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## **Late Quaternary variation of lignin composition in Core MD012421 off central Japan, NW Pacific**

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### **Abstract**

In order to understand the responses of terrestrial vegetation in central Japan to global climate changes, we have generated the record of lignin composition from Core MD01-2421 off central Japan in the NW Pacific during the last 145,000 years by TMAH-pyrolysis-GC/MS. The relative abundance of lignin was significantly low in early MIS-1 and MIS-5e and higher in MIS-5c to early MIS-4. This reflects glacial-interglacial changes in sea level and riverine runoff. The ratio of syringyl (S)- to vanillyl (V)-phenols (S/V ratio), which is a contribution index of angiosperms against gymnosperms, was lower in MIS-2, MIS-4 and MIS-6, reflecting the glacial-interglacial variation of air temperature. The ratio of cinnamyl (C)- to vanillyl (V)-phenols (C/V ratio), which indicates the contribution of grasses, was higher in late MIS-2, early-mid

MIS-3 and MIS-6. The periods of higher C/V ratio correspond to the periods of lower sea surface temperatures (SSTs), suggesting a dry and cold climate in late MIS-2, mid-MIS-3 and MIS-6.

Keywords: lignin, vegetation, TMAH pyrolysis, glacial, central Japan, IMAGES, WEPAMA

## **1. Introduction**

Central Japan is located near the atmospheric and oceanic boundaries between subarctic and subtropical regimes (Fig. 1). The paleoenvironmental change of this region is, therefore, sensitive to the latitudinal shift of the above mentioned boundaries in the northwestern Pacific region. Recently, the latitudinal displacement of the oceanic subarctic boundary was reconstructed from the penultimate glacial period (MIS-6) using a giant piston core MD01-2421 taken off the Honshu Island of central Japan in the NW Pacific. This record showed that the subarctic boundary was displaced in response to changes in the Earth's precession (Yamamoto et al., 2004; Aizawa et al., 2004; Koizumi et al., 2004; Oba et al., 2005).

Pollen studies demonstrated the remarkable difference of vegetation on the Japanese Islands between the Holocene and the last glacial maximum (LGM) (compiled in Tsukada, 1985; Takahara et al., 2000). At LGM, boreal conifer forests occupied modern cool-temperate deciduous broadleaf and mid-temperate conifer forest zones (NE Japan), and temperate coniferous forests occupied the modern warm-temperate evergreen forest zone (SW Japan). This difference in vegetation can be attributed to the decreased air temperature and precipitation in LGM (Tsukada, 1985).

Although the continuous records of pollen are scarce, splice records from on-land cores are available for the last glacial cycle (e.g., Tsukada, 1988). High-resolution records of pollen and spores were generated from marine core MD01-2421 during the last 145,000 years and demonstrated how the vegetation of central Japan changed in response to glacial-interglacial cycles (Igarashi and Oba, submitted).

Lignin is an abundant, stable phenolic macromolecule uniquely found in the cell walls of vascular land plants. Alkaline CuO oxidation yields four groups of structurally related products: p-hydroxy, vanillyl, syringyl and cinnamyl groups (Hedges and Mann, 1979) (Fig. 2). The vanillyl group is abundant in gymnosperms, whereas the syringyl group is specific to angiosperms. The cinnamyl group is abundant in non-woody tissues of vascular plants and grasses (Hedges and Mann, 1979; Goñi and Hedges, 1992). The relative abundance of vanillyl, syringyl and cinnamyl groups, therefore, is often used as an index of paleo-vegetation.

Lignin was investigated for a sediment core from Lake Biwa, Japan (Ishiwatari and Uzaki, 1987) and Lake Baikal, Siberia (Orem et al., 1997; Ishiwatari et al., 2005). A marine core was also analyzed from the Okinawa Trough (Ujiié et al., 2001). These studies showed glacial-interglacial or longer time scale variations of lignin abundance and composition, which are attributed to diagenesis, vegetation changes and sea level changes. The time resolutions of lignin records from Lake Biwa and the Okinawa Trough were low compared with high-resolution paleoenvironmental records that became common for the last decade, because of the drawback of the conventional lignin analysis that needs much time and effort.

