Tada, R., Murray, R.W., Alvarez Zarikian, C.A., and the Expedition 346 Scientists
Proceedings of the Integrated Ocean Drilling Program Volume 346
publications.iodp.org

https://doi.org/10.2204/iodp.proc.346.207.2021

Contents

Data report: bulk sediment organic matter, carbonate, and stable isotope stratigraphy from IODP Expedition 346 Site U1427 (250–530 m CCSF-D_Patched)[1]

Sonja Felder,[2] Andrew C.G. Henderson,[2] Melanie J. Leng,[3, 4] and Hilary J. Sloane[3]

Keywords: Integrated Ocean Drilling Program, IODP, *JOIDES Resolution*, Expedition 346, Asian Monsoon, Site U1427, mid-Pleistocene transition, total organic carbon, total nitrogen, C/N ratios, $\delta^{13}C_{org}$, calcium carbonate

Abstract

Bulk sedimentary characteristics are presented from Integrated Ocean Drilling Program Site U1427, covering the depths greater than 250 m core composite depth below seafloor (CCSF-D_Patched), which spans the mid-Pleistocene transition. Site U1427 is located in the southern Sea of Japan/East Sea and was drilled during Integrated Ocean Drilling Program Expedition 346. Total organic carbon ranges from 0.5 to 3.1 wt%, total nitrogen ranges from 0.04 to 0.32 wt%, and carbonate ($CaCO_3$) contents vary between 1.3 and 25.7 wt%. The carbon isotope ratio of organic matter ($\delta^{13}C_{org}$) values range from −24.9‰ to −20‰. There is a broad correspondence between the geochemical parameters and the shipboard color reflectance index (b*), and this relationship becomes more pronounced from ~375 m CCSF-D_Patched upward. The b* index has been used as an indicator of glacial–interglacial cycles at Site U1427. Using this inference, the data suggest reduced marine productivity during glacials, whereas interglacials are characterized by relatively higher marine productivity. The interpretation of C/N ratios at Site U1427 may be complicated by an inorganic nitrogen component.

Introduction

This report presents new data of total organic carbon (TOC), total nitrogen (TN), and calcium carbonate ($CaCO_3$) content as well as the carbon isotope ratio of organic matter ($\delta^{13}C_{org}$) in bulk sediments for the lower 250 m of the Integrated Ocean Drilling Program Site U1427 sediment column. Although studies on the upper ~250 m have previously been published (**Black et al.**, 2018; Gallagher et al., 2018; Sagawa et al., 2018; Saavedra-Pellitero et al., 2019), little has yet been done on the lower cored interval. The lower 250 m encompass the mid-Pleistocene transition, an enigmatic period of Earth's climate past, during which the periodicity of glacial and interglacial cycles shifted from a 41,000 year frequency to the modern 100,000 year frequency (Shackleton et. al, 1976; Pisias and Moore, 1981; Lisiecki and Raymo, 2005).

