Smectite, illite, and early diagenesis in South Pacific Gyre subseafloor sediment

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Abstract

Subseafloor sediment and basalt rock samples at seven sites in the South Pacific Gyre (SPG) were recovered by Integrated Ocean Drilling Program Expedition 329 (2010.10.8 ~ 2010.12.13). Microscopic and spectroscopic measurements on the structural Fe-redox states and the elemental composition of smectite, and polytypes of illite in the sediment at two sites (U1365 and U1369) were performed to understand the origin/formation mechanism of clay minerals in the oligotrophic open ocean. The dominant phases of clay minerals found in the present study were smectite and illite polytypes. Suggestive of non-uniform early diagenetic processes in the expansive SPG seafloor, higher ordering of illite polytypes ($1M$, $2M_1$, and $3T$) were identified at site U1369 while disordered $1M_d$ illite were found at U1365. Smectites of hydrothermal origin (Al-rich beidellite, and saponite) were observed at U1369. Fe-rich montmorillonite minerals that are likely associated with the terrigenous input, were dominant at U1365. Nontronite (Fe-rich smectite) was detected at both sites. Red-brown to yellow-brown semiopaque oxide minerals (RSO) were widely distributed with Fe-rich smectite near the basaltic crust at U1365. Lower observed heat flow at U1365 relative to U1369 provides a possible explanation for the observed variability in clay mineral speciation between these two sites. The presence of K-nontronite at the basalt/sediment interface at both sites indicates an oxidative basalt alteration; however variations in the oxidation states of structural Fe in nontronite measured by EELS indicate that reductive environment persists locally at the basalt/sediment interface.

Keywords: South Pacific Gyre; K-nontronite; diagenesis; Illite polytypism; IODP Expedition

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1. Introduction

Integrated Ocean Drilling Program (IODP) Expedition 329 recovered subseafloor sediment and basalt rock samples across a range of crustal ages and tectonic spreading rates in the South Pacific Gyre (SPG). The SPG is a unique depositional environment where the sedimentation rates are among the lowest (less than 1.6 to 1.9 m/Myr) of any seafloor setting on Earth, and sediments and basaltic basement have been continuously exposed to oxic conditions for their entire sedimentation history (D'Hondt *et al.*, 2009, 2015). The low sedimentation rates are due to extremely low influxes of terrigenous matters and low bioproduction in the euphotic zone (Anderson, 1986; Glasby, 1991; Claustre and Maritorena, 2003; D'Hondt *et al.*, 2009). Given these unique conditions, the formation of subseafloor sediments, particularly the composition and structure of clay minerals and their formation mechanism supposed to be different from those in the anoxic conditions of equatorial upwelling regions and high accumulation rates at the continental margins (D'Hondt *et al.*, 2015). IODP Expedition 329, for the first time, allows investigation of a vast range of mineralogical data throughout the entire sedimentary column of the SPG.

Smectites in subseafloor sediment can originate from aerial or fluvial influx of terrigenous material, or hydrothermal alteration of basalt (Biscaye, 1965; Chamley, 1989; Weaver, 1989; Fagel *et al.*, 2001). Variations of chemistry and crystalline structure within smectites reflect their origin and formation mechanisms (Wilson, 1999). Trioctahedral smectite, mainly occurring as the mineral saponite, likely forms through the hydrothermal alteration of basaltic basement igneous rocks (Zierenberg *et al.*, 1983; Cole, 1988; Cuadros *et al.*, 2008, 2013; Dekov *et al.*, 2008). Dioctahedral Al-rich smectite (beidellite) appears to form via interactions among hydrothermal solutions and sediment at high temperatures (~160

to 200 °C) (Haggerty and Baker, 1967; McMurthy *et al.*, 1983; Parra *et al.*, 1985, 1986; Fagel *et al.*, 2001). Fe-rich smectite, known as the mineral nontronite, is quite frequent in hydrothermally altered basalt (Zierenberg *et al.*, 1983; Cuadros *et al.*, 2008, 2013; Dekov *et al.*, 2008), although Pacific pelagic clays also possess nontronite that possibly forms through low temperature reactions within subseafloor sediment (Cuadros *et al.*, 2011).

Fe-rich smectite, particularly nontronite has variable crystal structure and chemistry. Variation of Fe(II)/Fe(III) in smectite structure is likely attributable to redox changes that may involve oxidation of organic matter (Eslinger *et al.*, 1979), or local microbial Fe-respiration (Gates *et al.*, 1998; Kostka *et al.*, 1996, 1999a,b; Stucki, 1998; Kim *et al.*, 2003, 2004; Zhang *et al.*, 2007a,b; Jaisi *et al.*, 2005, 2007a,b, 2011; Seabaugh *et al.*, 2006; Stucki and Kostka, 2006; Dong *et al.*, 2009). In contrast, the formation of K-smectite indicates an oxidative weathering process of subseafloor sediment in the presence of seawater (Hart *et al.*, 1974; Clayton *et al.*, 2000; Zhou *et al.*, 2001). Variations in mica polytypes associated with endogenous heat flow (Nespolo *et al.*, 2001) are common in sediments. In subseafloor hydrothermal deposits, micas develop the stacking order with a sequence of $1M_d$ - $1M$ - $2M_1$ depending on the hydrothermal activity and reaction time (Yoder, 1959; Velde, 1965). The structural assessments by Selected Area Electron Diffraction (SAED) pattern allows to detect the evolution of mica polytypes in hydrothermal regions (Inoue *et al.*, 1988; DiMarco *et al.*, 1989). Pelagic red clays in the Pacific Ocean constitute 49 % of seafloor sediment (Anderson, 1986). They are especially abundant in the southwestern Pacific Basin (Piper *et al.*, 1985). Fe-rich smectite and Fe/Mn-oxyhydroxides are the dominant mineral phases in Pacific pelagic clays (Singer *et al.*, 1984; Cuadros *et al.*, 2011).