Pyrolysis gas chromatography-mass spectrometry with *in situ* methylation with tetramethylammonium hydroxide (TMAH-pyrolysis-GC/MS) has been used recently for

the analysis of macromolecules such as lignin (e.g., Clifford et al., 1995; Hatcher et al., 1995). TMAH-pyrolysis-GC/MS yields lignin phenols that are equivalent to those produced by conventional alkaline CuO oxidation (Hatcher et al., 1995; Yamamoto, 2000). In this method, the organic matter is pyrolyzed in the presence of TMAH, and the pyrolysates are transformed to a methyl ester, a methoxy benzene, etc. The derivatized pyrolysates are analyzed with on-line GC/MS. This method enables us to analyze a small amount of sample (~0.1 mg C) more rapidly, compared to the conventional alkaline CuO oxidation method.

In this study, we have generated the record of lignin composition from Core MD01-2421 off central Japan in the NW Pacific by TMAH-pyrolysis-GC/MS during the last 145,000 years, in order to understand the responses of the terrestrial vegetation in central Japan to global climate changes.

## **2. Materials and methods**

A piston core MD01-2421 (45.82m long) was collected from off the coast of central Japan at 36°02'N, 141°47'E, at a 2224-meter water depth during IMAGES VII-WEPAMA Leg 2 in 2001 (Oba and Murayama, 2004) (Fig. 1). The lithology and age model were presented in Oba et al. (2005). A total of 95 samples were collected from the core. The average sampling interval was ~1.5 ka.

The rivers that potentially supply sediments to the coring site are the Tone, Naka and Kuji Rivers. The main stream of the Tone River flowed into Tokyo Bay until the 17<sup>th</sup> century when the Tone River artificially joined with Kinu and Kokai River. The river basins of the paleo-Kinu-Kokai, Naka and Kuji Rivers cover the northeastern sector of the Kanto Plain and the northern adjacent mountains.

Pyrolysis gas chromatography-mass spectrometry with *in situ* methylation with tetramethylammonium hydroxide (TMAH-pyrolysis-GC/MS) was carried out using a Japan Analytical Industry JHP-5 Curie point pyrolyzer that was directly connected to the injection port of a Hewlett Packard 5973 gas chromatograph-mass selective detector. The column used was a Chrompack CP-Sil5CB (length, 30 m; i.d., 0.25 mm; thickness, 0.25  $\mu$ m). The sediment sample (ca. 20 mg) was placed on a Ni-Co pyrofoil plate with 30  $\mu$ l of 5% TMAH in methanol and 20  $\mu$ l of internal standard solution (0.1 g/L n-nonadecanoic acid in hexane). The methanol and hexane were removed under vacuum, and the sample was wrapped in pyrofoil. The sample was heated at 590°C for 20 sec in the pyrolyzer, and the generated compounds were transferred to the GC splitless injection system at 300°C with a helium carrier gas. The oven temperature was programmed from 70°C to 310°C at 4°C/min after the initial hold time of 1 min, and then it was held isothermally at 310°C for 30 minutes. The mass spectrometer was run in the full scan ion-monitoring mode ( $m/z$  50-650). Electron impact spectra were obtained at 70 eV. Identification of lignin phenols was achieved by comparison of their mass spectra and retention times with those of authentic standards. Concentrations of lignin phenols were obtained according to the following equation:

$$\text{Conc}_A = 2 \times (\text{Area}_A/\text{RF}_A)/(\text{Area}_{\text{IS}}/\text{RF}_{\text{IS}})/W_{\text{SD}}$$

where  $\text{Conc}_A$  is the concentration of compound A,  $\text{Area}_A$  is the peak area of compound A on the ion chromatogram of its molecular ion,  $\text{Area}_{\text{IS}}$  is the peak area of internal standard (n-nonadecanoic acid) on the ion chromatogram of  $m/z$  74,  $\text{RF}_A$  and  $\text{RF}_{\text{IS}}$  are the response factors of compound A and internal standard, and  $W_{\text{SD}}$  is the sample weight.

