1. INTRODUCTION

The alteration of volcanic ash is considered to be an essential process in the diagenesis of marine sediments. For example, Weaver (1958) suggested that most of the expanded clays in marine sediments were derived from volcanic glass, and that potassium was fixed into expandable clays and later illite from the coexisting pore water. In several studies of chemical variations of interstitial water, previous workers have suggested that low-temperature alteration of ash affected interstitial water chemistry (e.g., Lawrence et al., 1979; Gieskes and Lawrence, 1981; Gieskes et al., 1990a, b). Matsubisa and Matsumoto (1986) attributed the variation of $\delta^{18}O$ and Mg content of interstitial waters recovered from the Nankai Trough during Leg 87 to ash alteration. From the onboard chemical analyses of interstitial waters retrieved from Site 808, Leg 87 (Fig. 1), Shipboard Scientific Party (1991) also pointed out that the chemical variations of interstitial water were partly affected by the alteration of ash.

In his report on the lithology and physical properties of sediments in subduction zones, Vrolijk (1990) discussed the importance of smectite-rich sediments. He suggested that smectite-rich strata derived from the alteration of volcanic ash are structurally weak and that décollement zones may be preferentially formed in the smectite-rich layers.

The alteration of ash is also thought to be an important process in the geochemical cycle of oceanic sediments. However, little is known about the mineralogical and chemical variations of volcanic ash itself, because it is difficult to obtain a suite of pure volcanic ash samples from the same sediment column.

The continental slope of Nankai Trough (Fig. 1) is a well-documented modern accretionary prism in the Pacific Ocean. We selected 72 samples of volcanic ash from Site 808, where a complete sediment column was obtained from the ocean floor, through the décollement, to the underlying basalt. Because these samples originally have a high volcanic glass content, they provide a good opportunity for establishing a model of ash alteration at the early stage of diagenesis.

In this paper, we present the alteration mineralogy and major-element chemistry of the ash samples and discuss the effect of ash alteration on the chemistry of interstitial fluids. The chemistry of bulk samples demonstrates that the decomposition of ash and the subsequent formation of authigenic smectite and zeolites play important roles in controlling interstitial water chemistry.

2. SAMPLES

Site 808 is located at the toe of the Nankai accretionary prism. The sediments at Site 808 (0 to 1290 mbsf) can be broadly classified into two groups: clastic material transported by turbidity currents (dominating the upper portion of the sediment column above ca. 600 mbsf), and hemipelagic sediments deposited on the oceanic crust of Shikoku Basin in the lower portion (Shipboard Scientific Party, 1991). The facies association reported by the Shipboard Scientific Party, with location of 72 ash samples, is shown in Figure 2. The age of the basal sediment is between 13.6 and 15 Ma (Shipboard Scientific Party, 1991). Ash layers are especially concentrated in the interval from 557 to 824 mbsf. This interval corresponds to the trench-to-basin transition and the upper Shikoku Basin facies (Fig. 2A); the age of these sediments is between 0.28 and 2.65 Ma (Shipboard Scientific Party, 1991). The décollement zone extends from 945 to 965 mbsf in the lower Shikoku Basin facies. Only five samples of ash were recovered from this interval.

The 13 ash samples between 1245 and 1275 mbsf are apparently different from the ash above 1245 mbsf. These 13 ash samples are white and contain quartz grains about 1 mm diameter, based on optical observation. They were collected from various locations within the same ash layer of 45 m thickness. This ash layer was silicified and well consolidated, and the original glass is completely altered.