This study aims to investigate the structure and mineral composition of smectite phases and illite polytypes in the subseafloor sedimentary sequence in the oligotrophic open

ocean of the SPG. Specific objectives of this research include (1) investigating the diversity of smectite phases, (2) determining the redox states of structural Fe in Fe-rich smectite, and (3) defining the elemental composition and formation mechanisms of clay minerals and polytypes of illite in the sediment of two oligotrophic sites (IODP Expedition 329 sites U1365 and U1369) that experienced long-term, low rates of sediment accumulation and persistent oxic conditions. Therefore, the present study provides insight into the processes of mineral formation and early diagenesis.

2. Samples and methods

2.1. Sampling locations

IODP Expedition 329 recovered seafloor sediment from seven sampling sites along two transects spanning the western half of the SPG. One transect (sites U1365 – U1368) crosses the center of the SPG at 26°S from the upper slope of the East Pacific Rise (EPR) to the western abyssal plain with increasing basement age from 13.5 Ma to 84-120 Ma (Gradstein *et al.*, 2004) (Fig. 1, Table 1). The entire sediment column at four sites and the upper 100 m of basement at three sites were cored along this transect. Water depths at these sites varied from 3740 meters below sea level (mbsl) to 5695 mbsl (Table 1). The other transect (sites U1369 – U1371) crosses the southern edge of the gyre at approximately 42°S and also sampled the entire sediment column at each site. Crustal ages is 75 Ma and water depths increase from 5075 m to 5305 m. Sediment cores were recovered at three sites where basement rocks were deliberately not cored. The thickness of the sediment column in the

SPG seafloor increases with the basement age and is greatest at site U1371 (131 m), a location that is influenced by upwelling along the southwestern edge of the SPG (D'Hondt *et al.*, 2009). Expedition 329 shipboard scientists characterized the overall stratigraphy and preliminary mineralogy for all recovered cores (Expedition 329 Scientists, 2011). Based on those results and to more fully characterize differences among the sites with respect to crustal age and position within the SPG, sites U1365 and U1369 were selected for further study. Sites U1367 and U1368 were excluded from further consideration because the dominant lithology at those sites is calcareous nannofossil ooze; site U1371 was excluded because its cores are composed primarily of siliceous ooze. Site U1365 is located 4500 km west of the EPR. It represents the location furthest from the ridge and resides on the oldest crust available within the SPG, dated at 124.6 Ma (Gradstein *et al.*, 2004). Sediment recovered at site U1369 resides upon crust dated at 58 Ma, approximately 2000 km west of the EPR.

2.2. Clay mineral separation

Samples from various depths were sub-cored from split cores at two sites (U1365 and U1369) based on the core description. A total of 16 and 10 clay samples were prepared from sites U1365 and U1369, respectively. In brief, sample preparation included: (1) chemical treatment with sodium acetate (NaOAc) - acetic acid (HOAc) buffer solution (pH 5.0) and hydrogen peroxide (30 % H₂O₂) to remove carbonate and organic matter (Jackson, 1969); (2) multiple washes with distilled water to remove any residues of the chemical reagents; (3) separation of the clay-size fraction (<1 µm) by centrifuge (Jackson, 1969); (4) reduction of clay dispersion volume by addition of sodium chloride (NaCl); (5) removal of excess salt by dialysis; and (6) final dried clay sample acquisition by freeze-drying (Malcolm,

1968).

2.3. X-ray diffraction (XRD) and optical microscopy

XRD analyses were performed on air-dried and glycolated samples using a Rigaku Mini-Flex II automated X-ray diffractometer with Cu-K α radiation at Yonsei University. Fine clay samples were dispersed in distilled water (0.5 mg/ml) and immersed in an ultrasonic water bath to minimize any flocculation induced by freeze-drying. Oriented powder mount samples were prepared by pipetting sediment dispersions onto glass slides and gently taping the bottom of the slide to coax the clay particles into settling on their *a-b* crystallographic plane. XRD profiles over ranges of 2θ degrees from 3° to 40° (air-dried), and 3° to 15° (glycolated) were recorded at scan speeds of 1.5°/min and step sizes of 0.02° with a receiving slit size of 0.3 mm and a divergence slit size of 1.25°. *Crystallographica Search-Match software* (version 2.0.3.1) was used to identify the composition of minerals constituting each clay sample. The smear slides for various depths were examined to estimate the mineral composition at x50 – x100 magnifications under the optical polarization microscopy. The semi-quantification of mineral contents was measured based on the visual percentage estimation using the comparator chart (Marsaglia *et al.*, 2013).