The response factors of lignin phenols ( $RF_{LG}$ ) and internal standard ( $RF_{IS}$ ) were determined by the analysis of the authentic standards (lignin phenols and n-nonadecanoic acid) according the following formula:

$$RF_{LG} = \text{Int}_M / \text{Int}_{50-650}$$

$$RF_{IS} = \text{Int}_{74} / \text{Int}_{50-650}$$

where  $\text{Int}_M$  is the intensity of molecular ion in the mass spectrum of ligninphenol,  $\text{Int}_{74}$  is the intensity of  $m/z$  74 fragment ion in the mass spectrum of n-nonadecanoic acid, and  $\text{Int}_{50-650}$  is the sum of ion intensities from  $m/z$  50 to  $m/z$  650. The response factors of lignin phenols and n-nonadecanoic acid obtained by this way were listed in Table 1. The standard deviations in replicate analysis (five times) were 10, 7, 15 and 8 % of the concentration for total syringyl phenol (S), total vanillyl phenols (V), total cinnamyl phenol (C) and total eight lignin ( $\Sigma 8$ ; S+V+C), respectively, and they were 0.01, 0.03 and 0.06 for S/V and C/V ratios and the ratio of acid to aldehyde of vanillyl phenol [(Ad/Al)<sub>v</sub> ratio], respectively.

### 3. Results and discussion

#### 3.1. Lignin abundance

$\Sigma 8$  (mg/10g-sediment), which is the total amount of eight lignin phenols belonging to vanillyl, syringyl and cinnamyl groups (Fig. 2), varied between 0.014 and 0.106, with an average of 0.050 (Fig. 3). The  $\Lambda$  (mg/100mg-TOC), which is the total amount of the above mentioned eight lignin phenols in 100 mg of TOC, varied between 0.009 and 0.145, with an average of 0.047 (Fig. 3). The  $\Sigma 8$  and  $\Lambda$  were much smaller than those of

riverine particles from the Tokachi River in northern Japan ( $\Sigma 8 = 0.13-0.88$  and  $\Lambda = 0.69-2.94$ ,  $n = 4$ , Inagaki, Yamamoto and Nagao, unpublished data).

A lignin study for a sediment core from Lake Biwa showed that lignin concentration decreased with increasing core depth during diagenesis, and the calculated half life is  $\sim 400,000$  years (Ishiwatari and Uzaki, 1987). Using this half life value, we estimated that the downward decrease of lignin concentration caused by diagenesis is  $\sim 22\%$  of the original concentration in the whole core range ( $\sim 145$  kyrs).

The  $\Sigma 8$  and  $\Lambda$  were significantly lower in early MIS-1 and MIS-5e than in the other periods (Fig. 3). Also, both periods were characterized by higher sea level stands than the other periods. Paleogeographical reconstructions displayed that the Kanto Plain, which is the sediment source region of the studied site, was covered by sea-water in MIS-5e to a large extent (the Shimosueyoshi Transgression), as well as to a lesser extent in early MIS-1 (the Jomon Transgression) (e.g., Kaizuka et al., 2000). The increased distance of source region and more stable sedimentation on the shelf in this high sea level stand period presumably resulted in a significant decrease in the transportation of terrigenous organic matter to the site of this core.

The  $\Sigma 8$  and  $\Lambda$  were higher in MIS-5c to early MIS-4 than they were in the other intervals (Fig. 3). Also, this period was characterized by a relatively high abundance of freshwater diatoms in this core (Koizumi et al., 2004). Increased riverine runoff might have resulted in an increase also of terrigenous input to the studied site.

