

Data report: elemental, Rock-Eval, and isotopic compositions of bulk sediments, IODP Expedition 311¹

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Abstract

Several geochemical analyses were performed on samples to assess their geochemical characteristics and variations according to vertical depth and site location. Total carbon, total organic carbon (TOC), and total nitrogen (TN) content decreased from northeast to southwest along the transect of Integrated Ocean Drilling Program Expedition 311 Sites U1329, U1327, U1325, and U1326. Variations with depth showed differing trends with sites and compositions. Most organic matter was at an immature stage and Type III evolution based on Rock-Eval pyrolysis. However, results from TOC/TN, $\delta^{13}\text{C}_{\text{org}}$, and $\delta^{15}\text{N}_{\text{org}}$ analyses showed that organic matter has an admixture of origin.

Introduction

Operations during Integrated Ocean Drilling Program (IODP) Expedition 311 drilled five sites across the northern Cascadia margin (see the “[Expedition 311 summary](#)” chapter). Among the five sites, the northeast–southwest transect of Sites U1329, U1327, U1325, and U1326 was cored to investigate gas hydrate occurrence and formation. Cold vent Site U1328 was also drilled. Based on recovered core sections, Sites U1329, U1327, U1326, and U1328 are divided into three lithostratigraphic units (I, II, and III) and Site U1325 is divided into five lithostratigraphic subunits (IA, IB, II, III, and IV) (see the “[Expedition 311 summary](#)” chapter). Characterization of elements (total carbon [TC], total nitrogen [TN], and total sulfur [TS]) and organic matter in bulk sediments according to transect and lithostratigraphic units could be helpful in understanding the depositional environment, diagenesis, and origin of organic matter and give additional information about gas hydrate occurrence. Hence, this study reports several geochemical results on bulk sediments from the northern Cascadia margin.

Methods

Elemental analysis

A total of 311 squeeze cake samples from Sites U1325–U1329 were used for geochemical analyses. A part of each squeeze cake was dried for 24 h using a freeze dryer at the Korea Institute of Geoscience and Mineral Resources. After drying the bulk sediment sam-

¹Kim, J.-H., and Lee, Y.-J., 2009. Data report: elemental, Rock-Eval, and isotopic compositions of bulk sediments, IODP Expedition 311. In Riedel, M., Collett, T.S., Malone, M.J., and the Expedition 311 Scientists, *Proc. IODP*, 311: Washington, DC (Integrated Ocean Drilling Program Management International, Inc.).

doi:10.2204/iodp.proc.311.207.2009

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ples were ground and homogenized in an agate mortar. TC and TN contents were measured by combustion method using a LECO CHN-900 apparatus with detection limits of 0.001% for TC and 0.01% for TN. TS contents were determined using a LECO SC-132 apparatus with a detection limit of 0.001%.

Rock-Eval pyrolysis

Using Rock-Eval pyrolysis, free and adsorbed hydrocarbons released during programmed heating of a sample are recorded as the first peak in a pyrogram (S_1) under low temperature. The second peak (S_2) in the pyrogram represents hydrocarbons released by kerogen cracking when the sample is heated to 550°C. The temperature at the maximum of the S_2 peak is defined as T_{\max} . CO₂, shown as the third peak (S_3) in the program, is also generated by kerogen degradation. When these components are normalized to the TOC content, the S_2 peak becomes the hydrogen index (HI = $S_2 \times 100/\text{TOC}$) and S_3 becomes the oxygen index (OI = $S_3 \times 100/\text{TOC}$) (Tissot and Welte, 1984; Peters, 1986). Rock-Eval pyrolysis and TOC were determined by Rock-Eval 6.

Isotope analysis

Powdered bulk samples were pretreated with 3N HCl to remove carbonate (CaCO₃) and inorganic nitrogen for the analysis of organic carbon ($\delta^{13}\text{C}_{\text{org}}$) and nitrogen ($\delta^{15}\text{N}_{\text{org}}$) isotope ratios. $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{org}}$ were measured by a VG Optima stable isotope ratio mass spectrometer at the National Instrumentation Center for Environmental Management. The analytical reproducibility was $\pm 0.1\text{\textperthousand}$ for $\delta^{13}\text{C}_{\text{org}}$ and $\pm 0.2\text{\textperthousand}$ for $\delta^{15}\text{N}_{\text{org}}$. All carbon and nitrogen isotopes are reported in the usual δ notation relative to Vienna PeeDee belemnite (VPDB) for carbon and atmospheric N₂ for nitrogen:

$$\delta (\text{\textperthousand}) = \left(\frac{R_{\text{Sample}} - R_{\text{Standard}}}{R_{\text{Standard}}} \right) \times 1000,$$

where R represents the ¹³C/¹²C ratio and ¹⁵N/¹⁴N ratio of the sample and standard for each isotope.