2.4. Transmission electron microscopy (TEM)

A JEOL JEM-2010 UHR TEM equipped with EDS (JEOL JED-2200) at the University of Tokyo was operated at 200 kV to examine structural and chemical variations of clay minerals on lattice fringe images, Selected Area Electron Diffraction (SAED) patterns,

and Energy Dispersive X-ray Spectrometer (EDS) analyses. TEM samples were impregnated with L.R. White resin (Kim *et al.*, 1995) to prevent structural artifacts caused by the dehydration of clay minerals under a vacuum in TEM. The cured samples were sliced to 70 nm in thickness using an ultramicrotome (ULTRACUT TCT; Leica, installed at the Korea Basic Science Institute, KBSI) and then placed on a holey carbon TEM Cu-grid. The lattice fringe images were used to differentiate the smectite layers (12-13 Å) from the illite layers (10 Å) while the EDS analyses were used to determine each mineral's elemental composition. The chemical composition of clay minerals were measured by Analytical Transmission Electron Microscopy (ATEM) with an acquisition time of 30 seconds under the bright-field imaging mode. Background signals of EDS spectra (emsa file format) were removed by *PeakFit - EDS S/W* (Kogure, the University of Tokyo, 2012) and fitted by the least square method (LSM). The mass percent of elemental components (K, Na, Ca, Si, Al, Fe, Mg, Ti, and Mn) were then calculated based on the relative peak intensity. The chemical formulas of the various clay minerals were determined by assuming that each unit cell contained 22-oxygen atoms.

2.5. Electron Energy Loss Spectroscopy (EELS)

Electron Energy Loss Spectroscopy (EELS) was performed at the KBSI using a TECNAI G² F30 ST FE-TEM (FEI Company, Hillsboro, Oregon, USA) equipped with a Gatan imaging filter operated at 300kV. The operational conditions for EELS acquisition included an entrance aperture of 2.0 mm, energy dispersion of 0.1 eV/channel, and full width at half-maximum (FWHM) to 1.0 eV for the zero-loss peak calibration. Fe *L*-edge spectra was acquired with an acquisition time of 5.0 s in the Scanning Transmission Electron

Microscope (STEM) mode.

Standard procedures were used to measure the Fe-oxidation state of clay preparations selected for EELS. The statistical optimum signal-window parameters for the integral ratio of Fe- L_2/L_3 edges were calculated using *Gatan Digital Micrograph* software. In particular, the background intensities were removed from EELS spectra through an application of standard power-law and double arctan functions. A window δ (30 eV) was selected in the background to extrapolate the curve over the post-edge window and the electron intensity under the extrapolated line was subtracted from a total intensity. Because the fit of the curve to the tail of a preceding edge shows similar power-law dependencies to the background (Williams and Carter, 2009), a double arctan function (Equation 1) was used as the background-function.

Equation 1

$$f(\Delta E) = \frac{h1}{\pi} \cdot \left[\arctan\left(\frac{\pi}{w1} \cdot (\Delta E - E1) + \frac{\pi}{2}\right) \right] \times \left[\frac{h2}{\pi} \right] \times \left[\arctan\left(\frac{\pi}{w2} \cdot (\Delta E - E2) + \frac{\pi}{2}\right) \right]$$

Two arctan functions (h1 and h2) associated with height (after the power-law was used to eliminate background effects) were then applied to the Fe L_3 and the Fe L_2 edges with fixed inflection points at $E1=710.0$ eV and $E2=721.2$ eV and fixed widths of $w1=w2=1$ eV. The calculated double arctan background-functions were subtracted from the signal integration window of each analysis. Fe-oxidation states were determined by the universal curve as a function of the integral ratio of Fe L_3/L_2 and the total ferric Fe concentration (van Aken *et al.*, 1998). EELS (50 signals) were collected for each sample and then summated.

3. Results and discussions

3.1. Core description

The split cores of sites U1365 and U1369 were scanned by Section Half Imaging Logger (SHIL) (IODP-USIO) and described based on the optical observation of smear slides of sediments with increasing depth (Fig. 2). The sediment column at U1365 is subdivided into four lithological units; 1) zeolitic metalliferous pelagic clay (unit IA; 0-8.35 mbsf), 2) metalliferous pelagic clay to zeolitic metalliferous pelagic clay (unit IB; 8.35-43.7 mbsf), 3) porcelanite and chert (unit II; 43.7-62.3 mbsf), and 4) metalliferous clay (unit III; 62.3-75.3 mbsf). In the subunit IA, proportions of clay decrease from 30 % to 20 %, and zeolite abundance increases from 10 % to 40 %, while both clay and Red-brown to yellow-brown Semiopaque Oxide minerals (RSO) vary erratically (10 % to 50 %) with a depth. Sediment in unit II includes chert, porcelanite and inter-bedded pelagic sediment. The mineral proportion of both clay and zeolite minerals decreases relative to unit I, while RSO increases from 20 % to 90 %. Unit III consists of black colored metalliferous clays with a high proportion of RSO. The unit located just above the basalt contact is distinctively colored compared to the brown and dark brown sediment in the upper units. The sediment column at U1369 is subdivided into two lithological units; 1) metalliferous zeolitic pelagic clay (unit I; 0 - 5.3 mbsf), and 2) zeolitic metalliferous pelagic clay (unit II; 5.3 - 15.6 mbsf). In the unit I, brown-yellowish sediment includes of zeolite less than 10 μm in length (38 – 63 %), RSO (24 - 38 %) and clays (~13 %) whose abundances vary with depth. In unit II, dark brown sediment contains clay (9 – 15 %), RSO (42 %) and zeolite crystals that are greater than 50 μm in length (35 – 70 %). The existence of chert layers at a depth of 43.7-62.3 mbsf of U1365 indicated a high biological productivity and high temperature of seawater (Keene, 1975; Muttoni and Kent, 2007). Dark black colored sediment appeared at the basal contact may indicate the alteration of basalt with seawater. Aeolian or terrigenous sediment may cause the variation of

