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# Geochemical indication of contrasting Holocene sediments related to sea–level change in coastal lagoon of the San'in district, Southwest Japan

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## Abstract

Geochemical analysis of Holocene sediments related to the sea–level change has been carried out for evaluation of changes in sedimentary environment. The Jomon transgression (from 10 k yrs BP) resulted in accumulation of organic black muds of the Shinjiko Formation, while succeeding regression in the Yayoi age (from 2400 yrs BP) led to deposition of the Asakumi Formation under backswamp condition of the fluvial system from the Kofun (4–6 C) to Heian (9–10 C) ages.

Changes in sedimentary environments are clearly demonstrated by geochemical indicators, such as TOC/TS and TOC/TN, $SiO_2/Al_2O_3$, $Al_2O_3/TiO_2$, and Ti/Zr ratios. Variation of $SiO_2/Al_2O_3$ and Ti/Zr is consistent with the grain size and sand contents. CIA is useful index of weathering degrees, showing relatively higher CIA for the Asakumi Formation than that of the Shinjiko Formation. Correlation of $Al_2O_3/TiO_2$ with grain size and sand contents is weak, suggesting that $Al_2O_3/TiO_2$ shows composition of the sources. K–metasomatism of Shinjiko muds is shown in the A–CN–K diagram, which occurred during unconformable disturvance between two formations.

**key words**: Holocene, coastal Jomon transgression, geochemistry

## Introduction

Geochemical approach to sediments is a useful tool for evaluation of sedimentary environment, weathering process and provenance change (e.g. Taylor and McLennan, 1985; McLennan et al., 1993; Nesbitt et al., 1996). Holocene sediments provide useful information on geochemical composition of muds, because they have little progressive alteration due to burial, diagenesis, and tectonic deformation compared with older sediments and sedimentary rocks. Thus geochemistry of such sediments is a key for characterization of sediments which were affected by transition from marine to non–marine conditions.

The coastal lagoons of the San'in region, Southwest Japan have been influenced by the Jomon transgression with high stand in sea–level at 6300 yrs BP, and succeedingly fluvial deltaic plains developed since the sea–level fall from 2400 yrs BP of the Yayoi age (Ota and Yonekura, 1987). Previous studies revealed detailed sea–level changes and concequent sedimentary environments, thus geochemistry of Holocene sediments is significant to understand a variation of sedimentary environment and nature of compositions of sediments.

## Geologic outline of coastal lagoon and study section

The Lakes Nakaumi and Shinji have remained as brackish lakes after the last sea–level rise in Jomon age (Tokuoka et al., 1990), which initiated at 10 k yrs BP (Ota and Yonekura, 1987; Ota et al., 1982; Umitsu, 1991) (Fig. 1). This transgression had its maximum flooding at 6300 yrs BP and was followed by the Yayoi fall in sea–level (2400 yrs BP) (Tokuoka et al., 1990). Sea water invasion was recorded in many archeological sites in the coastal lagoons, where black muds with higher concentration of total sulfur (over 1 wt% of normal marine sediments by Berner, 1984) and total organic carbon were formed (Nakamura and Tokuoka, 1997; Sampei et al., 1996). Sediments deposited during the Jomon transgression is called Shinjiko Formation in the coastal region of Lake Shinji (Tokuoka et al., 1995), and gradually changed into coarser clastics (Tokuoka et al., 1990). The Shinjiko Formation of lagoonal facies was overlain by the Asakumi Formation of fluvial dominated facies (Tokuoka et al., 1995). The previous lagoonal environment was probably influenced by invasion of fresh water to have resulted in brackish condition, and coastal plains were expanded in this region (Fig. 1).

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The examined section is situated at the archeological site of River Asakumi, called the Haranomae remain (HM in Fig. 1) (Tokuoka et al., 1995). Various rocks are distributed in the tributary of the River Asakumi, such as Miocene sediments and volcanic rocks varrying in composition from basalt to rhyolite (Yamauchi et al., 1980; Kano et al., 1994).

Sediments of the HM section are composed of the Shinjiko and Asakumi Formations, according to lithology and archeological remains (Figs. 2, 3).

### Shinjiko Formation

The Shinjiko Formation consists of visually homogeneous organic black to gray muds which grade upward sandy muds and sands with ca. 1.8 m thick. The upper part of the formation includes relatively well–sorted quartz sands compared to those of the Asakumi Formation (Tokuoka et al., 1995).

Grain size of this formation varies from 7.2 to 5.7 in phi scale in this section (Fig. 2), showing coarsening upward sequence. They increase sand contents from 10 wt%to 70 wt% (Fig. 3) (Tokuoka et al., 1995). Skewness of the samples of the Shinjiko Formation has relatively higher values ranging from –0.35 to –0.1 compared to those of the Asakumi Formation from –0.45 to 0.34 (Tokuoka et al., 1995). This suggests that sediments of the Shinjiko Formation were deposited under lagoon condition which gradully changed into fluvial dominated condition. The Shinjiko and Asakumi Formations have similar values of sorting ranging from 1.7 to 2.1 (Tokuoka et al., 1995).

The K–Ah (Kikai–Akahoya) volcanic ash of 6300 yrs BP of Machida and Arai (1978) is intercalated in the lowermost part of this formation. The Shinjiko Formation ranges from the middle Jomon to the Yayoi age (1–3 C) (BESPO, 1995).

### Asakumi Formation

The Asakumi Formation comprises laterally accreted beds, and the boundary to the underlying Shinjiko Formation is marked by erosional surface. The base of the Asakumi Formation consists of conglomerates, and is overlain by black to gray muds with intercalated sands (Figs. 2, 3). The conglomerate includes granule to pebble, and the matrix comprises mainly of sandy conglomerates and coarse sands, showing cross lamination. The clasts are andesite, basalt, rhyolite and mudstones, and archeological remains are also included. The strata strikes NE–SW direction and dips SE. The clasts show imbrication indicating paleo–current direction from NE to SW, which is similar to the present Asakumi fluvial system. Natural woods are arranged parallel to strike of the bed.