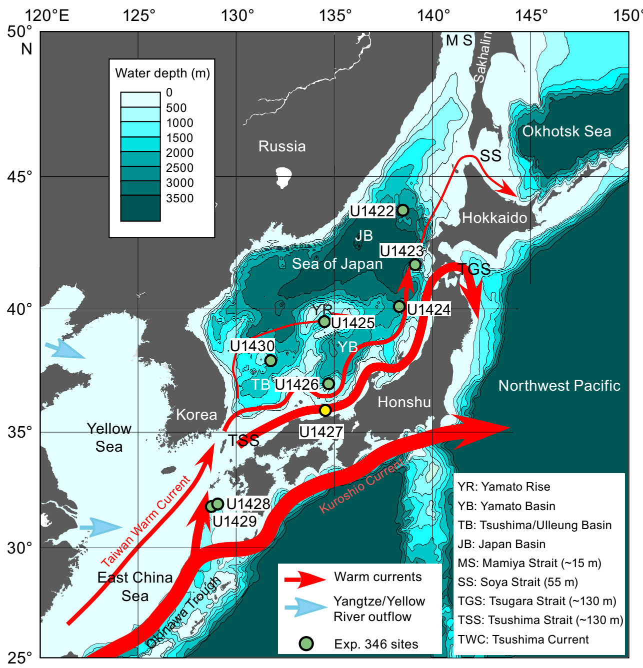
Site U1427 was cored during Integrated Ocean Drilling Program Expedition 346 (Asian Monsoon) and is located in the Sea of Japan/East Sea at a shallow water depth of about 330 m (Figure **F1**) (**Tada et al.**, 2015c). Marine productivity in the Sea of Japan/East Sea is mainly controlled by variations in East Asian summer monsoon intensity and glacio-eustatic sea level fluctuations as a result of their influences on nutrient input to the basin (Oba et al., 1991; Tada, 1994; Tada et al., 1999). The main nutrient source to the Sea of Japan/East Sea is thought to be the inflow of the Tsushima Warm Current through the Tsushima Strait in the south of the basin (Figure **F1**), although local nutrient input cannot be excluded at Site U1427 due to its close proximity to land. Glacio-eustatic sea level influences nutrient input by restricting the inflow of the Tsushima Warm Current at glacial sea level lowstands. During interglacials, nutrient input is high as a result of the unrestricted inflow of the Tsushima Warm Current, but at glacial sea level lowstands, the shallow Tsushima Strait, having a sill water depth of only ~130 m, is nearly dried up, reducing or preventing the inflow of the nutrient-enriched Tsushima Current and leading to reduced marine productivity in the basin (Oba et al., 1991; Tada, 1994; Tada et al., 1999; **Tada et al.**, 2015c). Variations in the East Asian summer monsoon affect productivity by controlling the relative contribution of nutrient-rich waters from the East China Sea to the Tsushima Warm Current, increasing nutrient contents at times of enhanced monsoonal precipitation (Oba et al., 1991; **Tada et al.**, 2015a; Saavedra-Pellitero et al., 2019). These variations in nutrient availability affect primary productivity and proxies recording marine productivity, such as TOC, TN, C/N ratios, $\delta^{13}C_{org}$, and $CaCO_3$ content.

[1] Felder, S., Henderson, A.C.G., Leng, M.J., and Sloane, H.J., 2021. Data report: bulk sediment organic matter, carbonate, and stable isotope stratigraphy from IODP Expedition 346 Site U1427 (250–530 m CCSF-D_Patched). *In* Tada, R., Murray, R.W., Alvarez Zarikian, C.A., and the Expedition 346 Scientists, *Proceedings of the Integrated Ocean Drilling Program*, 346: College Station, TX (Integrated Ocean Drilling Program). https://doi.org/10.2204/iodp.proc.346.207.2021

[2] School of Geography, Politics and Sociology, Newcastle University, United Kingdom. Correspondence author: **s.felder@ewetel.net**
[3] British Geological Survey, Nottingham, United Kingdom.
[4] School of Biosciences, Nottingham University, United Kingdom.

MS 346-207: Received 18 October 2020 · Accepted 25 March 2021 · Published 4 August 2021

Figure F1. Bathymetric map of the Sea of Japan/East Sea and Expedition 346 sites, including Site U1427 (modified from Tada et al., 2015c); major ocean currents (after Inoue, 1989, and Tomczak and Godfrey, 1994); outflow of the Yangtze and Yellow Rivers into the Yellow and East China Seas; and sill depths, including the Tsushima Strait (after Oba et al., 1991; Tada et al., 1999; Lee and Choi, 2015).



Methods and materials

A total of 517 samples were analyzed for the sediment organic parameters (TOC, TN, and $\delta^{13}C_{org}$), and 329 of these were analyzed for $CaCO_3$ content. For the organic parameters, ~300 mg of bulk sediment was decarbonated following the rinse method described in Brodie et al. (2011). Analysis was carried out in an element analyzer isotope ratio–mass spectrometer (EA-IRMS) at the British Geological Survey in Keyworth, United Kingdom. Three in-house standards showed relative standard deviations of <0.71 for TOC, <0.46 for TN, and <0.09 for $\delta^{13}C$. The isotope data are presented in the delta (δ) notation against Vienna Peedee belemnite (VPDB) and calculated using the following equation:

$$\delta R_{sample}\,[\text{‰ VPDB}] = \left(\frac{R_{sample} \times R_{standard}}{R_{standard}}\right) \times 100\,, \quad (1)$$

where R is the ratio of the heavy over the light isotope in a sample/standard (Coplen, 1994).