mineralogy for site U1365, far away from the center of gyre comparing with U1369.

3.2. X-ray diffraction (XRD)

XRD analyses of fine clay-sized sediment ($< 1 \mu\text{m}$) were performed from different depths at sites U1365 and U1369 (Fig. 3). Air-dried and ethylene-glycolated samples were examined to confirm the contents of smectite, chlorite, and kaolinite. The heterogeneous suite of clay minerals identified by XRD in the unit I (U1365) includes smectite (S), kaolinite (K) and illite (I) as well as clay-sized quartz (Q) and plagioclase (P). Smectite appears prominently through the depths of 4.59 - 42.8 mbsf compared with illite (4.59 - 34.86 mbsf), and kaolinite (4.59 - 17.49 mbsf). In unit III, goethite (G) and plagioclase (P) are present at depths between 71.83 and 75.16 mbsf. The discernible XRD reflections was not observed due to the amorphous RSO found in virtually all intervals of unit III. Because chert layers were identified in all intervals of the cores of unit II (43.7 - 62.3 mbsf) by visual observation, XRD was not performed for this unit. At site U1369, XRD diffractograms imply that illite (I), smectite (S), kaolinite (K), and chlorite (Ch) appear abundantly throughout all depths (1.16 - 15.52 mbsf) with minor amounts of plagioclase (P), phillipsite (Ph), K-feldspar (Kf) and goethite (G). XRD profiles for glycolated samples confirmed the occurrence of smectite and chlorite at U1369. The abundant, uniform occurrence of illite, chlorite, and kaolinite throughout all depths of sediment at site U1369 compared with the lower abundance and limited distribution at site U1365 (Fig. 3) indicates that the hydrothermal activity (Deer *et al.*, 1996; Dekov *et al.*, 2005) that aids in the formation of illite, chlorite, and kaolinite. These variations may result from differences in the pattern and magnitude of hydrothermal

circulation and advective heat flow. The observed heat flow at site U1369 is 18 mW/m², a value very low for its crustal age relative to conductive cooling models (Stein and Stein, 1994) and is highly indicative of ongoing fluid flow. In contrast, the observed heat flow at site U1365 is 58 mW/m², a value that is consistent with conductive cooling models for its crustal age.

3.3. Pore water chemistry

To explore the source of smectite and illite mineral variability at sites U1365 and U1369, the role of pore water was more fully considered. Pore water chemistry, including dissolved oxygen (DO), silicon (Si⁴⁺), potassium (K⁺), iron (Fe^{tot}), and nitrate (NO₃⁻) are provided by Expedition 329 Scientists (2011) (Fig. 4). At site U1365, DO profile decreases from 189.5 µM at the surface of sediment to 69.7 µM at the sediment/basalt contact. Dissolved Si⁴⁺ drastically increases from approximately 350 µM at the sediment/water interface up to 601 µM at 42.18 mbsf where chert and porcelanite layers (unit II) appear, Si⁴⁺ then decreases to 465 µM at the sediment/basalt contact (75.5 mbsf). K⁺ concentration fluctuates within the upper part of unit I (21.8 mbsf), and increases up to 15.4 mM at the lower part of unit I (42.18 mbsf). Below unit II (62.3 mbsf), the K⁺ concentrations appear nearly constant (~12 mM). Fe^{tot} concentration increases in value slightly with increasing depth. It achieves its peak value of 5.2 µM at the contact with the basaltic basement. The concentration of NO₃⁻ increases continuously from the sediment/water interface to the basal boundary of unit I (38.46 µM to 48.17 µM); however, NO₃⁻ values in unit III, below the chert and porcelanite layers of unit II, show a increase in concentration (33.3 µM to 38.65 µM, see solid arrow), relative to similar sediment found in unit I. At the site U1369, the concentration

of DO shows a slight decrease (157.6 μM to 118 μM) with increasing depth except near the sediment/basalt interface at 12.8 mbsf to 15.6 mbsf where oxygen values rebound from a low of 118 μM back to 136.1 μM . Si^{4+} concentrations fluctuate, slightly increasing with depth (240.8 μM to 276.4 μM). The K^+ concentration appears constant throughout the entire sequence of sediment with only some minor fluctuation (12.16 mM to 12.69 mM). Fe^{tot} also appears largely invariable, with values that are nearly constant in the range of 7.47 μM to 6.78 μM . Similar to the upper sections of U1365, NO_3^- increases continuously from approximately 38 μM to 41.2 μM . Contrary to the trend at U1365, NO_3^- at site U1369 shows a slight increase (40.3 μM to 41.2 μM , see open arrow) at the sediment/basalt interface.