Although the Asakumi Formation represents fluvial

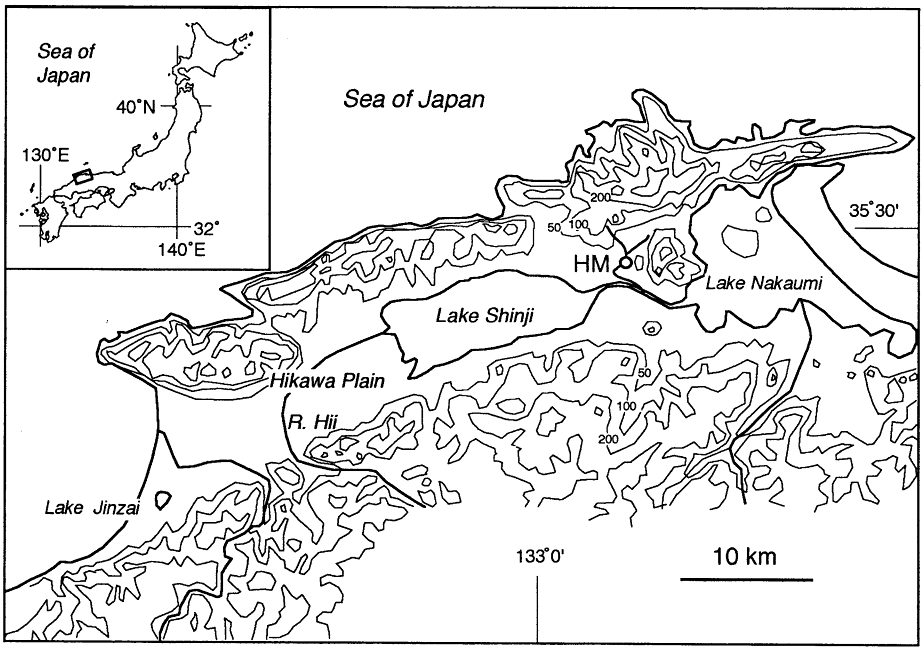

**Fig. 1** Index of the examined section (HA: Haranomae) and topography of the Nakaumi–Shinji lagoon in the San'in region, Southwest Japan, after Nakamura (1996).

**Table 1** Analyses of the Holocene sediments of the Shinjiko and Asakumi Formations at the Haranomae section (archeological site) in San'in district of Southwest Japan. Numbers are sample numbers in stratigraphically ascending order in each part, at 10– 20 cm thick intervals. SH is samples from the Shinjiko Formation ranging from middle Jomon (6300 yrs BP) to Yayoi ages (1–3 C). A, B and C indicate samples from three units of the Kofun (4–6 C), Nara–Heian (8–9 C) and Heian ages (9–10 C), respectively of the Asakumi Formation. Total Fe is given as $Fe_2O_3$*. LOI: Loss on ignition. p.v.: proposed values by Potts et al. (1992).