Results

Elemental composition

TC, TOC, and TN contents show spatial variation across the transect of four sites (Table T1; Figs. F1, F2). Their values gradually decrease from land toward open sea. That is, the highest values are at Site U1329 and the lowest values are at Site U1326. Variation with depth show a similar trend among these el-

ements. TC, TOC, and TN values slightly increase with depth at Sites U1329 and U1327, whereas they decrease with depth at Sites U1325 and U1326 (Fig. F1). In particular, TC values reach 7.34 wt% in the upper part of Site U1328 (Fig. F1), where many massive gas hydrates and authigenic carbonates were found on board (see the “Site U1328” chapter).

TOC and TN show a strong positive correlation ($R^2 > 0.80$) (Table T1). Also, moderate or strong positive correlations were observed between TC and TOC and between TC and TN, except for an abnormal value.

Organic matter from marine algae typically has an atomic TOC/TN ratio of 4–10; ratios from vascular land plants are ≥ 20 (Emerson and Hedges, 1988; Meyers, 1994). Most atomic TOC/TN ratios in tested Expedition 311 samples have a range of 4–10 (Table T1; Figs. F1, F2) and are relatively constant with depth.

TS content at Site U1328 is higher at the surface and shows a slightly increasing trend with depth. At Site U1326, TS content slightly decreases with depth (Fig. F1). TOC/TS ratios at Sites U1326 and U1328 have a slightly decreasing trend with depth, whereas they are slightly increasing at Sites U1325 and U1329 (Fig. F1).

Rock-Eval pyrolysis

Most analyzed S_2 and S_3 values from Expedition 311 samples are <3 mg hydrocarbon [HC]/g rock and 3 mg CO₂/g rock (Table T1; Fig. F3). S_2 values show vertical and spatial variations through the transect, whereas S_3 values do not show any trend (Fig. F3). S_2 values are higher at Sites U1329 and U1327, located nearer to land, than at other sites. Additionally, S_2 values at Sites U1329 and U1327 slightly increase with depth, whereas S_2 values at the other sites are relatively constant irrespective of depth (Fig. F3).

Most analyzed HI and OI values are 50–150 mg HC/g TOC and 100–300 mg CO₂/g TOC (Table T1; Figs. F3, F4). Plotting modified van Krevelen-type and S_2 versus TOC diagrams using analyzed values from Expedition 311, most samples are at Type III evolution. There is a strong positive correlation ($R^2 > 0.80$) between S_2 and TOC (Fig. F4).

Most analyzed T_{\max} values were $<435^\circ\text{C}$, which shows that organic matter in the samples is at a thermally immature stage. T_{\max} did not show vertical variation with depth (Table T1; Fig. F3). However, T_{\max} has the lowest values ($<350^\circ\text{C}$) in the upper part of lithostratigraphic Unit I (<50 meters below seafloor) at Site U1328 (Fig. F3). This interval contains massive in situ gas hydrates (see the “Site U1328” chapter). Additionally, the T_{\max} of Unit III at



Site U1326 has a lower value and shows variation (Fig. F3).

Isotopic composition

Marine organic matter typically has $\delta^{13}\text{C}$ values from $-22\text{\textperthousand}$ to $-20\text{\textperthousand}$ (Jasper and Gagosian, 1990; Meyers, 1994). Measured $\delta^{13}\text{C}_{\text{org}}$ values of Expedition 311 samples generally are from $-27.5\text{\textperthousand}$ to $-22.5\text{\textperthousand}$. $\delta^{13}\text{C}_{\text{org}}$ values are higher at Sites U1329 and U1327 compared to the other sites (Table T1; Figs. F1, F2). $\delta^{13}\text{C}_{\text{org}}$ values slightly increase with depth at Sites U1329, U1327, and U1328, whereas they show a slightly decreasing trend at Site U1325 (Figs. F1, F2).