DO profiles indicate that an oxidative environment persists throughout the sedimentary sequence as well as through the upper portions of the basaltic basement (Fig. 4). At site U1365, this observations is particularly noteworthy where thick chert layers (~20 m) likely impede or block the downward penetration of DO below unit II. RSO, an amorphous oxide that is sensitive to redox conditions, is abundant in the sediment immediately overlying the basalt contact at U1365 (Fig. 2). However, the amorphous Fe-oxyhydroxides could be a result of oxidation of dissolved Fe in hydrothermal fluids upon their mixing with oxygenated seawater (Millero *et al.*, 1987; Pichler and Veizer, 1999). The likely cause of this pervasive oxygen is diffusion of oxygen from fractured basaltic crust into overlying sediment (Orcutt *et al.*, 2013). D'hondt *et al.* (2015) speculate that this process has occurred throughout the entire SPG depositional history. Indeed, the observed concentration of DO at site U1369 actually shows a slight increase at the sediment/basalt interface (~14 mbsf to ~15 mbsf), and therefore, diffusion appears to be ongoing.

3.4. Transmission electron microscopy (TEM)

Bright-field TEM micrographs of clay minerals, including insets of corresponding EDS and SAED patterns, are displayed (Figs. 5 and 6). TEM images of clay packets (~30 nm, see circled area) in the upper part of unit I (4.59 mbsf) at site U1365 show a wavy structure with diffused corresponding SAED patterns and the elemental composition of the circled area ($\text{Al/Si} = 0.32$, $\text{Fe/Si} = 0.13$, $\text{Mg/Si} = 0.13$) indicating Fe-montmorillonite (Fig. 5a). Neighboring discrete clay packets (circled area, 50 nm in thickness) show the elemental compositions ($\text{Al/Si} = 0.58$, $\text{K/Si} = 0.04$) typical of illite (Fig. 5b). With $d_{001} = 1.0$ nm in the $00l$ Bragg reflections and diffused 1.0 nm spacings in $02l$ reflections row, these packets are likely disordered illite, polytype $1M_d$ (Fig. 5b). In unit III, fibrous and wavy smectite layers mixed with rounded Fe/Mn oxides prevail at the sediment/basaltic crust interface (75.52 mbsf). SAED and EDS results (Fig. 5c) reveal that clay in this unit includes Fe-rich smectite ($\text{Al/Si} = 0.11$, $\text{Fe/Si} = 0.18$) with diffused turbostratically disordered smectite Bragg's reflections ($d_{100} = 0.45$ nm). The abundance of iron in unit III is further supported by the presence of both goethite ($d_{110} = 0.42$ nm, $d_{111} = 0.25$), and hematite that are readily identifiable in XRD diffractograms obtained from samples from this interval (Expedition 329 Scientists, 2011).

TEM micrograph of clay packets in the lower part of sediment column (15.52 mbsf) at site U1369 shows a wavy structure with diffused SAED patterns ($d_{001} = 1.2$ nm) and the elemental composition of the circled area (Fig. 6a) shows a high Fe-content ($\text{Al/Si} = 0.48$, $\text{Fe/Si} = 0.22$) indicating Fe-rich smectite (nontronite). Variations in the illite polytypes found at U1369 are displayed in the SAED patterns of discrete clay packets (30 - 80 nm in thickness) with high Al/Si and K/Si contents ($\text{Al/Si} = 0.65 - 0.73$, $\text{K/Si} = 0.07 - 0.12$) (Figs. 6b, 6c, 6d). Three illite polytypes were identified:

- 1) $1M$, an ordered 1-layer polytype displaying distinct $00l$ reflections ($d_{001} = 1.0$ nm) and the repeated 1.0 nm spacings in $02l$ reflections row (Fig. 6b);
- 2) $2M_1$, an ordered 2-layer polytype exhibiting $00l$ reflections ($d_{001} = 1.0$ nm) with a well-defined repetition of 2.0 nm spacings in $02l$ reflections rows (Fig. 6c);
- 3) $3T$, an ordered 3-layer polytype showing $00l$ reflections with $d_{001} = 1.0$ nm and well-defined repetition of 3.0 nm spacings in $02l$ reflections rows (Fig. 6d).

Bright-field TEM micrographs of clay minerals from the sediment near the basaltic crust at sites U1365 and U1369 show a presence of K-bearing Fe-rich smectite (Fig. 7). TEM images of clay minerals in the lower part of unit III (70.16 mbsf) at site U1365 show an aggregation of clay packets (Fig. 7a). The elemental composition of the circled area shows ratios of ($Al/Si = 0.17$, $K/Si = 0.08$, $Fe/Si = 0.52$), consistent with K-bearing Fe-rich nontronite. Clay packets from a similar interval at site U1369 (unit II, 15.52 mbsf), also show prominent K content ($Al/Si = 0.36$, $K/Si = 0.06$, $Fe/Si = 0.32$), Fe-rich nontronite (Fig. 7b).