| | Oxides (wt %) | | | | | | | | | | | | Trace elements (ppm) | | | | | | | | | | | | wt % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| sample no. | SiO2 | TiO2 | Al2O3 | Fe2O3 | MnO | MgO | CaO | Na2O | K2O | P2O5 | Total | LOI | V | Cr | Co | Ni | Cu | Zn | Y | Zr | Nb | Rb | Sr | Ba | TOC | TN | TS |
| Asakumi Formation | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| C-11 | 71.05 | 1.09 | 18.08 | 5.65 | 0.05 | 1.04 | 0.59 | 1.01 | 1.56 | 0.04 | 100.15 | 13.67 | 108 | 114 | 4 | 53 | 24 | 36 | 32 | 201 | 13 | 71 | 117 | 396 | 3.21 | 0.18 | 1.74 |
| C-9 | 65.53 | 1.05 | 20.41 | 9.22 | 0.04 | 1.37 | 0.44 | 0.71 | 1.64 | 0.05 | 100.46 | 26.24 | 131 | 118 | 2 | 73 | 19 | 85 | 32 | 190 | 14 | 91 | 94 | 379 | 4.25 | 0.25 | 3.09 |
| C-7 | 71.63 | 1.05 | 18.22 | 5.44 | 0.05 | 1.40 | 0.59 | 1.05 | 1.60 | 0.06 | 101.09 | 11.82 | 96 | 108 | 3 | 43 | 20 | 71 | 35 | 192 | 10 | 73 | 128 | 358 | 2.55 | 0.16 | 1.16 |
| C-5 | 70.10 | 1.06 | 19.60 | 5.94 | 0.05 | 1.53 | 0.55 | 0.89 | 1.65 | 0.07 | 101.42 | 13.16 | 109 | 105 | 3 | 45 | 21 | 59 | 34 | 194 | 12 | 79 | 115 | 381 | 3.11 | 0.20 | 0.87 |
| C-3 | 68.61 | 1.08 | 19.15 | 6.81 | 0.05 | 1.51 | 0.53 | 0.84 | 1.58 | 0.06 | 100.23 | 13.24 | 131 | 111 | 3 | 45 | 19 | 114 | 33 | 199 | 15 | 75 | 111 | 374 | 2.86 | 0.19 | 1.55 |
| C-1 | 73.44 | 1.03 | 15.80 | 4.67 | 0.05 | 1.29 | 0.67 | 1.30 | 1.53 | 0.05 | 99.81 | 8.22 | 98 | 101 | 4 | 31 | 11 | 87 | 26 | 185 | 14 | 60 | 136 | 379 | 1.59 | 0.10 | 0.62 |
| B-10 | 73.54 | 1.08 | 17.87 | 2.88 | 0.05 | 1.02 | 0.61 | 1.28 | 1.64 | 0.05 | 100.01 | 8.16 | 83 | 109 | 3 | 33 | 10 | 57 | 29 | 198 | 12 | 65 | 134 | 371 | 1.75 | 0.12 | 0.12 |
| B-9 | 70.34 | 1.05 | 18.71 | 5.13 | 0.04 | 1.06 | 0.58 | 1.06 | 1.59 | 0.06 | 99.61 | 14.03 | 114 | 109 | 5 | 50 | 25 | 100 | 33 | 199 | 14 | 69 | 115 | 349 | 3.70 | 0.21 | 1.43 |
| B-7 | 70.87 | 1.06 | 17.96 | 6.50 | 0.05 | 1.35 | 0.59 | 1.13 | 1.56 | 0.06 | 101.12 | 14.12 | 109 | 108 | 3 | 59 | 21 | 142 | 34 | 198 | 12 | 71 | 121 | 411 | 3.24 | 0.18 | 2.05 |
| B-5 | 70.21 | 1.06 | 18.44 | 6.16 | 0.05 | 1.46 | 0.57 | 1.04 | 1.56 | 0.07 | 100.61 | 13.14 | 106 | 111 | 3 | 45 | 21 | 112 | 33 | 206 | 13 | 73 | 120 | 392 | 3.18 | 0.19 | 1.30 |
| B-3 | 70.36 | 1.06 | 18.02 | 5.63 | 0.05 | 1.41 | 0.58 | 1.13 | 1.57 | 0.07 | 99.89 | 10.61 | 103 | 115 | 4 | 42 | 17 | 88 | 31 | 198 | 12 | 72 | 120 | 356 | 2.44 | 0.16 | 0.54 |
| B-1 | 73.11 | 1.03 | 16.92 | 5.28 | 0.05 | 1.36 | 0.62 | 1.15 | 1.55 | 0.07 | 101.12 | 9.88 | 105 | 113 | 3 | 40 | 15 | 98 | 30 | 206 | 11 | 69 | 125 | 365 | 2.15 | 0.15 | 0.63 |
| A-10 | 73.16 | 1.08 | 17.46 | 4.84 | 0.05 | 1.08 | 0.64 | 1.17 | 1.55 | 0.05 | 101.07 | 12.04 | 103 | 104 | 4 | 50 | 22 | 99 | 32 | 205 | 11 | 66 | 127 | 379 | 2.97 | 0.16 | 1.23 |
| A-9 | 72.55 | 1.05 | 17.34 | 5.50 | 0.05 | 1.33 | 0.63 | 1.27 | 1.57 | 0.06 | 101.34 | 11.25 | 95 | 99 | 3 | 38 | 16 | 87 | 33 | 203 | 12 | 72 | 127 | 394 | 2.70 | 0.16 | 1.09 |
| A-7 | 73.31 | 1.18 | 16.01 | 5.38 | 0.06 | 1.34 | 0.63 | 1.32 | 1.54 | 0.06 | 100.82 | 8.61 | 105 | 117 | 4 | 38 | 9 | 95 | 29 | 212 | 12 | 64 | 131 | 333 | 1.52 | 0.11 | 1.02 |
| A-5 | 71.61 | 1.04 | 16.51 | 5.74 | 0.05 | 1.34 | 0.59 | 1.31 | 1.57 | 0.07 | 99.82 | 9.04 | 93 | 97 | 4 | 39 | 14 | 82 | 27 | 194 | 12 | 68 | 126 | 292 | 1.60 | 0.11 | 0.94 |
| A-3 | 72.48 | 0.98 | 16.67 | 5.30 | 0.05 | 1.33 | 0.56 | 1.10 | 1.59 | 0.05 | 100.10 | 8.95 | 82 | 86 | 4 | 33 | 14 | 90 | 26 | 187 | 13 | 68 | 119 | 371 | 1.74 | 0.12 | 0.57 |
| A-1 | 71.54 | 1.01 | 18.17 | 5.81 | 0.05 | 1.45 | 0.54 | 1.02 | 1.66 | 0.07 | 101.32 | 10.22 | 99 | 93 | 3 | 41 | 15 | 100 | 31 | 196 | 11 | 77 | 116 | 356 | 2.00 | 0.14 | 0.83 |
| Shinjiko Formation | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| SH-18 | 83.16 | 0.48 | 10.37 | 2.38 | 0.02 | 0.69 | 0.48 | 0.88 | 2.38 | 0.04 | 100.88 | 5.82 | 23 | 53 | 2 | 22 | 1.8 | 35 | 12 | 134 | 7 | 86 | 128 | 496 | 0.82 | 0.09 | 0.67 |
| SH-16 | 81.69 | 0.60 | 11.11 | 3.15 | 0.03 | 0.83 | 0.56 | 0.85 | 2.25 | 0.05 | 101.11 | 6.93 | 41 | 76 | 2 | 27 | 0 | 39 | 13 | 188 | 8 | 83 | 137 | 486 | 0.89 | 0.09 | 0.78 |
| SH-14 | 78.58 | 0.73 | 12.37 | 3.67 | 0.04 | 1.03 | 0.61 | 0.97 | 2.23 | 0.06 | 100.28 | 8.09 | 44 | 86 | 3 | 28 | 5.3 | 48 | 16 | 218 | 10 | 82 | 148 | 459 | 0.99 | 0.11 | 1.01 |
| SH-12 | 76.62 | 0.75 | 13.46 | 4.77 | 0.04 | 1.19 | 0.69 | 0.99 | 2.31 | 0.06 | 100.87 | 9.56 | 62 | 91 | 3 | 30 | 9.3 | 56 | 16 | 226 | 8 | 87 | 160 | 473 | 0.82 | 0.11 | 1.18 |
| SH-10 | 75.59 | 0.83 | 13.99 | 4.55 | 0.04 | 1.40 | 0.78 | 1.12 | 2.26 | 0.06 | 100.62 | 9.81 | 58 | 123 | 4 | 33 | 9 | 54 | 18 | 263 | 11 | 81 | 179 | 455 | 1.23 | 0.13 | 1.16 |
| SH-8 | 70.32 | 0.97 | 16.49 | 6.35 | 0.05 | 1.78 | 0.85 | 1.18 | 2.04 | 0.07 | 100.09 | 17.38 | 106 | 108 | 5 | 36 | 11 | 79 | 28 | 281 | 14 | 81 | 166 | 438 | 3.12 | 0.20 | 2.19 |
| SH-6 | 70.92 | 0.98 | 15.78 | 5.38 | 0.04 | 1.86 | 0.89 | 1.16 | 2.25 | 0.07 | 99.33 | 9.83 | 85 | 116 | 5 | 39 | 9.3 | 62 | 22 | 258 | 14 | 82 | 188 | 453 | 1.34 | 0.18 | 1.28 |
| SH-4 | 66.99 | 1.08 | 18.45 | 7.22 | 0.06 | 2.24 | 0.93 | 1.01 | 1.96 | 0.08 | 100.02 | 13.95 | 103 | 125 | 5 | 51 | 20 | 89 | 27 | 232 | 13 | 86 | 172 | 394 | 1.78 | 0.20 | 1.90 |
| SH-2 | 68.25 | 0.98 | 17.36 | 6.49 | 0.06 | 1.89 | 1.00 | 1.31 | 2.11 | 0.09 | 99.54 | 12.31 | 94 | 101 | 5 | 39 | 13 | 75 | 24 | 225 | 12 | 86 | 172 | 358 | 1.48 | 0.22 | 1.58 |
| SH-1 | 72.07 | 0.96 | 15.90 | 5.19 | 0.04 | 1.56 | 0.84 | 1.17 | 2.27 | 0.08 | 100.07 | 10.08 | 93 | 112 | 4 | 33 | 8.5 | 67 | 22 | 285 | 13 | 88 | 173 | 448 | 1.36 | 0.21 | 1.26 |
| SCo-1 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| p.v. | 64.13 | 0.64 | 13.96 | 5.25 | 0.05 | 2.78 | 2.68 | 0.92 | 2.83 | 0.21 | 93.45 | | 134 | 69 | 11 | 28 | 29 | 105 | 27 | 163 | 11 | 114 | 178 | 582 | | | |
| av.(n=10) | 65.30 | 0.63 | 13.89 | 5.44 | 0.05 | 2.67 | 2.61 | 1.23 | 2.78 | 0.35 | 94.94 | | 128 | 69 | 11 | 26 | 22 | 106 | 20 | 171 | 11 | 124 | 171 | 554 | | | |
| STD | 0.10 | 0.00 | 0.05 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.01 | | | 2.83 | 3.68 | 0.21 | 0.28 | 0.35 | 1.84 | 0.35 | 0.42 | 0.00 | 0.64 | 1.41 | 1.70 | | | |

sediments, it is mainly composed of muds in this section. Asakumi muds are characterized by relatively consistent grain size of 7.7–7.0 in phi scale (Fig. 2), and less sand contents ranging from 3 to 35 wt% for the examined samples (Fig. 3) (Tokuoka et al., 1995).

The Asakumi Formation consists of three units (A, B and C in Figs. 2 and 3, Table 1; the Kofun (4–6 C), Nara–Heian (8–9 C) and Heian ages (9–10 C), respectively, according to archeological remains (BESPO, 1995).

## Sample preparation and analytical method

Samples of the Shinjiko (SH) and Asakumi Formations (A, B and C) were collected at 10–20 cm intervals (n=28) (Table 1). Dried samples (at 110℃ for 24 hours) were utilized for analysis of major and trace elements and total organic C, total N and total S.

