Several 2:1-type clay minerals with unique morphology have been synthesized under different hydrothermal conditions by a new concept called Geonics, which is "adaptation of processes in the formation of natural geologic analogues". Illite particles exhibiting unique triangle-shaped particles up to a few hundred nm were obtained from an aluminous composition treated at 500°C and 100 MPa for a day. A long lath with a width of a few hundred nm and several tens of micrometers long obtained at 450°C and 100 MPa for 40 days is a regular mixed-layer structure wherein smectite and mica nanosheets alternate periodically. The hexagonal and rhombohedral illite was observed on the product synthesized at 500°C and 100 MPa for 40 days. The observations confirm that the assembly of silicate nanosheets and morphology should be controlled by chemical species, synthesis temperature, and duration.

Key words: geonics, illite, interstratification, nanolayer, smectite

1. INTRODUCTION

The nanotechnology has played important roles in the research field of materials science and engineering. Nanomaterials such as nanoparticles, nanosheets, etc. have been systematically investigated because of their unique shape-dependent optical and electrical properties that confer them with the ability to function as potential structural blocks for a new generation of environmental and energy-related materials. For understanding of their intrinsic shape-dependent properties, it is necessary to investigate their particle growth mechanism and the reaction process.

Clay minerals are abundant in nature, and are formed by weathering, diagenesis and hydrothermal alteration [1]. Clay minerals contain the two-dimensional tetrahedral sheet (T) and octahedral sheet (O). Common tetrahedrally coordinated cations are Si⁴⁺ and Al³⁺ while octahedrally coordinated cations are commonly Al³⁺, Fe³⁺, Mg²⁺, and Fe²⁺. Numerous combinations of T and O sheets are observed in clay minerals. The current research focuses on 2:1-type clay minerals wherein an octahedral sheet is sandwiched between two tetrahedral sheets (Figure 1). Normally, the layers are not electrostatically neutral. The excess layer charge is neutralized by various interlayer materials (cation, sheet etc.). Depending on the amount and species of sheets and interlayer material, the 2:1 layer structure can be classified into smectite, mica, illite, talc and so on. In another point of view, an assembly of two T-sheets and one O-sheet is a basic silicate nanosheet. These 2:1-type clay minerals can also be called self-assembled nanosheets.

Because of the relative high surface area and surface acid sites, smectite clay minerals are used as catalysts and catalytic support. Unfortunately typical clay minerals such as smectites do not show a distinct morphology. In the present work, we have synthesized several silicate nanolayers and nanoscale assembly of silicate nanolayers by "adaptation of processes in the formation of natural geologic analogues"; a new concept called Geonics.

Geonics is the term for describing the processes and technologies that mimic long term geological processes. The definition is the application of methods and systems found in nature to the study and design of engineering systems and modern technology. The concept of mimicking nature was originated by Janine Benyus in her book "Biomimicry: Innovation Inspired by Nature" [2]. She explains biomimicry as a method of solving problems that uses natural processes and systems as a source of knowledge and inspiration. It involves nature as model, measure and mentor. The concepts behind biomimicry are that the natural processes and systems have evolved over several billion years through a process of research and development commonly referred to as evolution. A reoccurring theme in natural systems is the cyclical flow of matter in such a way that there is no waste of matter and very low energy.

2. EXPERIMENTAL

2.1 Materials

SiO₂ (Extra pure grade, 99.9%) and Al₂O₃ (Extra pure grade, 99.99%) were obtained from High Purity Chemical Lab. Co., Ltd. MgO (Extra pure grade,
99.99%) was kindly donated from Ube Industries Ltd. Na₂CO₃ (Primary standard, 99.98%) was obtained from Asahi Glass Co., Ltd. All these chemicals were used without further purification.

2.2 Sample preparation
Sample preparation was conducted based on our previous study [3]. The starting materials were quenched glass made from the mixture of Na₂CO₃, Al₂O₃, MgO and SiO₂, having a stoichiometric dehydrated smectite composition.

