## Natural analogue study on long term alteration of bentonite (2) - Geochemical simulation-

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## Introduction

In the geological disposal of Japanese TRU waste, it is important to understand the long term alteration of bentonite that is a part of the engineered barrier system. In this study, the geochemical simulations were carried out on natural bentonite suffered from Ca-rich alteration.

## **Discussion of Results**

The alteration of bentonite in a tuffaceous bed at a Japanese island arc basin was focused as natural analogue. Based on the initial minerals estimated by MELTS[1], long term alteration of initial rock was calculated by PHREEQC[2]. In the simulation case, the initial marine sediments deposited in seawater at 5 Ma ago. This sedimentary age was based on experimental analysis of microfossils. In the simulation case, we programed that the sedimentary basin changed to land at 1 Ma ago. At the time, the porewater was set to be a 50:50 mixed rainwater-groundwater because a result of principal component analysis of present groundwater suggests this mixing ratio among rainwater and shallow hot spring water.

As a calculation result, coexistence of Na-, Camontmorillonite and zeolite were confirmed (Fig.2) for the past 5Ma. This coexistence is consistent with experimental results.



Fig.1 Calculated time-evolution of minerals in bentonite.

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[1] Ghiorso & Sack (1995) CMP **119**, 197-212. [2] Parkhurst & Appelo (1999) WRIR 99-4259.

## Biogeochemical cycling of nitrogen and carbon in the 3.2 Ga ocean: Results from DXCL-DP, NW Pilbara, Western Australia

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Records of geochemical cycling of bio-essential, redoxsensitive elements have keys to decipher misteries of the coevolution of Earth and life. In order to obtain insight into biogeochemical cyclig of those elements and early evolution of microbial biosphere from high-quality samples, we drilled through Mesoarchean strata in coastal Pilbara (Dixon Island-Clearverville Drilling Project, see [1]), and obtained 3.2 Ga old drillcores (CL1, CL2, and DX) of sulfide-rich black shales in the Cleaverville Group. We conducted a systemtic geochemical study involving sequential extractions of Fe, S, C, and N for phase-depdendenet contents and isotope compositions, in addition to major and trace element analysis, for >80 samples. Here we focus on geochemistry of N and C.

The average  $C_{org}$  contents are 0.60, 0.73m and 1.21 wt.% for CL1, CL2, and DX, respectively, with a maximum value of 3.0 wt.%. The  $\delta^{13}C_{org}$  values range from -30.7 to -25.7% (CL1), -32.6 to -27.8% (CL2), and -31.8 to -26.0% (DX). The average  $\delta^{15}N_{org}$  values are -3.8±0.9% for CL1 and CL2 and -2.0±1.0% for DX, while the  $\delta^{15}N_{clay}$  values are -3.4±0.6% for CL1 and CL2, and -0.1±2.4% for DX. These data may be explained by the following processes.

Microbially mediated redox-cycling of nitrogen, possibly involving denitrification and microbial (cyanobacterial?)  $N_2$ fixation are most likely mechanism to fully explain the obtained data set, while microbially mediated non-redox cycling of NH<sub>3</sub> is also possible. Sources of N are N<sub>2</sub> from the coeval atmosphere and/or NH<sub>3</sub> from submarine hydrothermal activity. Denitrifiction occurs in anoxic environments where sulfate reducton may also occurr, which is supported by sulfur isotope compositions of sulfide in the same sample set. These results are in contrast with a previous study using chert [2], but consistent with more recent study by [3].

This study suggests operation of microbial N in the Mesoarchean. The atmosphere-hydrosphere system would have been sufficiently oxidized to allow redox-cycling of nitrate.

[1] Yamaguchi *et al.* (2009) *Sci. Drill.* 7, 34-37. [2] Beaumont & Robert (1999) Precam. Res. 96, 63-82. [3] Godfrey & Falkowsky (2009) Nature Geosc. 2, 725-729.