Analyzed $\delta^{15}\text{N}_{\text{org}}$ values are from $-3\text{\textperthousand}$ to 6\textperthousand . $\delta^{15}\text{N}_{\text{org}}$ values are higher at Sites U1329, U1327, and U1328 than at Sites U1325 and U1326. $\delta^{15}\text{N}_{\text{org}}$ values slightly decrease with depth at Sites U1329, U1327, and U1325, whereas they show a slightly increasing trend at Site U1328 (Table T1; Figs. F1, F2).

Acknowledgments

This study used samples provided by the Integrated Ocean Drilling Program (IODP) and was financially

supported by Korea Integrated Ocean Drilling Program (K-IODP) of Ministry of Land, Transport and Maritime Affairs (MLTM).

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Initial receipt: 25 June 2008

Acceptance: 27 October 2008

Publication: 8 May 2009

MS 311-207

Figure F1. Element concentrations, ratios, and isotope profiles. TC = total carbon, TOC = total organic carbon, TN = total nitrogen, TS = total sulfur. A. Site U1325. B. Site U1326. C. Site U1327. ([Continued on next page.](#))

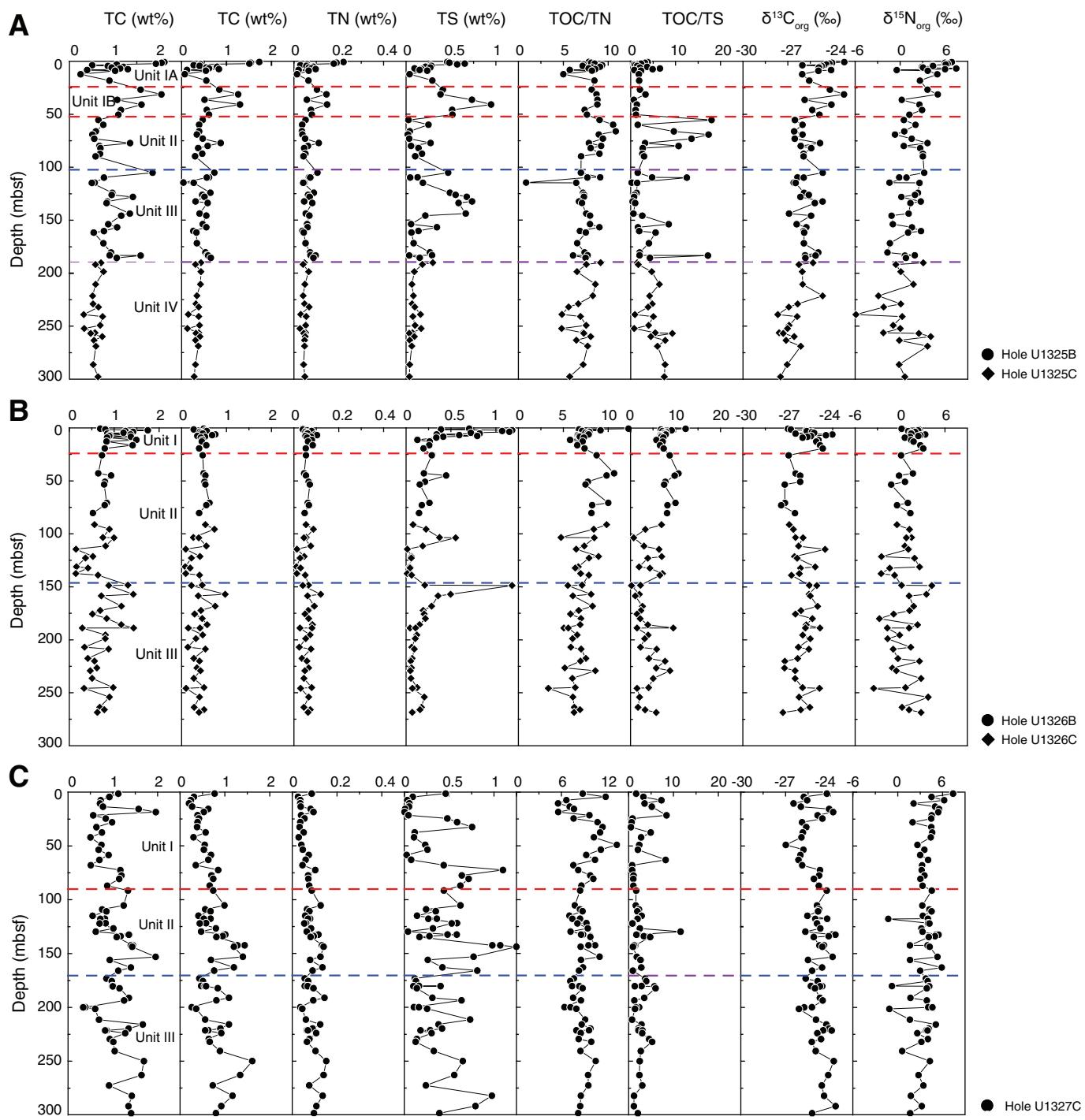


Figure F1 (continued). D. Site U1328. E. Site U1329.