### Total organic carbon and total nitrogen

Total organic carbon (TOC), and total nitrogen (TN) are measured using a CHN–corder (Yanako MT–3). The method is outlined in Suzuki et al. (1986) and Sampei (1991).

### Total Sulfur

Total sulfur (TS) was measured on 200 mg samples by combustion and infrared absorption spectrometry using a HORIBA EMIA–120 following the procedure of Terashima (1979). The errors (coefficient of variation) inherent to this analysis were less than 3%.

### Major and trace elements

Major elements ($SiO_2$, $TiO_2$, $Al_2O_3$, $Fe_2O_3$*, MnO, MgO, CaO, $Na_2O$, $K_2O$, and $P_2O_5$) and trace elements (V, Cr, Co, Ni, Cu, Zn, Y, Zr, Nb, Rb, Sr, and Ba) were analyzed using the RIX 2000 XRF system (Rigaku Denki Co. Ltd.) of Shimane University. Analysis were made on glass beads prepared with lithium tetraborate flux with a sample (ignited base) to flux ratio of 1:5, as detailed by Ichikawa et al. (1987) and

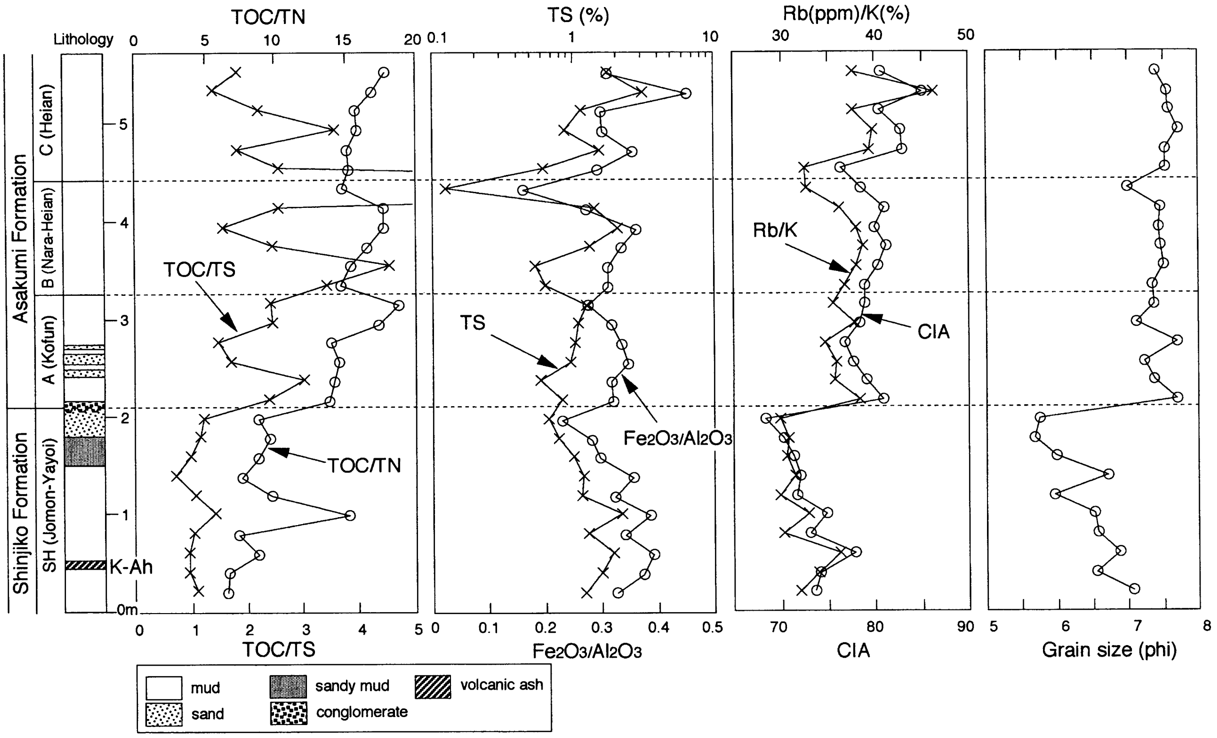

**Fig. 2** Stratigraphic variation of LOI, TOC, TN, TS, $Fe_2O_3/Al_2O_3$, CIA and Rb/K of the muds at the archeological site in Shimane University (SU section), San'in district of Southwest Japan. K–Ah represents Kikai–Akahoya tephra of 6300 yrs BP. Bed numbers are indicated.

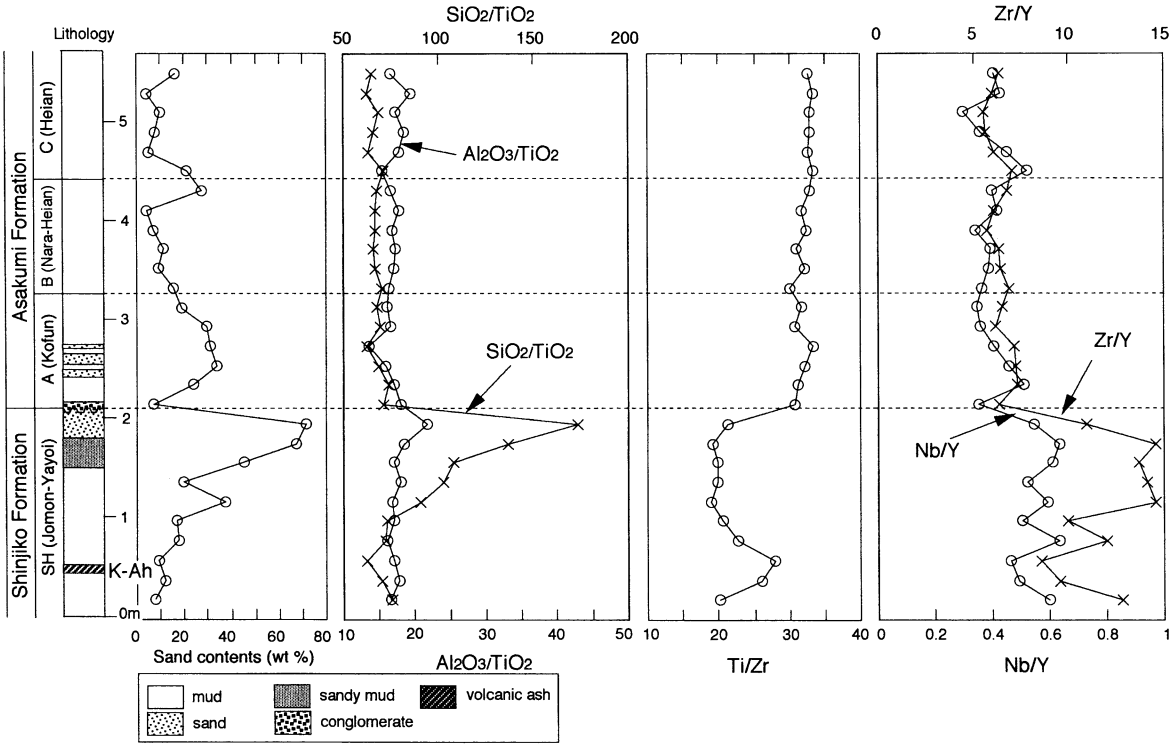

**Fig. 3** Stratigraphic variation of $Al_2O_3/TiO_2$, $SiO_2/Al_2O_3$, Ti/Zr, Nb/Y, Zr/Y and sand contents of the Shinjiko and Asakumi Formations at the Haranomae section in San'in district of Southwest Japan. Age determination is based on archeological remains (BESPO, 1995). K–Ah represents Kikai–Akahoya volcanic ash of 6300 yrs BP (Nakamura and Tokuoka, 1997). Sand contents is after Tokuoka et al. (1995).