3. ANALYTICAL METHOD

Mineralogical compositions were determined by X-ray diffraction using a Ni-target CuKα radiation at 30 kV and 10 mA. Randomly mounted air-dried bulk samples of ca. 200 mg were used for this purpose. For identification of illite/smectite mixed-layered minerals (I/S), glycolated samples were also scanned. The illite content in the I/S, however, was not determined in this study. The weight % of clay minerals was estimated from the peak height of the (001) reflection. Pure smectite diluted by powdered quartz glass was used for calibration. Reproducibility of clay contents for duplicated samples was within ±5%.
For major chemical analyses, the samples were ultrasonically stirred with ultrafiltrated water to remove dissolved salts, and the residues were collected by centrifugation and sedimentation. This procedure was repeated at least four times and the ash was dried for 24 hr at 110° C. The dried samples were ignited at about 900° C for 1 hr. After ignition the ash samples are regarded as free from organic matter and volatile components such as carbonate and water. Lithium borate and a heat-treated, powdered sample (10:1) was fused in a 5% Au-containing platinum crucible for 8 min. at 1200° C to make a glass bead for quantitative analysis by X-ray fluorescence (XRF). The elemental analyses performed by XRF are Si, Al, Ti, Mg, Ca, Fe as Fe$^{3+}$, Mn, Na, K, and P. All elemental compositions are expressed as weight % of the oxide form. Accuracy and reproducibility of measurement were checked by standard rock samples supplied by the Geological Survey of Japan. Measurement error of each element is within ±2%.

RESULTS AND DISCUSSION

Mineralogy

Minerals identified by the X-ray diffraction pattern of bulk ash layers are listed in Table 1. As noted before, the weight % of the constituent minerals except for total clay was not estimated. Thus, the mineral abundances are uncorrected intensities of characteristic peaks of each mineral.

Because the studied ash layers are ocean floor deposits derived from subaerial volcanism, the samples also contain detrital minerals. All ash samples contain quartz, feldspar, chlorite, and calcite. Most of the calcite must be originally of biogenic origin. The intensities of X-ray diffraction peaks of quartz, feldspar, and chlorite are slightly greater in the uppermost 556 mbsf of the sediment column, where most sediments were affected by turbidity currents, in contrast to the lower portion, below 556 mbsf. Illite of 2M$_1$ polytype, indicating a detrital origin, is also a component of the uppermost 557 mbsf of sediment, though its concentration decreases with depth. Hornblende was frequently observed in the interval from 580 to 850 mbsf, which supports the possibility of a volcanic origin.

Figure 2B shows the alteration mineral assemblage of the ash layers. The relative concentrations of the alteration minerals estimated from X-ray diffraction data are plotted as a function of depth in Figures 2C-2E. The first downhole appearance of smectite recognized as the appearance of a 15-Å peak, was detected in the bulk sample from 200 mbsf. Below 557 mbsf, the concentration of clay minerals drastically increases with depth. A broad and asymmetric peak of the (001) clay mineral reflection suggests the occurrence of mixed-layered I/S in ash from 645 mbsf, where the temperature is about 60° C. From the on-board analysis, I/S formation was indicated by X-ray diffraction patterns of samples from the sediment column at ca. 530 mbsf (Shipboard Scientific Party, 1991). Underwood et al. (this volume) observed that I/S was detected in shales from 550 mbsf. They also reported that the illite composition in I/S increases with depth, with the illite content in I/S reaching almost 80% at the base of the sediment column at about 120° C. Both of the reported depths of I/S appearance are shallower than its possible appearance in ash. The X-ray diffraction peak of (001) clay mineral reflection in the ash samples becomes sharper and more symmetric with increasing depth, and illite formation in mixed-layered I/S does not occur even in the samples from the base of the sediment column, where smectite is still the most abundant phase of the authigenic clay minerals.

Mixed-layered I/S is widely recognized as a transition mineral phase in the transformation of smectite to illite during diagenesis (e.g., Weaver, 1958; Dunoyer de Segonzac, 1970). For the sedimen-
Formation mechanisms of I/S mixed-layered minerals between volcanic ash and the chemical compositions of each mineral interfere with the transformation of smectite to illite. Further information on I/S in volcanic ash and the chemical compositions of each separated mineral phase will be necessary to clarify the different formation mechanisms of I/S mixed-layered minerals between volcanic ash and shales.