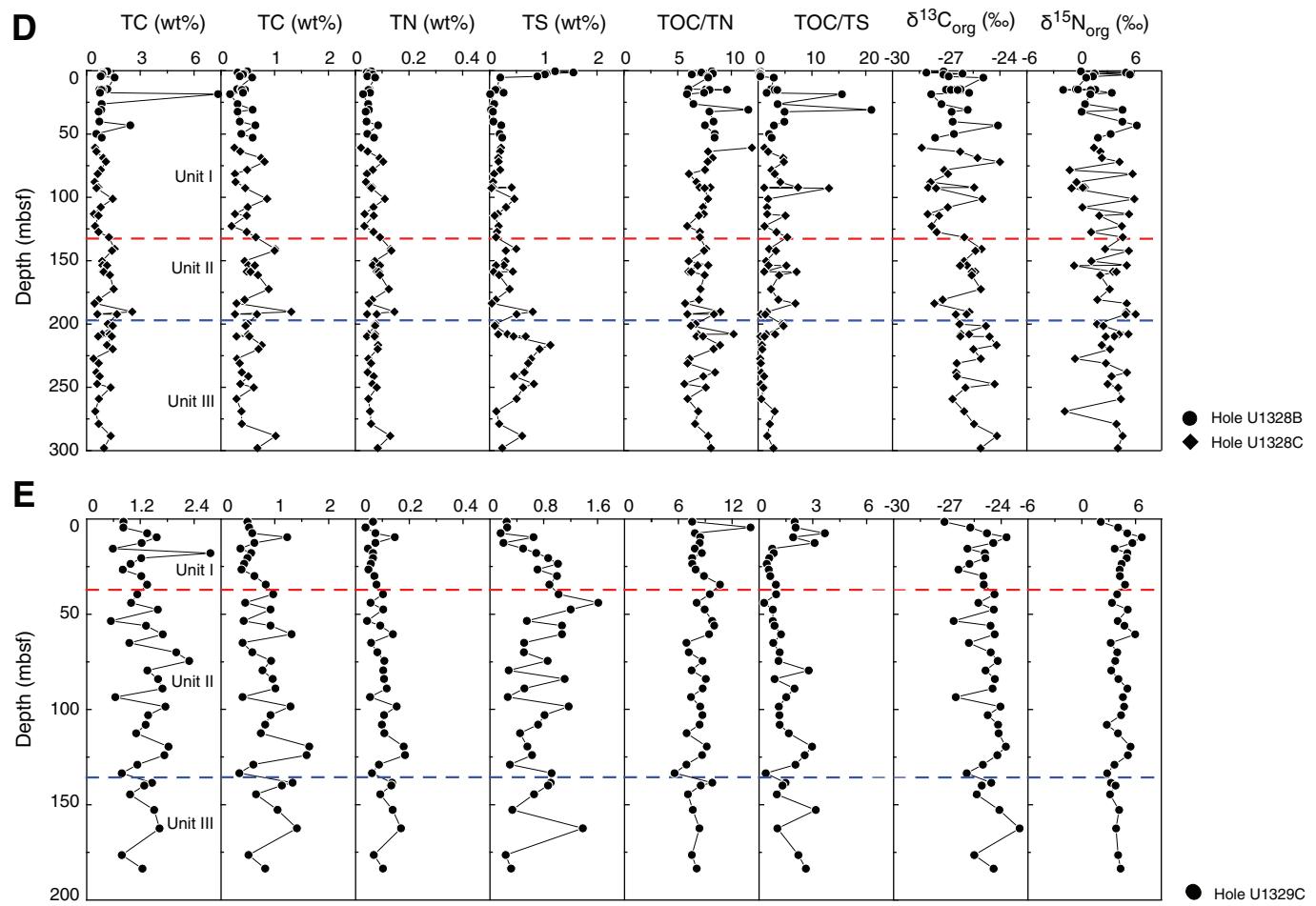


Figure F2. Element concentration, ratio, and isotope values by lithostratigraphic unit. Horizontal line = median, bottom box = first quartile (Q_1), top box = third quartile (Q_3), whiskers = lowest and highest observations inside the regions $Q_1 - 1.5(Q_3 - Q_1)$ and $Q_3 + 1.5(Q_3 - Q_1)$, respectively. * = outliers. A. Total carbon (TC). B. Total organic carbon (TOC). C. Total nitrogen (TN). D. Total sulfur (TS). E. TOC/TN. F. TOC/TS. G. Carbon isotope. H. Nitrogen isotope.