The mixture of aluminous smectite (Na-beidellite) composition, which is Na₃Al₄(Al₄Si₄O₂₄)O₂₂, was fused by an infrared focusing-image furnace, and then quenched into water. The other oxide mixtures having a stoichiometric montmorillonite composition with Na₃Al₄Mg₆Al₃Si₇O₂₂ placed inside a Pt-crucible was fused with an electric furnace and quenched in water. The glass was crushed and fractionated to be less than 10 mm by hydraulic elutriation. The mixture of pulverized glass and distilled water in the ratio of 1:1 by weight was sealed in a gold tube, and then treated at a pressure of 100 MPa and at the desired temperatures and durations.

2.3 Characterization
The products were examined by powder XRD method after quenching (Rigaku RINT2000). Two samples were prepared following the method used in a previous study [3]; (1) compression-free (CF) sample, and (2) ethylene glycolated (EG) sample. The CF sample was prepared by crushing and mounting the product on a backgroundless quartz plate without compression to reduce the influence of preferred orientation. For the EG sample, a suspension of the product in water was allowed to settle on a glass slide and dried at room temperature (RT), then placed in a sealed container with ethylene glycol, and heated overnight at 60 °C. The EG sample is used for the identification of smectite which expands to 1.7nm after overnight at 60 °C. The pattern was obtained from the compression-free (CF) sample, which was dispersed by distilled water on Cu grids using a JEM-1010 (JEOL) operating at 100 kV.

3. RESULTS AND DISCUSSION
3.1 Unique-shaped Illite particle from aluminous smectite composition
The term illite was proposed as a group name for clay-size micaceous components in argillaceous sediments. Authigenic illite precipitated from formation water in sandstone pores appear frequently in the form of laths.

The occurrence of illite was observed in the different natural system. In shales and mudstone, the lath- and hexagonal-shaped crystallites were found. In the hydrothermal deposits, the lath-shaped crystals changed to the hexagonal forms as the bulk composition became more mica rich. In sandstone, both laths and hexagonal shapes were present. Recently the experimental constraints on the morphology of illite were carried out [4]. The experimental results confirmed that the lath-shaped illite was formed due to a slow growth rate from supersaturated solutions. The lath-shaped illite is a metastable form and the hexagonal crystal is ultimately stable.

Another experimental approach addressed the question how illite could growth as different morphologies [5]. Three different crystal morphologies of illite, hexagonal habits, rhombs, and lath and fibers, were described. For the case of lath-shaped illite, it has a dioctahedral 1M mica structure, and the laths are parallel to the a crystallographic axis [6]. Elongated habits of illites display aspect ratios (length/width) ranging from 3 – 50 or more. Three variations in the idiomorphic forms, crystal morphologies of illite may explained by the growth rate on the prismatic faces (010), (110) and (1 1 0) fronts. The hexagonal lamella form when the equal growth rate of three fronts. The rhombs may develop when the growth rate on the (010) is faster than the other two fronts. The elongated laths and fibers form when the

in size coexisted with lath-shaped and irregular shaped phase (Figure 3a). AFM image of the product confirmed the triangle-shape particle in TEM analysis (Figure 3b). The triangle particle could not be completely exfoliated, but the average thickness is about 3 nm.

Fig. 2. XRD pattern of the triangle-shaped illite

Fig. 3. TEM (a) and AFM (b) images of the triangle-shaped illite.
growth rate on the (010) is slower than the other two fronts. From the similar mineral shapes in natural and synthetic conditions in the previous studies [4, 5], they estimated that the physical and chemical conditions of crystallization did not change the shapes of illite to a great extent. Unfortunately a triangle-shaped particles was rare in nature and experimental results. Present experiment is out of the temperature range of diagenetic mineral genesis and very short duration. Our previous study [3, 7] showed the time-temperature diagram of the reaction sequence in beidellite composition at hydrothermal confirmed that beidellite reacted to the rectorite below 450 °C, and then changed to illitic phase. Therefore the present results indicated that the kinetic crystallization was very effective to produce a triangle shape. The precise characterizations have not yet done. These results signify that the distinct morphologies of illite should be controlled by chemical species, synthetic temperature and duration.