Hydrothermal activity is reflected in the illite polytypes ($1M$, $2M_1$, and $3T$) at site U1369 compared with U1365. Illite polytypes $2M_1$ and $3T$, in particular, are commonly associated with hydrothermal processes: polytype $2M_1$, for example, is reported in hydrothermally altered subseafloor sediments from the Aleutian trench (DSDP 180) (Eslinger and Yeh, 1981) and in subseafloor hemipelagic mud from the Chile Triple Junction trench (Kurnosov *et al.*, 1995). The highly ordered illite polytype, $3T$, on the other hand, has been synthesized in a lab-scale hydrothermal condition (Warshaw, 1960) and detected in a hydrothermal vein system in the Creede mining district, Colorado, USA (Horton, 1983). The preponderance of beidellite and saponite at site U1369 close to EPR is strongly indicative of hydrothermal origins associated with active mid-ocean ridges (Parra *et al.*, 1985, 1986; Fagel *et al.*, 2001), as previously reported for northern North Atlantic sediment (Fagel *et al.*, 2001).

However, the smectite found in site U1365, where Fe-rich nontronite and RSO coexist within metalliferous sediment located near the sediment/basalt contact, is likely the product of non-hydrothermal processes. The deposition of smectite in SPG pelagic sediment also likely due to the terrigenous input. The Fe-rich montmorillonite in the upper part of site U1365 sediment seems to be an influx of terrestrial component (Aoki *et al.*, 1979; Fagel *et al.*, 2007), or alteration of volcanic ash (Peterson and Griffin, 1964) because the location of site U1365 is close to the continental margin. Indeed, Fe-rich montmorillonite does not appear in the sediments of site U1369 near the EPR, where the hydrothermal alteration or seawater/basalt alteration are likely to be a dominant process, resulting in the formation of Fe-rich nontronite, thermodynamically favored relative to the other clay minerals.

3.5. Electron Energy Loss Spectroscopy (EELS)

Clay samples from sites U1365 and U1369 were examined by TEM-EELS (Fig. 8a). The Fe L_3 and L_2 edges appear near 708 and 721 eV. The integral ratio of Fe L_3/L_2 in samples with substantial K were calculated by statistical analysis in *Digital Micrograph software* as 4.38 and 1.88 for sites U1365 (74.04 mbsf) and U1369 (15.52 mbsf), respectively. The corresponding percentages of Fe(III), estimated by means of the universal curve as a function of integral white-line ratio of Fe L_3/L_2 versus Fe(III) concentration, are thus ~47 %, and ~4 %, (Fig. 8b). The sample of Fe-rich smectite (nontronite) without K-content in the metalliferous sediment (Fig. 5c) contains more Fe(III) significantly (~78 %) (Fig. 8b).

The accuracy of the estimated concentrations of Fe(III) in the nontronite of sites U1365 and U1369 are assessed by two means: First, the results are compared to the integral ratio of Fe L_3/L_2 of well characterized bio-reduced nontronite (77.8 % of Fe(III) for 6-month

bio-reduced N_{Au}-1 measured by 1-10 phenanthroline) as determined by Koo *et al.*, (2014). Their results ($\text{Fe } L_3/L_2 = 6.82$, 78 % Fe(III)) show strong similarity to those presented herein; both sets of results fall on the fit line of van Aken *et al.*, (1998). Secondly, our results confirm with hematite crystals for 100 % Fe(III) standard obtained from site U1371 (Mitsunobu *et al.*, 2012). Their data, based on micro-XANES analysis, also plots on the van Aken *et al.*, (1998) universal curve, with $\text{Fe } L_3/L_2 = 9.58$ corresponding to the 100% ferric iron (Fig. 8b).

Regardless of thermal history of sediment or location, K-bearing nontronite exists only in sediment located near crustal basalt (Fig. 7), suggesting the *in-situ* formation of smectite from basalt alteration with sea water. Since the unaltered basalt contains low K in the study area (Zhang *et al.*, 2012), seawater is the most likely source of K (Fig. 4). The mechanism of K uptake is likely by diffusive exchange with seawater in the presence of dissolved oxygen (Clayton *et al.*, 2000). However, the mechanism of K-fixation into the nontronite structure is not fully understood due to the following observations: 1) the Fe(III) measured by EELS on the K-nontronite in basal sediment shows a range of 4 – 47 % (Fig. 8) promoting K-fixation into the more negatively charged nontronite compared with ferric dominant nontronite; 2) the composition of basalts immediately underlying the sediment are marked by a dominant (60 % ~ 66 %) Fe(III) phase (Zhang *et al.*, 2012), however the reactions of basalt alteration that lead to nontronite formation could change in the Fe-redox state; and 3) the redox state of Fe in nontronite is ferric (~78%) (Fig. 8b). Consequently, a redox reaction -in direct opposition to an oxidative diffusive exchange- is needed to explain the observed Fe(II) found in these K-bearing nontronites.

