>
<td>Stellerite</td>
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<td></td>
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</tbody>
</table>

※ Yellow: Bleached Zone
※※ Gray: Fractured Zone
6. Interaction between smectite and hyperalkaline groundwater

Lithology of Alteration Zone between Pillow lava and Bentonite layer

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

× 4

Grain structure

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

Correspondence with XRD pattern of Goethite
6. Nontronitization of Ca-Smectite

Electron diffraction analysis

Electron diffraction pattern of Feather structure

<table>
<thead>
<tr>
<th>8</th>
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<tbody>
<tr>
<td>Na</td>
<td>0.0082</td>
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<tr>
<td>Ca</td>
<td>0.4699</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Mg</td>
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<tr>
<td>K</td>
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<td>Ti</td>
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<tr>
<td>Si</td>
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</table>

Nontronite from point analysis of Fe accumulation band by EPMA

Correspondence with XRD pattern of smectite
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

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>Na-Cp</th>
<th>Ca-Cp</th>
<th>K-Cp</th>
<th>Ca-H</th>
<th>K-H</th>
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<tbody>
<tr>
<td>SiO₂</td>
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<tr>
<td>Al₂O₃</td>
<td>14.25</td>
<td>13.18</td>
<td>13.27</td>
<td>12.70</td>
<td>14.95</td>
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<td>2.81</td>
<td>0.75</td>
<td>1.84</td>
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<tr>
<td>K₂O</td>
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<td>1.16</td>
<td>9.94</td>
<td>1.00</td>
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<table>
<thead>
<tr>
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<th>Phillipine</th>
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<tbody>
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<td>K₂O</td>
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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

- Emplacement of Ophiolite
- Island Arc Volcanism
- Pelagic-semipelagic sediments
  - Basic (ol, px, hb, feld)
  - Felsic (feld, px, ol, qz)
  - Volcanoclastics (Tuffaceous: pumic, ash, glass)
- Diagenesis
- Zeolites
- Bentonite (Na-smectite)
- Bentonite (Ca-smectite)
- Smectite – chlorite Mixed Layer
  - Chlorite
- Hyperalkaline fluids (GW) coming up along fractures
  - Manganite
  - Serpentine
  - "Interaction"
- "Interaction"
  - Ca – Zeolites (Clinoptilolite + Heulandite)
  - Ca – Smectite
  - Ca – Zeolites
  - Ca – Smectite
  - Nontronite
  - Ca – Zeolites
- Iron Concentration Zone (Goethite)
- Compositional zoning patterns
  - Ca – Mg
  - Ca – Mg – Fe
  - Ca – Fe

- Pillow Lava (Zambales Ophiolite)
- Altered Pillow Lava
- Altered Bentonite
- Bentonite - Zeolites Beds

- Pelagic-semipelagic sediments
- Compositional zoning patterns
- Pelagic-semipelagic sediments
- Volcaniclastic sediments
  - Tuffaceous: pumic, ash, glass
  - Felsic (feld, px, ol, qz)
  - Basic (ol, px, hb, feld)
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$^{2+}$ oxidized and Si, Al, Na and Ca were selectively leached, consequently 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 Bentonite and Hyperalkaline groundwater.