Alt. is altitude of the sample horizon for Shinjiko Formation and the unit A of the Asakumi Formation. Units B and C laterally deposited to the unit A, so that their thickness is used for determination of the sample horizon.

fundamentally followed by Norrish and Hutton (1969).

Results are shown in Table 1. For analytical errors, standard deviations of analyzed values (n=10) of USGS standard SCo-1 (Cody Shale) are shown in comparison with the proposed values from Potts et al. (1992).

### LOI (Loss on ignition)

Loss on ignition was determined by ignition of powdered samples at 1100℃ in a muffle furnace for 1 hour.

## Geochemical characteristic of the samples

### TOC, TN and TS

TOC of the Shinjiko Formation shows relatively lower values ranging from 0.82 wt%to 3.12 wt% (with average value of 1.38 wt%) than those of the Asakumi Formation (Table 1, Fig. 2). TOC of the Asakumi Formation gradually increases ascendingly, ranging from 1.52 wt%to 4.25 wt% (with average of 2.59 wt%). TOC/TN ratios increase ascendingly in the section with some variation, which is related to increasing TOC values (Fig. 2). This suggests that derivation of TOC from higher plant might be dominated during the deposition of the Asakumi Formation.

TS of the Shinjiko Formation gradually decreases from 1.16 wt%to 0.67 wt%, and in the Asakumi Formation TS varies. The uppermost sample of the unit B shows strong depression, suggesting dominance of fluvial input or regression of sea-level. TOC/TS ratio is valuable indicator for marine (TOC/TS ratio under 5) and non-marine condition (TOC/TS over 5) (Berner and Raiswell, 1984). According to stratigraphic variation of TOC/TS ratio in this section, marine or brackish condition can be inferred for the Asakumi Formation, except for one sample shown by the lowest sulfur concentration mentioned above. Stratigraphic variation of $Fe_2O_3/Al_2O_3$ ratio correlates with TS profile (Fig. 2), which may indicate iron concentration as sulfide minerals by sulfur reducing reaction (Berner, 1984; Calvert and Pedersen, 1993).

### $SiO_2$, $TiO_2$, $Al_2O_3$ and $Fe_2O_3$

$SiO_2$ of the Shinjiko Formation increases toward upsection from 67 to 83 wt% (Table 1), and correlates well to sand contents (Fig. 3). It also has relatively higher concentration than the Asakumi Formation. $SiO_2$ of the Shinjiko Formation has negative correlation with $Al_2O_3$ (with correlation coefficient, $r^2=0.997$), indicating mixing of quartz sands and clays and quartz grain fractionation in finer sediments (Fig. 4). $SiO_2$ of the Asakumi Formation plots above this correlation line, showing dominance of $Al_2O_3$ compared to those of the Shinjiko Formation. $SiO_2/TiO_2$ ratio shows gradual increase in the Shinjiko Formation, and this ratio shows relatively small variation in the Asakumi Formation than that of the Shinjiko Formation. But it gradually decreases upsection.

$TiO_2$ and $Al_2O_3$ are relatively immobile during sedimentary process, and may be useful for evaluation of source rocks (e.g. Taylor and McLennan, 1985; Condie, 1993; Sugitani, 1996; Yamamoto et al., 1986). $TiO_2$ shows correlation with $Al_2O_3$ in the Shinjiko Formation ($r^2=0.98$). The Asakumi Formation has higher values than that of the Shinjiko Formation with relatively constant values (=1.05 wt%) excluding one sample (Fig. 4). $Al_2O_3/TiO_2$ ratio slightly increases in the upper part of the Shinjiko Formation (21.7), but has rather constant values in the Asakumi Formation (average value of $Al_2O_3/TiO_2=16.9$), showing no significant correlation with grain size and sand contents (Figs. 2, 3).

$Fe_2O_3$ shows correlation with $Al_2O_3$ in the Shinjiko Formation ($r^2=0.98$), but has weak correlation with $Al_2O_3$ in the Asakumi Formation.

### Alkali and alkaline earth elements

$Na_2O$ and CaO are variable during sedimentary process (e.g. Wronkiewicz and Condie, 1987; Nesbitt and Young, 1989). $K_2O$, Rb and Ba are relatively immobile during this process than other alkali and alkaline earth elements.

$Na_2O$, CaO and Sr of the Shinjiko Formation show correlation with $Al_2O_3$ ($r^2=0.76$, 0.97 and 0.80, respectively), while these of the Asakumi Formation show negative correlation with $Al_2O_3$ ($r^2=0.88$, 0.79, 0.80, respectively). This suggests that two formations were deposited under mutually different conditions. $Na_2O$, CaO and Sr were probably adsorbed on clays of the Shinjiko Formation, while they are absorbed during deposition of the Asakumi Formation due to weathering.

$K_2O$ of the Shinjiko Formation shows negative correlation with $Al_2O_3$ ($r^2=0.79$) and Ba does so ($r^2=0.85$), suggesting diagenetic enrichment in $K_2O$ and Ba. In the Asakumi Formation, these elements don't show correlation with $Al_2O_3$. $K_2O$ of the Asakumi For-