The determination of the $CaCO_3$ content was made by direct total inorganic carbon (TIC) measurement using a multiEA 4000 HT system 1500 by JENA Analytics at Newcastle University, United Kingdom. For each analysis, about 50 mg of ground, homogenized bulk sediment was automatically acidified with phosphoric acid and analyzed (Jezierski, 2015; Analytik Jena AG, 2012). Three in-house standards showed relative standard deviations of <0.4 for TIC. Using the TIC values, $CaCO_3$ contents were calculated via the molar mass of $CaCO_3$:

$$\text{stoichiometric coeff.} = \frac{CaCO_3 \text{ molar mass}}{\text{C atomic weight}} = \frac{[40 + 12 + (3 \times 16)]}{12\text{ g/mol}} = \frac{100\text{ g/mol}}{12\text{ g/mol}}. \quad (2)$$

The resulting stoichiometric coefficient of 8.33 was used to calculate the $CaCO_3$ content from TIC, assuming all TIC is bound to calcium carbonates (calcite or aragonite):

$$CaCO_3\,(\text{wt\%}) = (\text{TC} - \text{TOC}) \times 8.33 = \text{TIC} \times 8.33. \quad (3)$$

For completeness, Equation **E3** shows the calculation of TIC from total carbon (TC) and TOC (after Bernard et al., 1995).

The data in this study (geochemical data and shipboard b* index) (**Tada et al.**, 2015b) are presented in Table **T1**. The CCSF-D_Patched depth scale has been used in publications on the upper 250 m of sediment cores at Site U1427 (**Black et al.**, 2018; Gallagher et al., 2018; **Itaki et al.**, 2018; Sagawa et al., 2018; Saavedra-Pellitero et al., 2019; **Peterson and Schimmenti**, 2020). For reference, Table **T1** also contains depth on the core depth below seafloor, Method A (CSF-A) scale (i.e., the depth in meters below seafloor as established on board the ship).

Results

The TOC, TN, C/N ratios, $\delta^{13}C_{org}$, and $CaCO_3$ data are plotted against shipboard color reflectance index b* (Figure **F2**; Table **T1**). The high-resolution b* record was used during Expedition 346 as an indicator for glacials/interglacials. Glacial sediments have lower b* values, whereas interglacial sediments have relatively higher b* values (**Tada et al.**, 2015c). During glacials, low b* coincides with low $CaCO_3$ and TOC contents (Figure **F2**), indicating reduced marine productivity and corroborating previous studies (**Tada et al.**, 2015c; **Black et al.**, 2018; Gallagher et al., 2018; Sagawa et al., 2018; Saavedra-Pellitero et al., 2019). In addition, glacials are characterized by enhanced contributions of terrigenous organic matter as indicated by lower $\delta^{13}C_{org}$ values (Figure **F2**). In marine algae, $\delta^{13}C_{org}$ varies with marine productivity via the preferential uptake of ^{12}C, but the $\delta^{13}C_{org}$ values are also influenced by variations in terrigenous organic matter input. In simple terms, marine plankton typically show $\delta^{13}C_{org}$ values between −20‰ and −22‰, and $\delta^{13}C_{org}$ of terrigenous material generally has lower $\delta^{13}C_{org}$ values around −27‰ (e.g., Jasper and Gagosian, 1993; Meyers, 1994). Glacial exposure of shelves and migration of the Yellow/Yangtze River mouths to positions closer to the Tsushima Strait, potentially combined with local riverine input at Site U1427, likely led to the glacial increase in terrigenous contributions to the sediments. In contrast, interglacials are characterized by relatively higher $CaCO_3$, TOC, and $\delta^{13}C_{org}$ values, indicating reduced terrigenous and enhanced marine organic matter contributions to the sediments as a result of enhanced marine productivity (Figure **F2**).