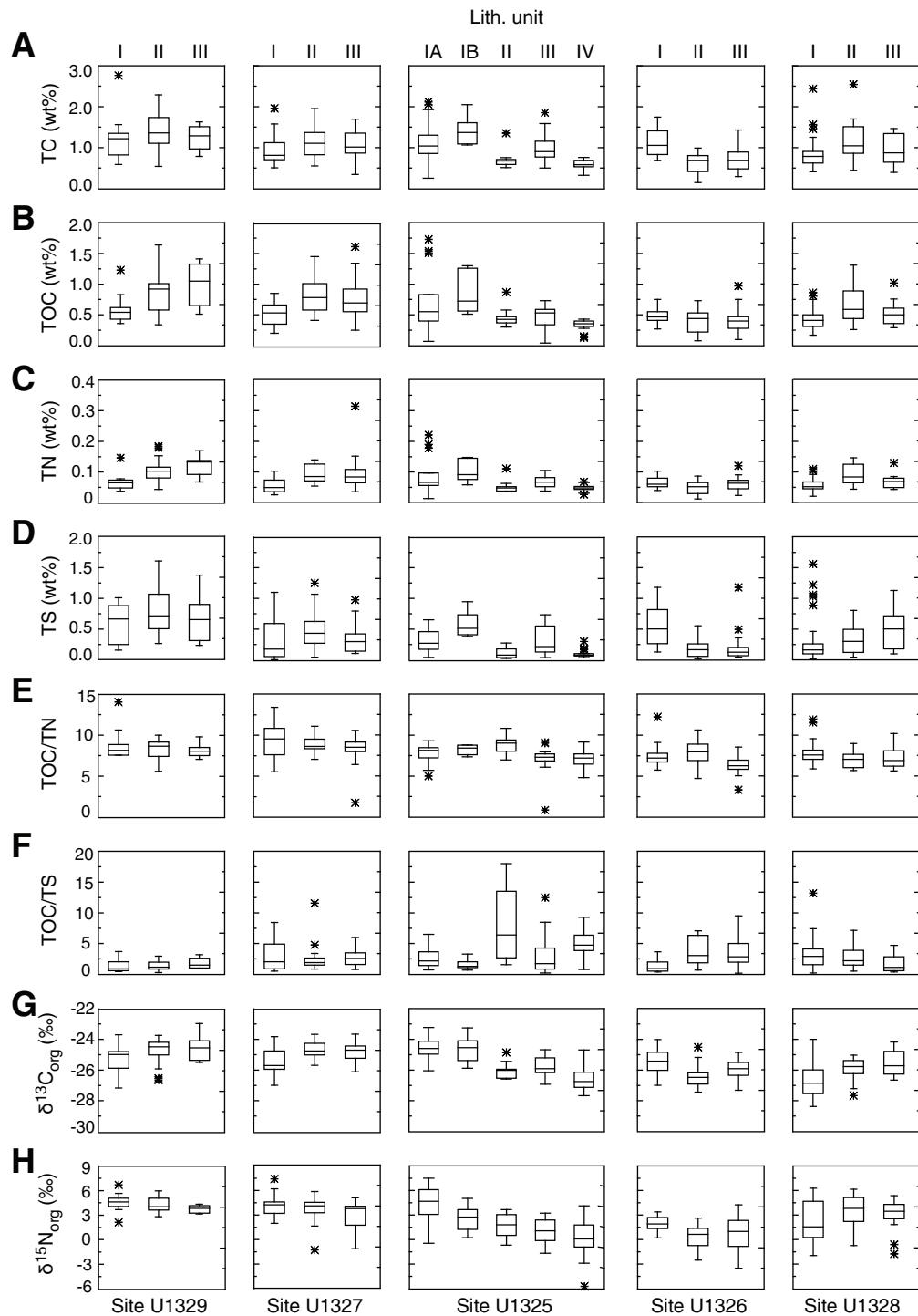


Figure F3. Rock-Eval pyrolysis profiles. S_2 = second peak, S_3 = third peak, T_{\max} = temperature at S_2 , HI = hydrogen index, HC = hydrocarbon, TOC = total organic carbon, OI = oxygen index. A. Site U1325. B. Site U1326. C. Site U1327. (Continued on next page.)