### 3.2. Lignin composition

The ratio of acid to aldehyde of vanillyl phenol  $[(Ad/Al)_v]$  systematically increases as the lignin is degraded by aerobic fungi, and the ratios of highly degraded lignin



exceeds ~0.4 in alkaline CuO oxidation method (Goñi et al., 1993). The TMAH procedure is more sensitive for calculation of  $(Ad/Al)_v$  ratios than the alkaline CuO oxidation procedure (Hatcher et al., 1995). The sensitivity of  $(Ad/Al)_v$  ratios to fungal degradation by the TMAH procedure are ~15 times higher than those by the CuO oxidation (Hatcher et al., 1995; Filley et al., 2000). Fresh, moderately degraded, highly degraded lignins have the  $(Ad/Al)_v$  ratios of ~0.5, ~3, 7-12, respectively in the TMAH procedure (Hatcher et al., 1995). In Core MD01-2421, the  $(Ad/Al)_v$  ratio ranged from 0.9 to 3.3, with an average of 1.6 (Fig.3), which suggests that the lignin was not highly degraded, but slightly or moderately degraded by aerobic microbes. Relatively high values were observed in late MIS-5e and early MIS-4 (Fig.3). These two periods were characterized by a higher abundance of neritic-littoral warm diatom species (Koizumi et al., 2004), suggesting that an intensified northward coastal current transported more degraded terrigenous organic matter from the shelf to the studied site.

The ratios of syringyl (S)- to vanillyl (V)-phenols (S/V ratio) and of cinnamyl (C)- to vanillyl (V)-phenols (C/V ratio) were used for the assessment of paleo-vegetation (e.g., Hedges and Mann 1979; Goñi and Hedges, 1992). A laboratory degradation of birch wood by a white-rot fungus *Phelbia tremellosus* linearly increased the  $(Ad/Al)_v$  ratio and decreased the S/V ratio (Hedges et al., 1988). There is, however, little correlation between S/V and  $(Ad/Al)_v$  ratios ( $r = 0.02$ ) in this core, implying that the variation of the S/V ratio was not significantly altered by aerobic degradation.

The S/V ratio, which is a contribution index of angiosperms against gymnosperms (Hedges and Mann 1979), ranged from 0.14 to 0.48, with an average of 0.26. The values fell within the range of mixture of angiosperms and gymnosperms (Fig. 4). S/V ratio shows maximal peaks at late MIS-5e, MIS-5d, MIS-5a, early MIS-3 and MIS-1 (Fig. 3).

The peaks at MIS-5d, MIS-5a and MIS-1 correspond to the maximal peaks of pollen Tp index [warm broad leaf pollen/(cool needle leaf pollen + warm broad leaf pollen)] (Fig. 3). The minimal peaks of S/V ratio at MIS-5e/5d, -5c/5b and -5a/4 boundaries correspond to the peaks of pollen of the Japanese cedar *Cryptomeria* (Fig. 3). These correspondences imply that the variation of S/V ratio has reflected the changes of terrestrial vegetation.

The correspondence between the S/V ratio and Tp index was not good exceptionally in MIS-5e. The S/V ratio was not high compared with high Tp index in this period (Fig. 3). Igarashi and Oba (submitted) interpreted that the MIS-5e has a different pollen assemblage from the MIS-1, being attributed to a more intense transgression in MIS-5e than MIS-1. The landward retreat of source region in MIS-5e presumably affected the S/V ratio more than Tp index. The long distance transportation of lignin particles could result in the preferential degradation of more labile syringyl phenols compared with vanillyl phenols, although  $(Ad/Al)_v$  ratio was not significantly high in MIS-5s. Alternatively, the source region of lignin might be different from that of pollen in MIS-5e. We need further investigations for this issue.