3.2 Morphological changes in Na-montmorillonite composition: Regular Interstratifications of Silicate Nanolayers

Montmorillonite is one of the important dioctahedral smectites. Montmorillonite occurs commonly as the principal constituents of rocks known as bentonite clay deposits. It also found widespread in soils, sedimentary and metamorphic rocks, and deposits of hydrothermal origin. The continuous conversion of dioctahedral smectite, mainly montmorillonite, to illite through illite-smectite interstratified clay mineral is of great interest for geoscience as a sensitive indicator in estimating the degree of diagenesis of sediments and alteration process in active and fossil geothermal areas [8].

Interstratification describes a phyllosilicate structure where two or more types of layers occur in a vertical stacking sequence. The illite-smectite interstratified clay mineral is ubiquitous in low-temperature geological environment.

Figure 4 shows the XRD patterns of the products prepared from the quenched glass with Na-montmorillonite composition at the conditions of 400, 450 and 500 °C and 100 MPa for 40 days after treatment with ethylene glycol.

The product from the hydrothermal experiment at 400 °C and 100 MPa for 40 days was identified to be a dioctahedral smectite based on the basal spacing expansion after ethylene glycol treatment (1.7 nm), and a $d_{100}$ of 1.49. The long spacing of 2.7 nm for EG-treated sample synthesized at 450 °C and 100 MPa for 40 days was identified to be regularly interstratified smectite-illite, wherein smectite (1.7 nm for EG) and illite (1.0 nm) nanosheets alternate periodically. The 1:1 regularly interstratified illite- smectite was also confirmed by the rational reflections in the XRD patterns. The sample at 500 °C and 100 MPa for 40 days was identified to be illite, because the basal reflection at 1.0 nm did not be expanded after the treatment with ethylene glycol. The reaction sequences were comparable to those observed in the previous studies; smectite converted to illite through illite-smectite interstratified clay mineral [1, 3, 9].

Figure 5 (a) and (b) showed the TEM images of the products synthesized at the conditions of 100 MPa for 40 days at 450 °C and 500 °C, respectively. The product at 450 °C and 100 MPa for 40 days indicated the aggregate of lath-shaped minerals with a few hundred nm in width and several ten micrometers in length. The aspect ratios (length/width) ranging over 100, which was larger than that of the natural lath-shaped illite. The elongated hexagonal plates were observed on the product synthesized at 500 °C and 100 MPa for 40 days.

The combined results from XRD and TEM confirmed the distinct sequential morphology changes in montmorillonite system; smectite reacted to illite with elongated hexagonal plate through regularly interstratified illite- smectite with high-aspect ratio lath-shape. The results were consistent with the observations in the natural hydrothermal alteration conditions [10]. The sequential phase changes with distinct morphology were observed. Smectites with flake-like or moss-like morphology changes to rigid lath-shape or clear hexagonal platy illite through tiny lath-shaped interstratified clay minerals.

4. CONCLUSION

We have succeeded the self-assembled silicate nanolayers with different morphology and stacking order (interstratification) in the hydrothermal conditions by GEONICS. Silicate nanosheets with unique morphologies should be a new class of nanomaterials particularly its characteristic high degree of two-dimensionality at molecular-level thickness. These nanosheets can be assembled and organized into
functionalized nanostructured systems for sophisticated electronic, magnetic or photochemical applications.

There must be great opportunity and competitive space in the material science for the study of geosciences to contribute innovative solutions to our key technological challenges, if only we begin thinking differently and collaborating with researchers from different fields.

REFERENCES

(Received December 8, 2008; Accepted May 12, 2009)