The reduced Fe in K-nontronite could result from local microbially mediated Fe-reduction. The less negatively charged nontronite associated with Fe-reduction has a strong tendency to fix K into the interlayer to balance the layer charge (Kim *et al.*, 2004 and Koo *et*

al., 2014). The microbial Fe(III) reduction in nontronite in marine sediment, a possible mechanism for the liberation of Fe(II) in anoxic environments, was previously reported (Vorhies and Gaines, 2009). Microbial activity, particularly Fe-respiration, is widely suspected of causing alterations in clay chemistry, structure and Fe(II) content (Kostka *et al.*, 1996; Gates *et al.*, 1998; Kostka *et al.*, 1999a, b; Kim *et al.*, 2004; Stucki, 2006; Dong *et al.*, 2009). In the present study, microbes from the sediment/basalt contact were insufficiently cultured to test the effect of their activity on subseafloor redox conditions (D'hondt *et al.*, 2015). Nonetheless, biotic redox reaction by microbial Fe-respiration cannot be excluded as a probable cause of the spatial variability of clay mineral in the SPG. Metagenome analysis for denitrification genes suggests that anoxic/hypoxic microenvironments may persist locally in the subseafloor sediment (Tully *et al.*, 2016). Recently, K-nontronite was clearly identified as an intermediate phase of illite in the interaction of Fe-reducing microbe and Fe-rich nontronite when 35 – 43 % of microbial Fe-reduction in nontronite was reached (Koo *et al.*, 2014). Furthermore, in sites U1365 and U1369, the slight increases in nitrate concentration in the sediment and basal basalt contacts (33.3 μM to 38.65 μM for site U1365 and 40.3 μM to 41.2 μM for site U1369, see arrows in Fig. 4e) are possibly caused by ammonium oxidation coupled with Fe-reduction in a process known as “feammox” or through the oxidation of reduced nitrogen species (Yang *et al.*, 2012). However, because the concentrations of ammonium for both sites were below their limits of detection, the exact cause of variations in the concentrations of nitrate are not determined (D'hondt *et al.*, 2011; Zehr *et al.*, 2011).

4. Conclusions

A series of microscopic, spectroscopic, and chemical analyses of clay minerals in

subseafloor sediment beneath the SPG reveals that clay mineral compositions were resulted from various origins/mechanisms of clay mineral formation in the open ocean. Illite polytypes provide snapshots of hydrothermal activity in sediment, and variation of Fe(II)/Fe(III) in nontronite and the appearance of K-nontronite at the basal basalt/sediments interface suggest that local reductive reaction occurs during the formation of K-nontronite despite the fact that dissolved oxygen prevails throughout the sediment column down to the basaltic basement. It is particularly worthy of note that the variability of clay mineral structure and composition identified by this study was formed under pervasive/persistent oxic conditions.

Acknowledgements

We would like to thank the scientific parties of IODP expedition 329 for their indispensable discussions and comments. This research was a part of the project titled ‘International Ocean Discovery Program’, funded by the Ministry of Oceans and Fisheries, Korea. HRTEM analyses were supported by Korea Basic Science Institute (KBSI) project (T35520), and partially supported by DOE grand to H. Dong (G01928).

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Figure captions

Fig. 1. Bathymetry map of the SPG showing drilling sites by IODP Expedition 329 (U1365 ~ U1371). Sediments cored at sites U1365 and U1369 (outlined in red) were used for the present study.

Fig. 2. Lithology of the sediment columns for the sites U1365 and U1369. Mineral compositions are indicated by colors (green = clay, gray = zeolite, red = RSO), and the insets of representative smear slide images show corresponding mineral compositions of pelagic sediment.

Fig. 3. XRD patterns of air dried and glycolated clay less than 1 μm of the seafloor sediment for the sites U1365 and U1369 at various depths displaying composition of smectite (S), chlorite (Ch), kaolinite (K), illite (I), quartz (Q), plagioclase (P), phillipsite (Ph), K-feldspar (Kf), and goethite (G).

Fig. 4. Pore water chemistry of sediment columns at the sites U1365 and U1369 (IODP expedition 329 scientists., 2011) showing (a) dissolved oxygen penetration down to sediment/basalt interface, (b) slightly increase in silicon with a depth and high silicon concentration around chert (U1365 unit II), (c) slightly increase in potassium concentration with a depth, (d) constant iron concentrations with a depth, and (e) increase in nitrate

concentration with a depth (see arrows showing abrupt increase at sediment/basalt interface).

Fig. 5. Bright-field TEM micrographs of the fine clay fraction ($<1\mu\text{m}$) with the insets of EDS spectra and the corresponding SAED patterns (circled area) for the site U1365 sediments showing (a) Fe-montmorillonite (4.59 mbsf), wavy structures with diffused corresponding SAED patterns ($d_{001} = 1.3 \text{ nm}$), and elemental compositions ($\text{Al/Si} = 0.32$, $\text{Fe/Si} = 0.13$); (b) $1M_d$ illite (4.59 mbsf), discrete packets with distinct Bragg's reflections ($d_{001} = 1.0 \text{ nm}$) and diffused 1.0 nm spacings in $02l$ reflections row, and elemental compositions ($\text{Al/Si} = 0.58$, $\text{K/Si} = 0.04$); and (c) Fe-rich smectite with Goethite (75.52 mbsf), wavy structures mixed with round shaped RSO, with turbostratically oriented SAED pattern of smectite ($d_{100} = 0.45 \text{ nm}$) and goethite ($d_{110} = 0.42 \text{ nm}$, $d_{111} = 0.25 \text{ nm}$) and the corresponding elemental composition of smectite ($\text{Al/Si} = 0.11$, $\text{Fe/Si} = 0.18$)