The C/V ratio, which indicates the contribution of non-woody tissues and grasses (Hedges and Mann 1979), ranged from 0 to 0.64, with an average of 0.29. The C/V ratio sensitively decreases by aerobic degradation of lignin (Hedges and Weliky, 1989; Opsahl and Benner, 1995). However, there is little correlation between S/V and  $(Ad/Al)_v$  ratios ( $r = 0.02$ ), implying that the variation of the C/V ratio was not altered by aerobic degradation. This C/V ratio shows maximal peaks at MIS-6, early-mid MIS-3 (~48 ka) and late MIS-2 (Fig. 3). The MIS-6 and MIS-2 were characterized by the occurrence of *Larix* pollen in this core (Fig. 3), which indicates a cold and dry climate

(Igarashi, 1996). The alkenone SST record from this core indicated that the SST was lower in these three periods than others, implying the southward displacement of the subarctic boundary (Yamamoto et al., 2004). Such displacement might be associated with the southward displacement of the Baiu Front, the early summer rain front. This displacement caused a decrease of summer monsoon precipitation in central Japan. This decreased precipitation presumably induced the expansion of grassland.

The good correspondence of lignin composition to pollen assemblages in Core MD01-2421 implies that the lignin composition in marine core can be used for paleo-vegetation reconstruction. The application of marine cores has several advantages. It helps in generating a long-term continuous record, as well as in examining the linkage between the land and the ocean. We expect further applications for future reconstruction of past terrestrial vegetation.

#### **4. Conclusions**

$\Sigma 8$  was significantly lower in early MIS-1 and MIS-5e, and it was higher in MIS-5c to early MIS-4, reflecting glacial-interglacial changes in sea level and riverine runoff. The S/V ratio was lower in MIS-2, MIS-4 and MIS-6, reflecting the glacial-interglacial variation of air temperature. The C/V ratio was higher in late MIS-2, early-mid MIS-3 and MIS-6, suggesting a dry and cold climate in these periods. The good correspondence of lignin composition to pollen assemblages in Core MD01-2421 implies that the lignin composition in marine core can be used for paleo-vegetation reconstruction.

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## Figure captions

Fig. 1. Map showing the locations of Core MD01-2421.

Fig. 2. The degradation products of lignin by alkaline CuO oxidation (Hedges and Parker, 1976; Hedges and Mann, 1979). The hydroxy groups are converted to methoxy groups in TMAH pyrolysate.

Fig. 3. Changes in total organic carbon (TOC) (Ueshima et al., 2005),  $\Sigma 8$ ,  $\Lambda$ , S/V, C/V, (Ad/Al)<sub>v</sub>, pollen Tp index, *Cryptomeria* and *Larix* pollen % of total pollen (Igarashi and Oba, submitted), and alkenone-derived sea surface temperature (SST) (Yamamoto et al., 2004) in Core MD01-2421 during the last 145,000 years.

Fig. 4. Liginphenol C/V versus S/V and C/(C+V) versus S/(S+V) in samples from Core MD01-2421. Compositional ranges of major vascular plants are also shown in this diagram. G: gymnosperm woods, g: gymnosperm needles, A: angiosperm woods, a: angiosperm leaves and grasses (Hedges and Mann, 1979).