Major-Element Chemistry

The analytical data pertaining to the major chemical constituents of the bulk ash samples are given in Table 2, and some important concentration trends are plotted in Figure 3. The range of observed TiO₂/Al₂O₃ ratios (0.01 to 0.05; Fig. 3B) is within the expected range for ash with an andesitic to rhyolitic composition derived from the Japanese Islands. For example, andesites from Sakurajima, one of the biggest and most active volcanoes in Japan, have TiO₂/Al₂O₃ ratios of 0.03 to 0.08 (Oba et al., 1980), while the ratio for pumice from Asama volcano is about 0.035 (Sato et al., 1989). Rhyolitic rocks have a smaller ratio than the andesites (e.g., 0.02 to 0.03 for volcanic glass tephras from Aso volcano; Machida and Momose, 1985). The apparent ratio of TiO₂/Al₂O₃ of bulk ash may be higher than that of pure glass because of the contamination of basic minerals such as chlorite and amphiboles. The higher TiO₂/Al₂O₃ ratio in the upper portion of the Site 808 sediment column as compared to the lower portion is concordant with the higher intensities of chlorites and amphiboles in the upper portion. If chemical analysis of pure glass were to be performed, the ash samples would become more rhyolitic than the present estimation.

Although decrease of the TiO₂/Al₂O₃ ratio with depth indicates a more rhyolitic ash composition, the SiO₂/Al₂O₃ ratio also generally decreases with increasing depth (Fig. 3). This is due to a higher solubility of Si relative to Al in the interstitial water. SiO₂ is generally released to interstitial waters when volcanic glass decomposes, whereas Al and Ti tend to remain in the solid phase.

In Figure 4, the relation of MgO/Al₂O₃ and K₂O/Al₂O₃ to SiO₂/Al₂O₃ are shown for ash from five depth intervals defined by the
Table 1. Peak intensities by X-ray diffraction of minerals in volcanic ash from Site 808.

<table>
<thead>
<tr>
<th>Sample</th>
<th>mbf</th>
<th>Qtz</th>
<th>Feld</th>
<th>Ill</th>
<th>Chl</th>
<th>Cal</th>
<th>Ho</th>
<th>Clay</th>
<th>CP</th>
<th>Anal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H-1, 71-73 cm</td>
<td>3.7</td>
<td>100.0</td>
<td>77.8</td>
<td>15.3</td>
<td>22.8</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2H-1, 77-79</td>
<td>7.1</td>
<td>100.0</td>
<td>56.5</td>
<td>31.5</td>
<td>39.7</td>
<td>62.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3H-1, 41-43</td>
<td>17.6</td>
<td>100.0</td>
<td>91.0</td>
<td>21.7</td>
<td>25.9</td>
<td>12.7</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Abbreviation of minerals and peaks measured for intensities are as follows. Qtz: quartz. Ill: illite (9.8Å); Chl: chlorite (7.6Å); Cal: calcite (3.0Å); Ho: hornblende (8.6Å); Clay: clay minerals (15Å); CP: clinoptilolite (9.6Å); Anal: analcite (5.6Å).

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### Table 2. Analytical data of major-element chemistry of volcanic ash from Site 808.