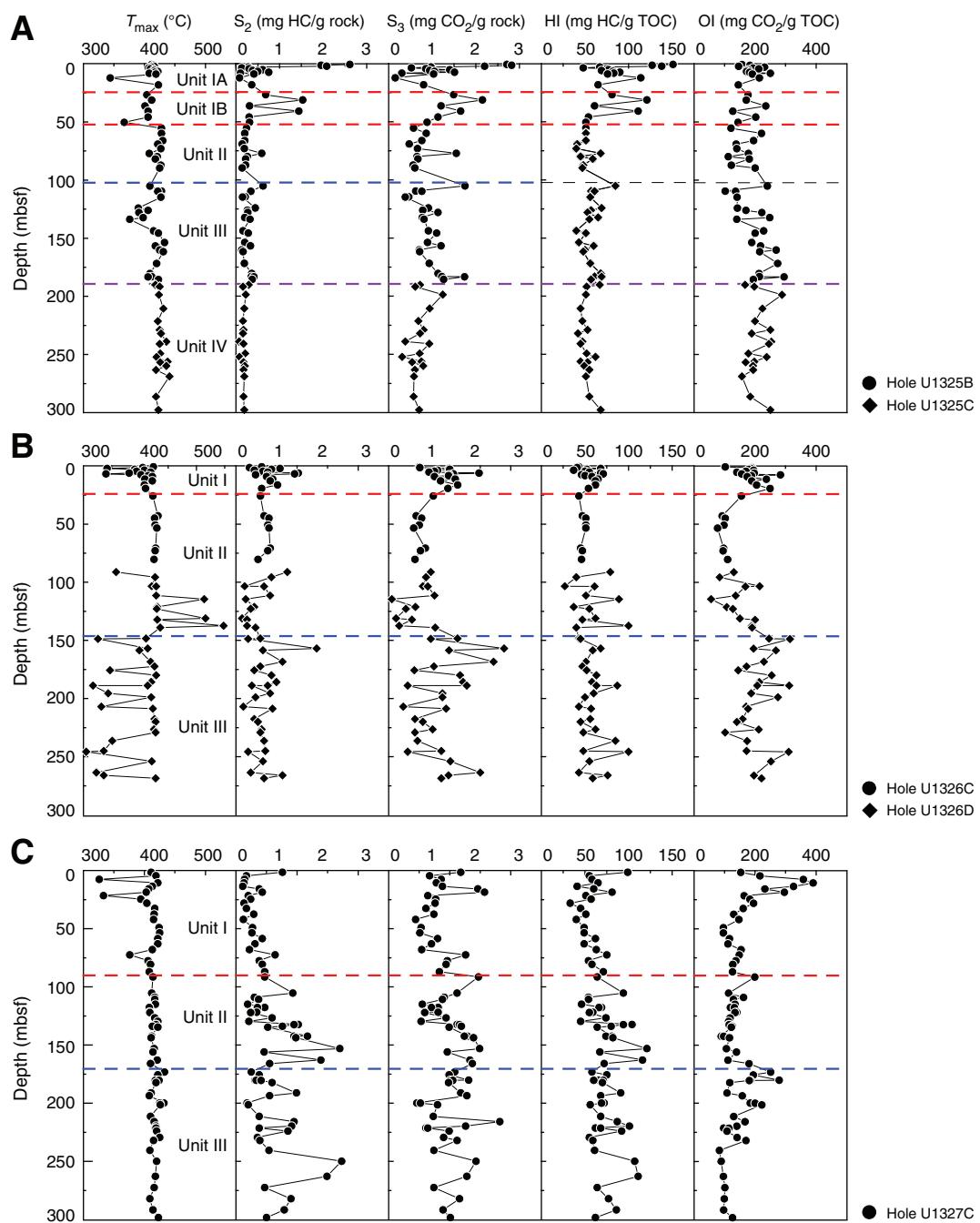


Figure F3 (continued). D. Site U1328. E. Site U1329.

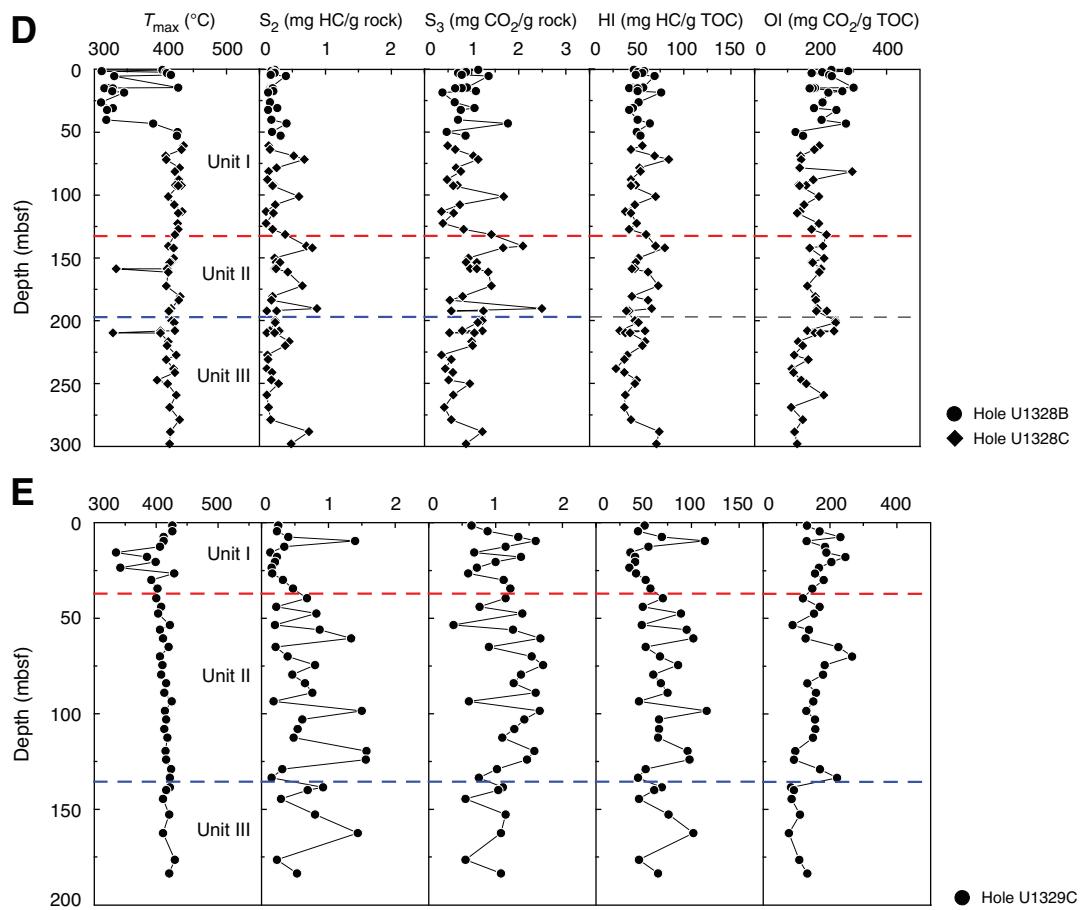


Figure F4. Modified van Krevelen-type diagrams and cross-plots. HI = hydrogen index, HC = hydrocarbon, OI = oxygen index, TOC = total organic carbon. A. Site U1325. B. Site U1326. C. Site U1327. ([Continued on next page.](#))