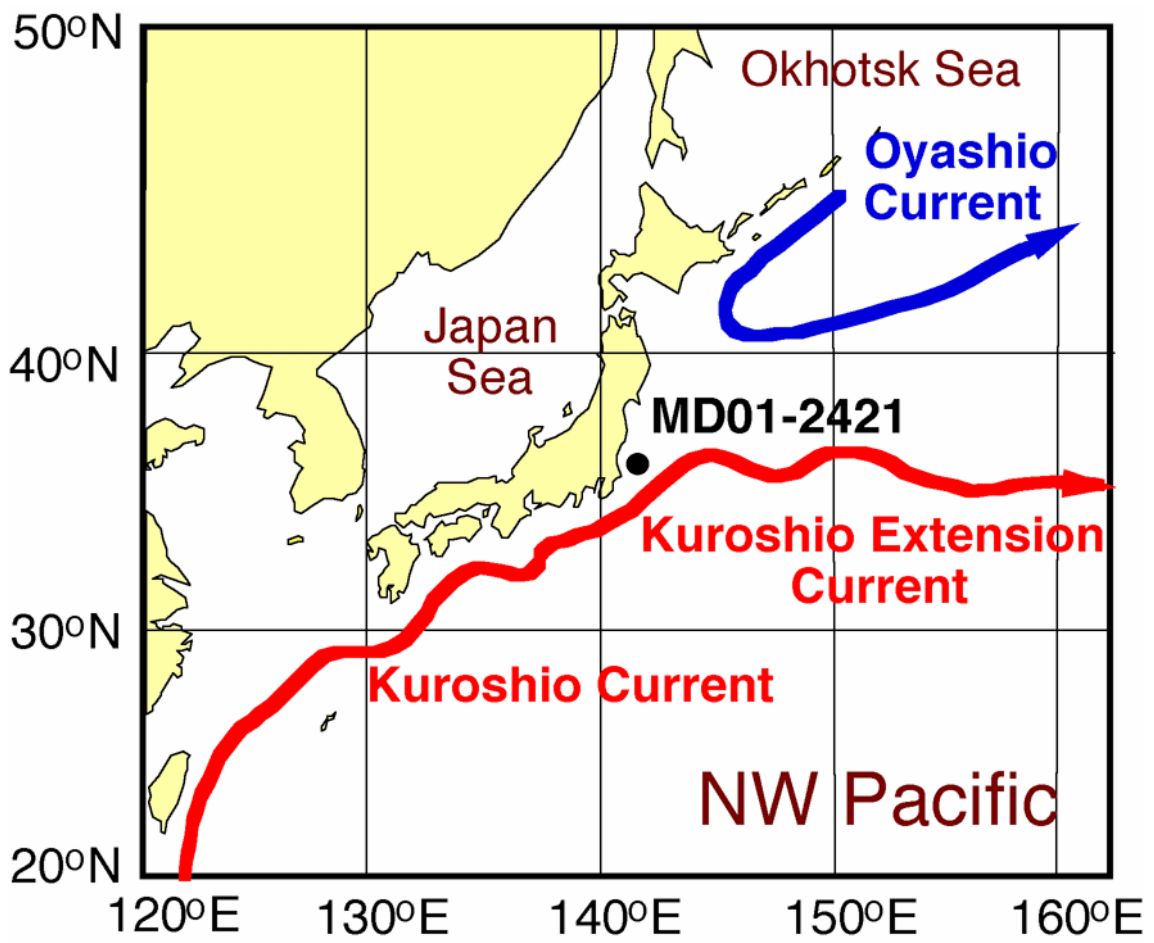


Fig. 1