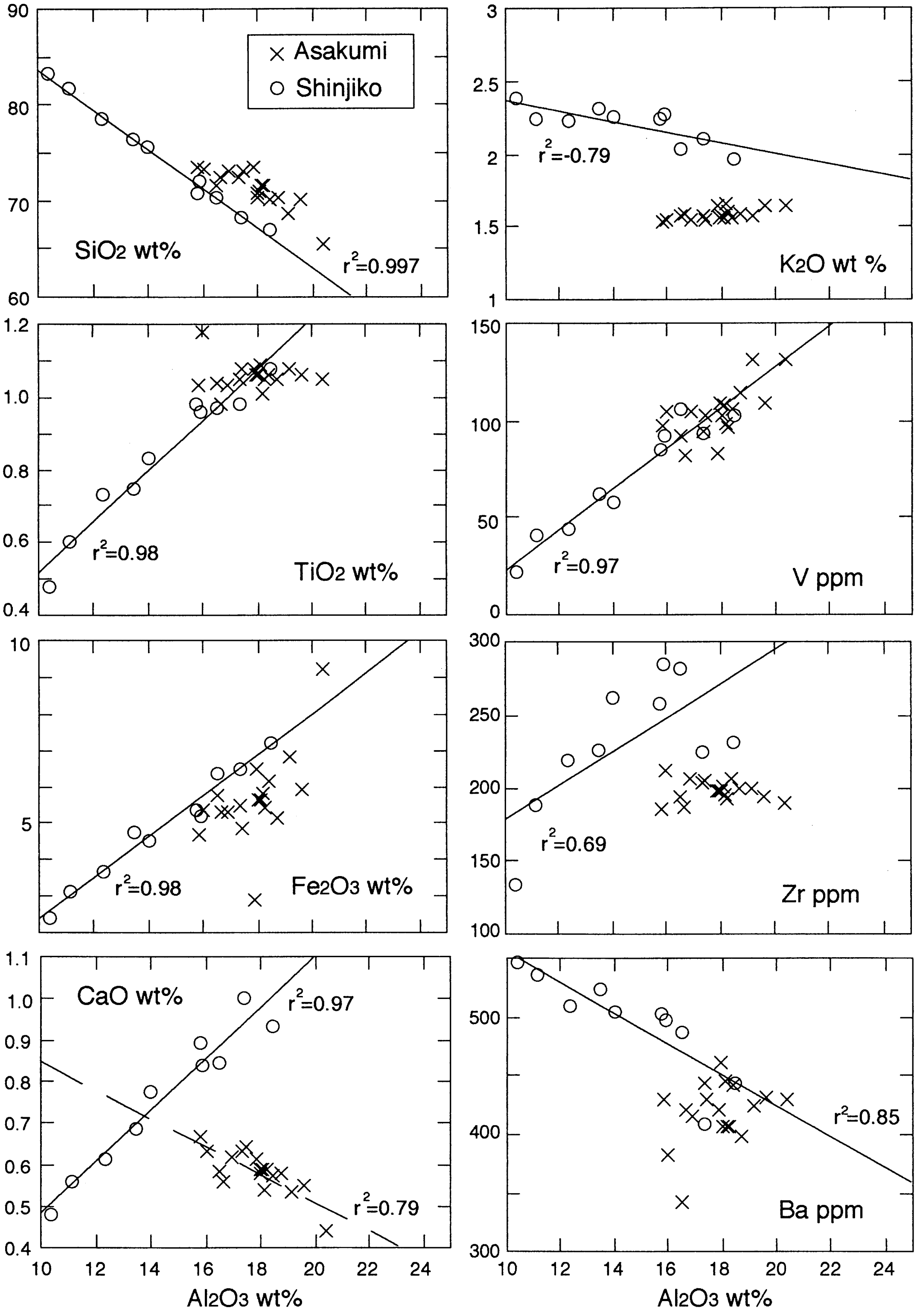

**Fig. 4** Major element oxides (in wt%) and trace elements (ppm) vs. $Al_2O_3$ for Shinjiko Formation (open circle) and Asakumi Formation (cross), showing calculated regression lines where appropriate.

mation shows small variation (Fig. 4). Rb of the Shinjiko Formation has consistent values, but in the Asakumi Formation shows correlation with $Al_2O_3$ ($r^2=0.85$).

MgO of the Shinjiko Formation has strong correlation with $Al_2O_3$ ($r^2=0.98$), but is rather constant in the Asakumi Formation (with average value of 1.32, STD =0.293). This may indicate that MgO of the Shinjiko Formation is incorporated with clay minerals, and concentration of these elements of the Asakumi Formation may have been influenced by a diagenetic alteration.

### Transition elements

Vanadium, Cr, Co, Ni and Cu behave similarly to each other during sedimentary process (e.g. Taylor and McLennan, 1985; Calvert and Pedersen, 1993; Jones and Manning, 1994). Vanadium of the Shinjiko Formation has strong correlation with $Al_2O_3$ ($r^2=0.96$), and other elements, Cr ($r^2=0.82$) and Zn ($r^2=0.98$) show similar correlation, suggesting adsorption of these elements on clays. In the Asakumi Formation, they show no apparent correlation with $Al_2O_3$, and have rather consistent values. MnO also shows correlation with $Al_2O_3$ in the Shinjiko Formation ($r^2=0.90$), and is rather consistent in the Asakumi Formation.

### Y, Nb and Zr

Yttrium, Nb and Zr are immobile during sedimentary process and may reflect source rock composition (e.g. Taylor and McLennan, 1985; Condie, 1993).

Y and Nb of the Shinjiko Formation show strong positive correlation with $Al_2O_3$ ($r^2=0.95$ and 0.85, respectively), and Zr does correlation with $Al_2O_3$ ($r^2=0.69$, in Fig. 4). In the Asakumi Formation, Y has higher concentration than those of the Shinjiko Formation, and Nb show similar concentration to those of the Shinjiko Formation. Zr of the Asakumi Formation has relatively lower concentration than that of the Shinjiko Formation. Zr may have been fractionated in the Asakumi Formation and plot below the correlation line of the Shinjiko Formation. Contrasting concentration of Y, Nb and Zr in the Shinjiko and Asakumi Formations is demonstrated in element ratios of Ti/Zr, Nb/Y and Zr/Y (Fig. 3). These ratios show variation in the Shinjiko Formation, but they have significantly consistent values in the Asakumi Formation. This suggests that muds with consistent composition were formed from the Kofun to the Heian ages of the Asakumi Formation, although sedimentary environment was influenced by fluvial input as shown by variation of TS, TOC/TN and TOC/TS ratios.

### Weathering condition

Weathering process and diagenetic alteration may significantly influence the chemical compositions of sedimentary rocks, and their effects are evaluated using $Al_2O_3$– ($CaO^*$+$Na_2O$) –$K_2O$ (A–CN–K) diagram. In this diagram, elements are plotted as molar proportion, where $CaO^*$ represents Ca in silicate–bearing minerals only (Nesbitt and Young, 1989: Fedo et al., 1995). The CIA (=Al/ (Al+Ca+Na+K) x 100, Nesbitt and Young, 1982) is a useful measure for evaluation of weathering degree, particularly the conversion of feldspar to secondary clay minerals such as kaolinite and illite, and sorting effect (Nesbitte et al., 1996) (Fig. 5).

Muds of the examined section show contrasting trends in this diagram, namely samples of the Shinjiko Formation plot parallel to A–CN join, and those of the Asakumi Formation plot on a line towards K–apex (Fig. 5). The trend of the Asakumi Formation initiates from the Daito granodiorite suggesting derivation from such source. The trend of the Shinjiko Formation indicates K–metasomatism (Fedo et al., 1995) towards upsection and $K_2O/Al_2O_3$ ratios increase from 0.10 to 0.23. The CIA of the Asakumi Formation gradually increase with some variation (Fig. 2), which correlates well with variation of grain size. This demonstrates that highly weathered finer grained material was derived towards upsection. Rb (ppm) /K (%) ratio correlates to profile of the CIA (Fig. 2) exhibiting that Rb/K ratio may also be a useful index of evaluation of weathering.

### Changes in geochemical composition related to the Jomon transgression and succeeding sea–level fall

Geochemical composition of the Shinjiko and Asakumi Formations shows contrasts which are closely related to change in sedimentary environment. $SiO_2$ concentration over 80% in the Shinjiko Formation (Table 1) suggests gradual abundance of quartz grains and coarsening upward variation. Zr and $TiO_2$ concentrations may be related to grain size fractionation (Taylor and McLennan, 1985; Garcia et al., 1994). Relatively higher values in Zr/Y in the middle to upper part of the Asakumi Formation (excluding top sample) are due to Zr enrichment related to this effect (Fig. 2).