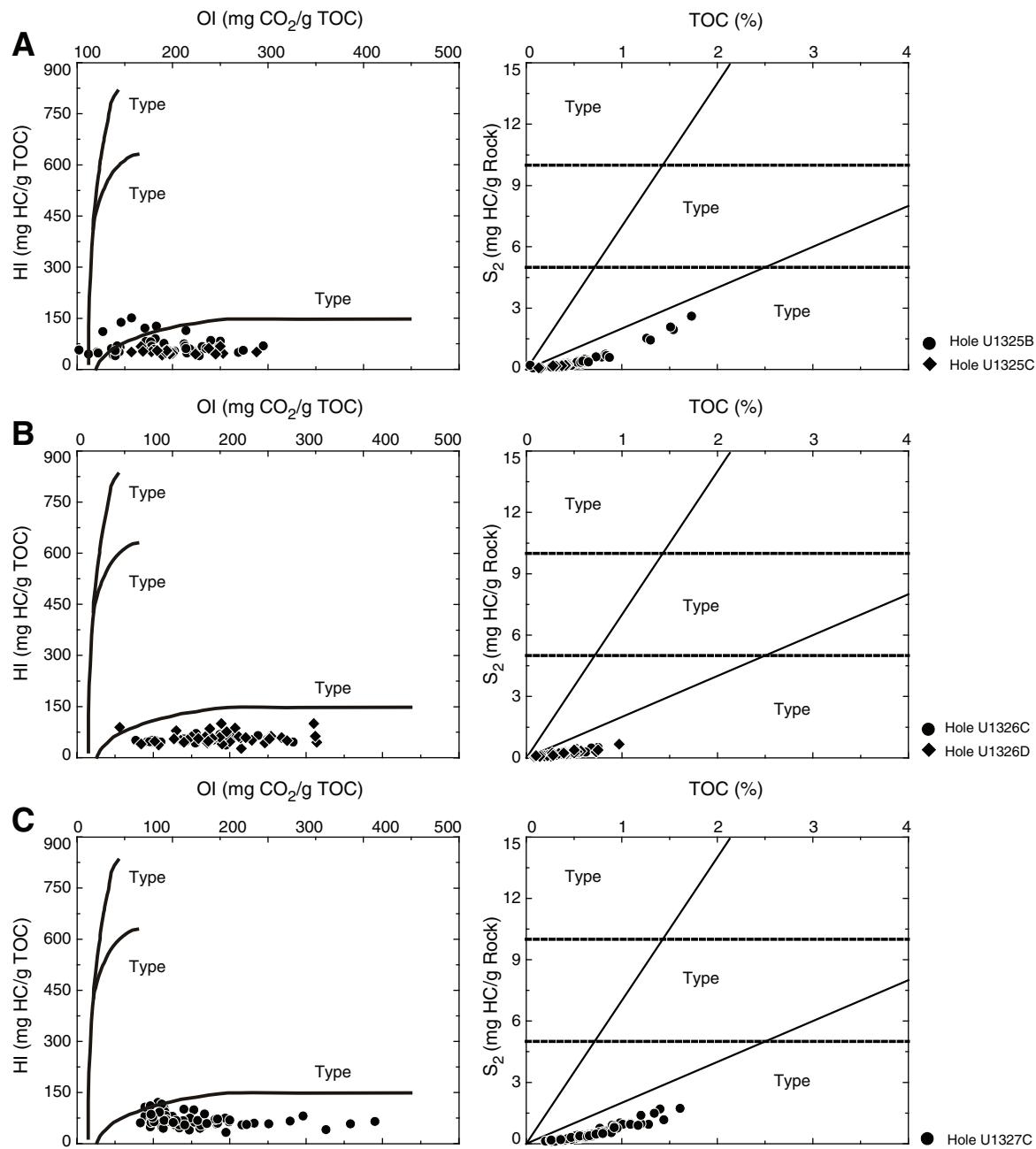


Figure F4 (continued). D. Site U1328. E. Site U1329.