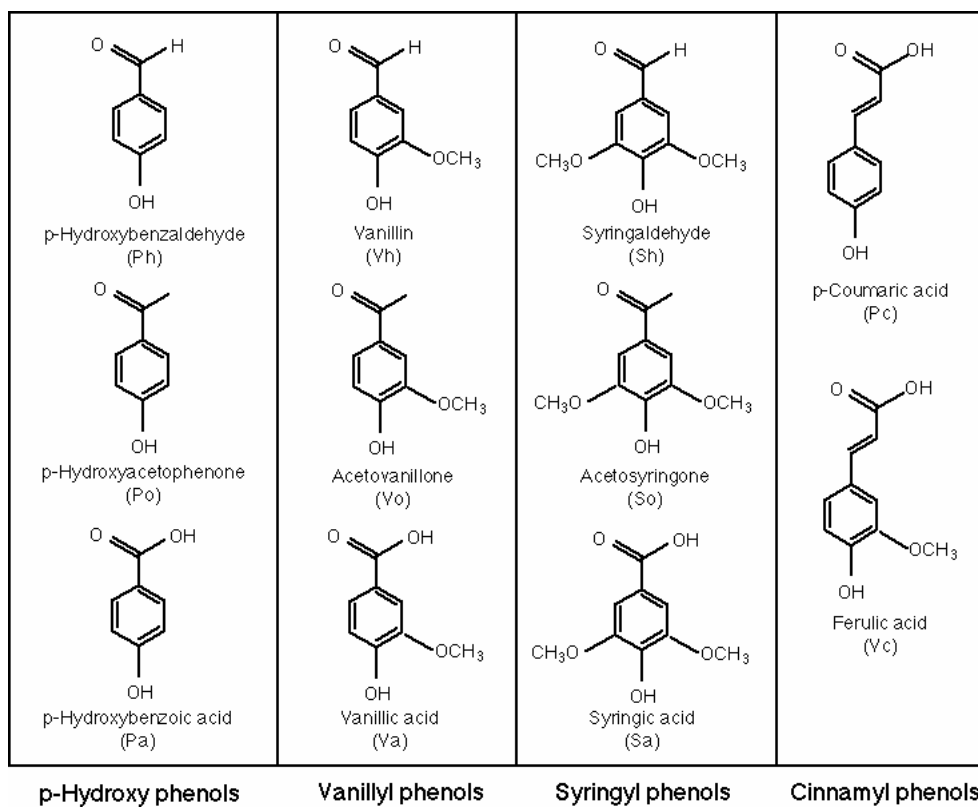


Fig. 2

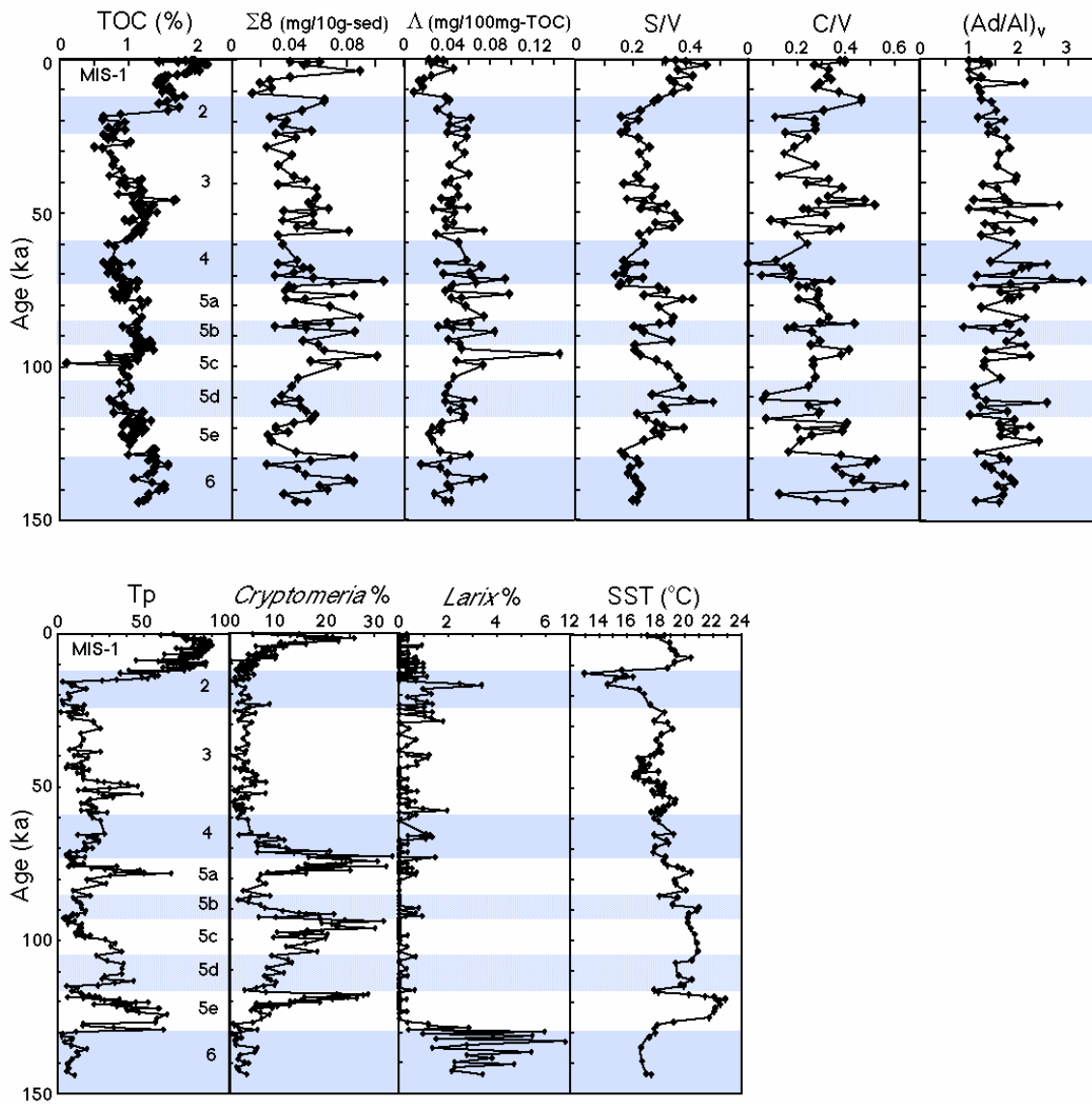