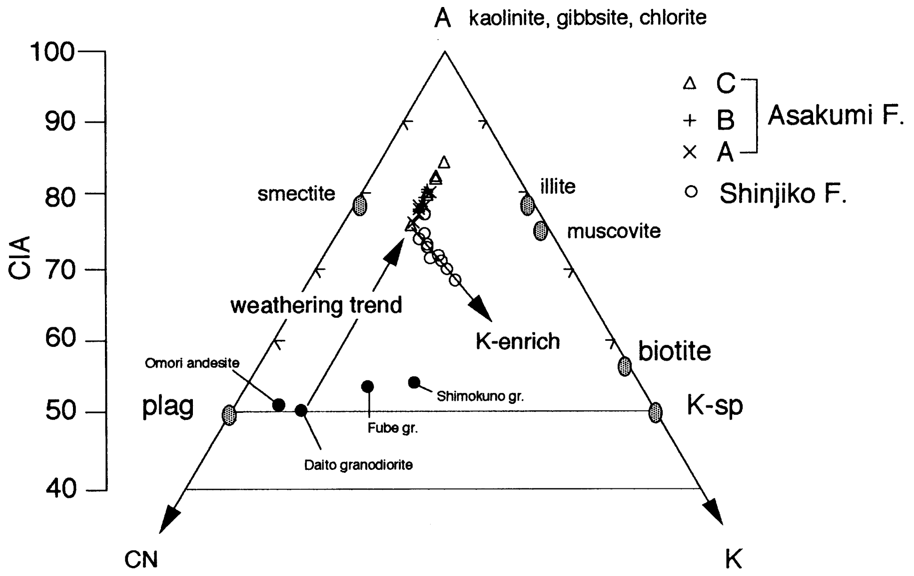

**Fig. 5** $Al_2O_3$– $(CaO+Na_2O)$ –$K_2O$ diagram and the CIA (chemical index of alteration) for the Shinjiko and Asakumi Formations (A, B and C units) at the Haranomae section in San'in district of Southwest Japan. Compositions of granites (Shimokuno and Fube granites), granodiorite (Daito granodiorite), and andesite (Omori andesite) are also given for estimation of source composition. Data from Murakami and Imaoka eds. (1987), and Kano et al. (1994).

Gradual dominance of fluvial detritus to the Shinjiko Formation of the Yayoi age might have effects on such compositional variation. Relative decrease in TS and $Fe_2O_3/Al_2O_3$ is suggestive of dominance of fresh water invasion during the regression of the Yayoi age (Tokuoka et al., 1990). These changes in sedimentary environment might attribute to an alteration of clay minerals, such as $K_2O$ metasomatism in A–CN–K diagram (Fig. 5) and Ba enrichment. Gradual decrease in the CIA and Rb/K ratio were caused by $K_2O$ enrichment towards the boundary of the formations. A sharp gap in mud compositions at the formation boundary is suggestive of chemical alteration of muds during unconformable disturbance of sedimentation.

TOC/TN ratio shows gradual increase in the Asakumi Formation suggesting growing influence of terrigenous TOC by the fluvial system. The delta front of this river system forwarded after Yayoi age (Nakamura, 1996; Nakamura et al., 1996), and the marine–brackish transitions occurred frequently as indicated in TOC/TS fluctuation in the Asakumi Formation (Fig. 2). Their CIA and Rb/K ratio are relatively higher than those of the Shinjiko Formation, and show gradual increase upsection. They, however, have decreased at the boundary of the units B and C (Nara–Heian and the Heian ages). Higher values of the CIA and Rb/K ratio indicate that relatively weathered material was formed locally under warming and humid climate (Sampei et al., 1996), or sediments were transported as a finner particles rich in clays. According to homogeneous composition of Asakumi muds shown by $Al_2O_3/TiO_2$, Ti/Zr, Nb/Y and Zr/Y ratios, particulated matter was accumulated in flood plain or backswamp pond of the Asakumi fluvial system. These immobile element ratios are not influenced by marine and non–marine transition and redox condition.

## Conclusion

Geochemical signature of Holocene sediments is to evaluate change in sedimentary environment and its effect on sediment composition. The sedimentary environment is a result of equilibrium of marine and fluvial system in the examined section, which may be evaluated by TOC/TS and TOC/TN ratios. The fluvial input of terrestrial organic matter can be estimated by variation in TOC/TN, and increasing TOC/TN ratio may indicate development of fluvial system in the examined section. TOC/TS is valuable for estimation of marine and non–marine conditions, and fluctuation of TOC/TS may be related to variation of fluvial input or change in sea–level.

The CIA and Rb/K ratio are useful indicators of degrees of source material weathering, and their variation is shown in marine–nonmarine transition sediments.

On the A–CN–K diagram, K–enrichemnt is indicated for the samples related to unconformable disturbance from marine to brakish conditions.

$SiO_2/TiO_2$ closely related to grain size, but $Al_2O_3/TiO_2$ is not significantly influenced by sorting effect of the examined samples. Consistent mud composition shown by immobile element ratios such as $Al_2O_3/TiO_2$, Ti/Zr, Nb/Y and Zr/Y, may unravel an effect on mud composition related to variation of sedimentary environment.

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## References

Berner, R. A., 1984. Sedimentary pyrite formation: An updated. *Geochim. Cosmochim. Acta*, 48, 605-615.

Berner, R. A. and Raiswell, R., 1984. C/S method for distinguishing freshwater from marine sedimentary rocks. *Geology*, 12, 365-368.

BESPO (Board of Education, Shimane Prefectural Office), 1995. *Report on the Haranomae Archeological Remains,* 198 pp.

Calvert, S. E. and Pedersen, T. F., 1993. Geochemistry of recent oxic and anoxic marine sediments: implication for the geological record. *Marine Geol.*, 113, 67-88.

Condie, K. C., 1993. Chemical composition and evolution of the upper continental crust: Contrasting results from surface samples and shales. *Chem. Geol.*, 104, 1-37.

Fedo, C. M., Nesbitt, H. W. and Young, G. N., 1995. Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols, with implications for paleoweathering conditions and provenance. *Geology*, 23, 921-924.

Garcia, D., Fonteiller, S. M. and Moutte, J., 1994. Sedimentary fractionations between Al, Ti, and Zr and genesis of strongly peraluminous granites. *Jour. Geol.*, 102, 411-422.

Ichikawa, H., Sakai,T., Watanabe, T. and Iizumi, S., 1987. Quantitative analysis of seven trace elements in silicate rocks using fused disc–samples by X–ray fluorescence method (Rh–tube). *Geol. Rep. Shimane Univ.*, 6, 161-169.

Jones, B. and Manning, D. A. C., 1994. Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. *Chem. Geol.*, 111, 111-129.