<table>
<thead>
<tr>
<th>Sample</th>
<th>mfo (%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>P₂O₅</th>
<th>TiO₂</th>
<th>H₂O</th>
<th>Total IL*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H-1, 7-13 cm</td>
<td>3.7</td>
<td>67.58</td>
<td>0.58</td>
<td>16.16</td>
<td>5.04</td>
<td>0.09</td>
<td>2.16</td>
<td>1.91</td>
<td>2.84</td>
<td>2.75</td>
<td>0.11</td>
<td>98.21</td>
</tr>
<tr>
<td>2H-1, 77-79 cm</td>
<td>7.1</td>
<td>56.52</td>
<td>0.63</td>
<td>15.21</td>
<td>5.08</td>
<td>0.08</td>
<td>3.39</td>
<td>1.54</td>
<td>2.91</td>
<td>1.83</td>
<td>0.24</td>
<td>97.67</td>
</tr>
<tr>
<td>3H-2, 41-43 cm</td>
<td>17.6</td>
<td>63.29</td>
<td>0.76</td>
<td>16.58</td>
<td>7.93</td>
<td>0.53</td>
<td>2.69</td>
<td>1.54</td>
<td>2.31</td>
<td>0.41</td>
<td>0.15</td>
<td>97.09</td>
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<td></td>
<td></td>
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<td>101.41</td>
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<tr>
<td>94X-9, 92-94</td>
<td>193.6</td>
<td>67.37</td>
<td>0.68</td>
<td>15.54</td>
<td>5.52</td>
<td>0.09</td>
<td>2.17</td>
<td>2.92</td>
<td>2.84</td>
<td>2.00</td>
<td>0.12</td>
<td>98.23</td>
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<td>100X-2, 142-144</td>
<td>98.7</td>
<td>67.61</td>
<td>0.60</td>
<td>13.62</td>
<td>5.54</td>
<td>0.21</td>
<td>2.07</td>
<td>3.46</td>
<td>2.57</td>
<td>2.14</td>
<td>0.18</td>
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<td>100X-3, 52-54</td>
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<td></td>
<td></td>
<td>100.35</td>
</tr>
<tr>
<td>11X-1, 115-117</td>
<td>208.0</td>
<td>64.85</td>
<td>0.77</td>
<td>16.96</td>
<td>6.99</td>
<td>0.20</td>
<td>2.63</td>
<td>2.43</td>
<td>2.93</td>
<td>1.74</td>
<td>0.11</td>
<td>96.11</td>
</tr>
<tr>
<td>20X-2, 32-37</td>
<td>289.7</td>
<td>68.91</td>
<td>1.54</td>
<td>8.37</td>
<td>0.91</td>
<td>0.11</td>
<td>3.88</td>
<td>2.59</td>
<td>2.83</td>
<td>3.11</td>
<td>0.14</td>
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<td>131R-88B</td>
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<td>131R-88C</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>101.40</td>
</tr>
</tbody>
</table>

*IL* is ignition loss.
Figure 3. Variation of major chemical constituents of volcanic ash with depth.
mineral assemblages shown in Figure 2B. The plots of MgO/Al2O3 vs. SiO2/Al2O3 for samples shallower than 646 mbsf show a negative correlation, although coexisting basic detrital minerals such as chlorite and hornblende obscure this relation. This negative correlation indicates the mixing of andesitic ash and felsic detrital minerals. Below 646 mbsf, the SiO2/Al2O3 and MgO/Al2O3 ratios of the same ash are positively correlated, suggesting the possibility that a single process is affecting the SiO2 and MgO concentrations of ash in the deeper portion.

Above 1200 mbsf, the K2O/Al2O3 ratio has a less-clear relation to the SiO2/Al2O3 ratio than the case of MgO/Al2O3. The presence of detrital minerals, such as quartz, K-feldspar, K-mica, and hornblende may hide the simple mixing relation observed between SiO2/Al2O3 and MgO/Al2O3. However, the plots of K2O/Al2O3 vs. SiO2/Al2O3 for samples below 1200 mbsf, where the ash samples are strongly altered, show a weakly positive correlation similar to that between MgO/Al2O3 and SiO2/Al2O3. This means that K behaves in a similar way to Si and Mg in this depth range.

The Fe2O3/Al2O3 ratios of all ash samples are positively correlated with the MgO/Al2O3 ratios (Fig. 5). The positive correlation is much better in the samples above 810 mbsf, with more scatter in data from deeper samples. Iron is not abundant in interstitial waters, while Mg is one of the major cations there. The data plotting above the general correlation trend in Figure 5 may indicate the incorporation of excess Mg in the solid phase from coexisting interstitial water. An increase of the Mg concentration of the solid phase with depth is consistent with the Mg depletion of coexisting pore fluids (Shipboard Scientific Party, 1991). This indicates that Mg of the pore fluids is fixed in smectite during diagenetic alteration.