Fig. 3

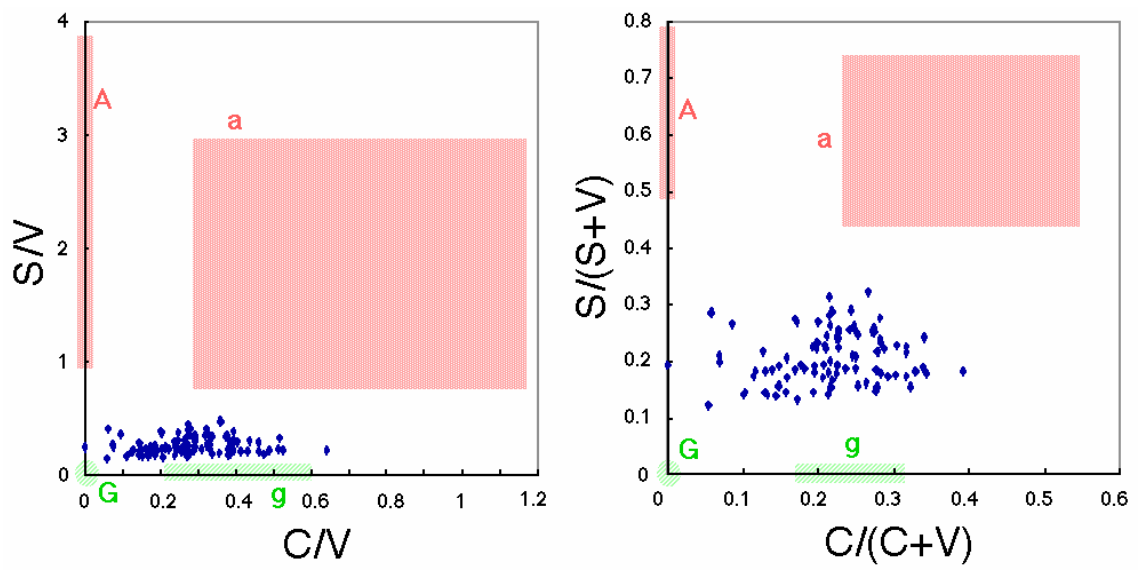


Fig. 4