Kano, K., Yamauchi, S., Takayasu, K., Matsuura, H. and Bunno, M., 1994. *Geology of the Matsue district. With geological Sheet Map at* 1:50,000, Geol. Surv. Japan, 126 pp.

Machida, H. and Arai, F., 1978. Akahoya ash– A Holocene widespread tephra erupted from the Kikai caldera, South Kyushu, Japan. *Quat. Res.*, 17, 143-163.

McLennan, S., Hemming, S., MacDaniel, D. K. and Hanson, G. N., 1993. Geochemical approach to sedimentation, provenance and tectonics. *Geol. Soc. Am. spec. paper*, 284, 21-40.

Murakami, N. and Imaoka, T. (eds), 1987. Acid to intermediate igneous activity in West Chugoku and its adjacent areas, Southwest Japan. *Professor Murakami N. Mem. Vol., Fac. Liberal Arts, Yamaguchi Univ.*, 419 pp.

Nakamura, T., 1996. Holocene environmental change and archeological remain in coastal lagoon in Shimane Prefecture, Southwest Japan. *Bull. Geol. Soc. Shimane Pref. Japan*, 11,14-20.

Nakamura, T. and Tokuoka, T., 1997. The Akahoya (K–Ah) tephra discovered from the SB–1 drilling in the lake Shinji and reexamination of the Holocene paleogeographic changes. *Geol. Rept. Shimane Univ.*, 15, 35-40.

Nakamura, T., Tokuoka, T., Onishi, I., Sampei, Y., Takayasu, K., Takehiro, F., Nishio, K. and Watanabe, M., 1996. Holocene environmental changes and lowland historic sites in eastern part of the Shimane Prefecture. *Laguna,* 3, 9-11.

Nesbitt, H. W., Fedo, C. M. and Young, G. M., 1996. Quartz and feldspar stability, steady and non–steady –state weathering, and petrogenesis of siliciclastic sands and muds. *Jour. Geol.*, 105, 173-191.

Nesbitt, H. W. and Young, G. M., 1982. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature,* 299, 715-717.

Nesbitt, H. W. and Young, G. M., 1989. Formation and diagenesis of weathering profiles. *Jour. Geol.*, 97, 129-147.

Norrish, H. W. and Hutton, J. T., 1969. An accurate X–ray spectrographic method for the analysis of a wide range of geologic samples. *Geochim. Cosmo-*

*chim. Acta*, **33**, 431-453.

Ota, Y. and Yonekura, N., 1987. *Quaternary Maps of Japan II Prehistoric Remains and Paleogeography*, Japan Association of Quaternary Research (eds.), Tokyo Univ. Press.

Ota, Y., Matsushima, Y. and Moriwaki, H., 1982. Note on the Holocene sea–level study in Japan.–On the basis of "Atlas of Holocene sea–level records in Japan"–. *Quat. Res.*, **21**, 133-143.

Potts, P. J., Tindle, A. G. and Webb, P. C., 1992. *Geochemical reference material compositions*. Whittles Publishing, 313 pp.

Sampei, Y., 1991. CHN–corder. *Earth Sci.*, **45**, 285-289.

Sampei, Y., Matsumoto, E., Tokuoka, T. and Inoue, D., 1996. Organic carbon accumulation rate during the last 8,000 years in lake Nakaumi, Southwest Japan: Coastal lagoon sediments as carbon sink. *Quat. Res.*, **35**, 113-124.

Sugitani, K., 1996. Study of sedimentary paleoenvironment of siliceous sedimentary rocks using some geochemical indicators. *Chikyukagaku* (*Geochemistry*), **30**, 75-89.

Suzuki, N., Yamamoto, J., Muranaka, H., Takayasu, K., Yamauchi, S., Onishi, Y., Tokuoka, T., Shimada, I., Mitsunashi, T., 1986. Analysis of geological materials by YANAKO CHN corder (MT 3) I.–determination of sedimentary organic carbon by low temperature combustion method and acid treatment–combustion method, and its use on line with personal computer. *Geol. Rep. Shimane. Univ.*, **5**, 19-34.

Taylor, S. R. and McLennan, S. M., 1985. *The Continental Crust: its composition and evolution.* Blackwell, Oxford, 312 pp.

Terashima, S., 1979. The determination of total carbon, total sulfur, carbonate and non–carbonate in geological materials by infrared absorption spectrometry. *Bull, Geol. Surv. Japan*, **30**, 609-627.

Tokuoka, T., Onishi, Y., Nakamura, T. and Takayasu, K., 1995. Paleoenvironment of the Haranomae archeological site and its neighbor, San'in district, Southwest Japan. In *Haranomae Archeological Remains*, Board of Education, Shimane Prefectural Office, 181-195.

Tokuoka, T., Onishi, Y., Takayasu, K. and Mitsunashi, T., 1990. Natural history and environmental changes of Lakes Nakaumi and Shinji. *Mem. Geol. Soc. Japan*, **36**, 15-34.

Umitsu, M., 1991. Holocene sea–level changes and coastal evolution of Japan. *Quat. Res.*, **30**, 187-196.

Wronkiewicz, D. J. and Condie, K., 1987. Geochemistry of Archean shales from the Witwatersrand Supergroup, South Africa: Source–area weathering and provenance. *Geoch. Cosmoch. Acta*, **51**, 2401-2416.

Yamamoto, K., Sugisaki, R. and Arai, F., 1986. Chemical aspect of alteration of acidic tuff and their application to siliceous deposits. *Chem. Geol.*, **55**, 61-76.

Yamauchi, S., Mitsunashi, T. and Yamamoto, Y., 1980. Miocene of the Shimane Peninsula. *Guide book for the geoexcursion, the 87 th Ann. Meet. Geol. Soc. Japan*. 39 pp.

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### （要　旨）

**石賀裕明・中村唯史・三瓶良和・高安克己・徳岡隆夫, 1998, 地球化学的指標による西南日本山陰地域の完新世海水準変動に伴う堆積物の検討, 島根大学地球資源環境学研究報告,** 17, 21–30

縄文海進とこれに続く弥生の海退の地質学的な記録は山陰の沖積平野に残されている．その記録の1つが松江市の朝酌川の遺跡発掘現場に見られる．地層は宍道湖層と朝酌層からなり，宍道湖層の下部にはアカホヤ火山灰（約6,300年前）が挟まれる．宍道湖層は粒度や含砂率から上方粗粒化を示す．朝酌層は砂層を主とするが薄い泥層を挟む．どちらの地層も全有機炭素，イオウ濃度は1 wt%以上のものが多く汽水環境で堆積した可能性を示唆する．堆積物の元素組成からは，宍道湖層では粒度組成の変化とともに $SiO_2$/TiO，Ti/Zr が変化する．朝酌層ではこれらの組成には大きな変化はない．堆積物の源岩の風化の程度の指標 CIA [CIA＝（Al/Al+Na+Ca*+K）×100；各元素はモル比で示され，Ca*は珪酸塩鉱物に含まれるもの］は宍道湖層では次第に低くなり（＜70），K に富んだ組成へと変化する．朝酌層は宍道湖層よりも高い CIA（＞80）を示し，後背地の堆積物の風化が進行したことを示す．