**Interaction Between Ash And Interstitial Water**

There appears to be a close relation between the chemical compositions of interstitial water and volcanic ash as a function of depth at Site 808 (Shipboard Scientific Party, 1991). In Figure 6, the H2SiO4 concentration and K/Cl and Na/Cl ratios of the interstitial waters analyzed during Leg 131 are plotted as a function of depth. H2SiO4 gradually increases from 500 µM just below the seafloor to 650 µM at 180 mbsf, and then rapidly increases to more than 800 µM between 180 and 200 mbsf. The concentration of H2SiO4 remains high to a depth of 550 mbsf and then sharply decreases to about 200 µM. The K/Cl ratio of the interstitial waters is characterized by an overall decrease between 0 and 650 mbsf with deflections in this trend near 200 mbsf and 550 mbsf (Fig. 6). The Mg/Cl ratio of the pore waters (not shown in this paper) varies in a similar manner to the K/Cl ratio.

As noted earlier, smectite starts to appear at 200 mbsf and the smectite content drastically increases below 550 mbsf (Fig. 2). Clinoptilolite and analcime first appear in the sediments at 650 and 810 mbsf, respectively. The first occurrence of smectite and the decrease of the K/Cl ratio of the interstitial water in the uppermost 200 mbsf indicate that smectite formation is associated with the removal of K from the interstitial waters. Smectite contains 45 wt% SiO2 in its structure, while andesitic glass contains 60 to 65 wt% SiO2. When smectite is formed from andesitic glass, SiO2 is released to the interstitial water. This also occurs in the uppermost 200 mbsf at Site 808.

The decrease in the K/Cl ratio of the interstitial waters at 550 mbsf corresponds to the first occurrence of mixed-layered I/S in shales (Underwood et al., this volume). Below 646 mbsf, where clinoptilolite (and maybe I/S) in the ash first appear, the H2SiO4 concentration and K/Cl ratio of the interstitial waters vary little compared with waters between 550 and 646 mbsf.

As described earlier, the SiO2/Al2O3, MgO/Al2O3, and K2O/Al2O3 ratios of bulk ash layers illustrate the mixing between andesitic glass
Figure 6. Variation of \(H_4SiO_4\), K/Cl, and Na/Cl of interstitial waters with depth in relation to alteration mineral assemblages. Analytical data of interstitial water is by Taira, Hill, Firth, et al. (1991).
and detrital minerals in the sediment column above 657 mbsf. By comparing the chemical characteristics of interstitial waters and ash, we suggest that glass decomposition exceeds smectite formation above 646 mbsf. The decrease of the H$_4$SiO$_4$ concentrations of interstitial waters between 550 and 650 mbsf is probably due to clinoptilolite formation. However, quartz overgrowths precipitating on detrital quartz may occur after illitization of smectites in sedimentary cements (Boles and Franks, 1979). Although an increase of the quartz content of the ash was not observed by X-ray diffractometry in the interval between 550 and 810 mbsf, the precipitation of quartz is also a possible sink for dissolved SiO$_2$.

Analcite is considered to be the major reservoir of Na in this sediment column. The relative intensity of X-ray reflection patterns of analcite tends to increase with the Na content of bulk ash layers (Fig. 7). Because Na is the most abundant cation in interstitial waters, a small variation (in the concentration of dissolved sodium) is hard to detect. In this sediment column, analcite occurs below 810 mbsf. Sodium fixation into analcite is not obvious in the interval between 810 and 1200 mbsf because of the low content of analcite and rare occurrence of ash layers. The decrease of the Na concentration of the interstitial water below 1200 mbsf (Fig. 6C) can be explained by the abundant formation of analcite at these depth (Fig. 2C). Thus, mineral formation by ash alteration also appears to affect the Na content of the interstitial water at the base of this sediment column.

**SUMMARY AND CONCLUSIONS**

The mineralogy and major-element chemistry were determined for 72 volcanic ash samples recovered from the sediment column between 4 and 1275 mbsf at ODP Site 808 in the Nankai Trough. The first occurrence of ash layers increases over the same interval, probably as a result of smectite and/or chlorite formation. Analcite forms below 810 mbsf (and particularly below 1240 mbsf), which may cause the observed decrease in the Na concentration of the interstitial water. Thus, the alteration of volcanic ash has a major influence on the chemistry of interstitial waters at Site 808.

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**REFERENCES**