Fig. 6. Bright-field TEM micrographs of the fine clay fraction ($<1 \mu\text{m}$) with the insets of EDS spectra and the corresponding SAED patterns (circled area) for the site U1369 sediments showing (a) Fe-rich smectite (15.52 mbsf), wavy structures with diffused Bragg's reflections ($d_{001} = 1.2 \text{ nm}$), and elemental compositions ($\text{Al/Si} = 0.48$, $\text{Fe/Si} = 0.22$); (b) $1M$ illite (15.52 mbsf), discrete packets with distinct Bragg's reflections ($d_{001} = 1.0 \text{ nm}$) and the repeated 1.0 nm spacings in $02l$ reflections row; (c) $2M_l$ illite (15.52 mbsf), distinct Bragg's reflections ($d_{001} = 1.0 \text{ nm}$) with repetition of 2.0 nm spacings in $02l$ reflections rows; and (d) $3T$ illite (15.52 mbsf), distinct Bragg's reflections ($d_{001} = 1.0 \text{ nm}$) with repetition of 3.0 nm spacing in $02l$ reflections rows. The corresponding elemental composition of illite (b, c, d)

shows high Al/Si and K/Si contents (Al/Si = 0.65 - 0.73, K/Si = 0.07 - 0.12).

Fig. 7. Bright-field TEM micrographs of the clay fraction ($<1\ \mu\text{m}$) for sediment/basalt interface at the sites U1365 and U1369 showing (a) K bearing Fe-rich smectite (U1365, 70.16 mbsf) with Al/Si = 0.17, K/Si = 0.08, and Fe/Si = 0.52; and (b) K bearing Fe-rich smectite (U1369, 15.52 mbsf) with Al/Si = 0.36, K/Si = 0.06, and Fe/Si = 0.32.

Fig. 8. EELS spectra of Fe $L_{2,3}$ for the K-bearing Fe-rich smectite (nontronite) at the basalt/sediment interface showing (a) distinct peaks separation at 708 and 721 eV, and (b) the plotted integral ratio of Fe L_3/L_2 on the universal curve as a function of Ferric iron concentration and Fe L_3/L_2 (van Aken et al., 1998).

Table 1
Summary of 7 drilling sites by IODP Exp. 329 in the SPG. The entire sediment column at four sites and the upper 100 m of basaltic basement at three sites were cored. Each coring site has various basement ages (0 - 75 Ma) and water depths (5075-5305 m) depending on their location within SPG.

Sequence	Site	Lattitude	Longitude	Water Depth (mbsl)	Total Sediment Thickness (m)	Basement Age (Ma) (Gradstein et al., 2004)
1	U1365	-23° 51'	-165° 39'	5695	75	84-120
	U1366	-26° 03'	-156° 54'	5127	30	84-120
	U1367	-26° 29'	-137° 56'	4289	27	33.5
	U1368	-27° 55'	-123° 10'	3740	16	13.5
2	U1369	-39° 19'	-139° 48'	5277	16	58
	U1370	-41° 51'	-153° 06'	5075	68	73.6-79.5
	U1371	-45° 58'	-163° 11'	5305	131	71.5-72.9

Figure 1

Figure2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure8

Abstract

Subseafloor sediment and basalt rock samples at seven sites in the South Pacific Gyre (SPG) were recovered by Integrated Ocean Drilling Program Expedition 329 (2010.10.8 ~ 2010.12.13). Microscopic and spectroscopic measurements on the structural Fe-redox states and the elemental composition of smectite, and polytypes of illite in the sediment at two sites (U1365 and U1369) were performed to understand the origin/formation mechanism of clay minerals in the oligotrophic open ocean. The dominant phases of clay minerals found in the present study were smectite and illite polytypes. Suggestive of non-uniform early diagenetic processes in the expansive SPG seafloor, higher ordering of illite polytypes ($1M$, $2M_I$, and $3T$) were identified at site U1369 while disordered $1M_d$ illite were found at U1365. Smectites of hydrothermal origin (Al-rich beidellite, and saponite) were observed at U1369. Fe-rich montmorillonite minerals that are likely associated with the terrigenous input, were dominant at U1365. Nontronite (Fe-rich smectite) was detected at both sites. Red-brown to yellow-brown semiopaque oxide minerals (RSO) were widely distributed with Fe-rich smectite near the basaltic crust at U1365. Lower observed heat flow at U1365 relative to U1369 provides a possible explanation for the observed variability in clay mineral speciation between these two sites. The presence of K-nontronite at the basalt/sediment interface at both sites indicates an oxidative basalt alteration; however variations in the oxidation states of structural Fe in nontronite measured by EELS indicate that reductive environment persists locally at the basalt/sediment interface.

Keywords: South Pacific Gyre; K-nontronite; diagenesis; Illite polytypism; IODP Expedition