Intriguingly, the C/N ratios do not always follow the trends and patterns of the above geochemical proxies. In general, C/N ratios of marine algae are lower than 10, and organic matter of land plants typically shows values higher than that (Scheffer and Schachtschabel, 1984; Meyers and Lallier-Vergès, 1999). At Site U1427, C/N ratios vary between ~2 and 16 across the interval 250–530 m CCSF-D_Patched, indicating a mixed marine-terrigenous source of organic matter and corroborating previous studies of the upper 140 m and the shipboard low-resolution data (**Black et al.**, 2018; **Tada et al.**, 2015c). However, interpretation of C/N ratios often differs from the other proxies presented here. C/N ratios tend to be lower during glacials, indicating enhanced marine organic matter and contradicting the interpretation of $CaCO_3$, TOC, and $\delta^{13}C_{org}$. In two intervals, ~390–320 and ~300–270 m CCSF-D_Patched, C/N ratios become variable, missing a clear glacial–interglacial trend (Figure **F2**). Vari-

Figure F2. Total organic carbon (TOC), total nitrogen (TN), C/N ratios, $\delta^{13}C_{org}$ and calcium carbonate ($CaCO_3$) content of sediment samples and shipboard color reflectance index b* against depth (m CCSF-D_Patched). Shaded areas indicate glacials.

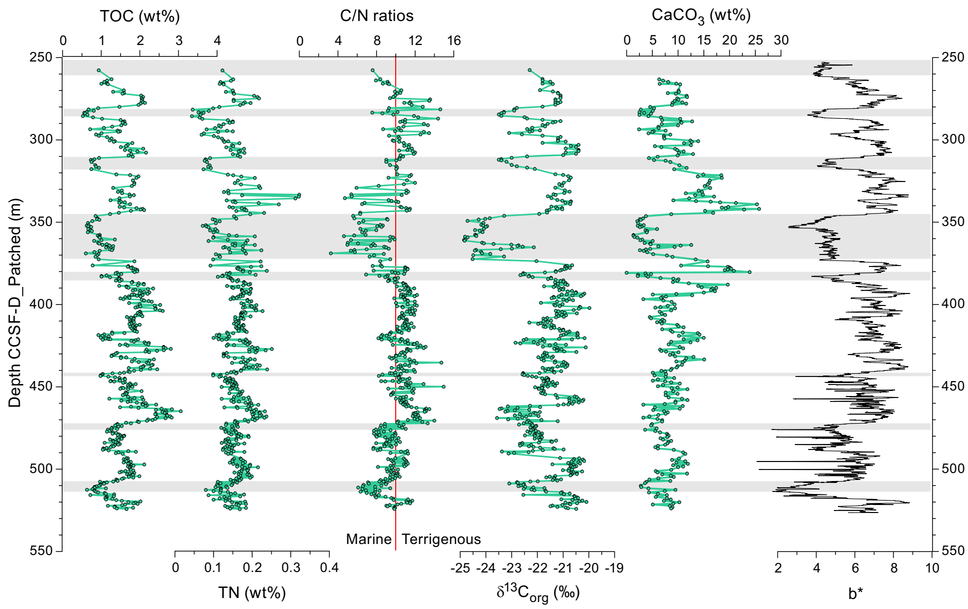


Table T1. $\delta^{13}C_{org}$ of organic matter ($\delta^{13}C_{org}$), total organic carbon (TOC), total nitrogen (TN), and calcium carbonate ($CaCO_3$) contents and TOC-TN (C/N) ratios, Site U1427. **Download table in CSV format.**

ations in C/N ratios are usually controlled by the relative contributions of marine and terrigenous organic matter; however, in the Sea of Japan/East Sea, an eolian contribution cannot be excluded, and/or, although rarely mentioned, an additional inorganic, clay-bound component of nitrogen may have played a role at Site U1427, complicating the interpretation of C/N ratios (Schubert and Calvert, 2001; Seki et al., 2019).

Acknowledgments

This study used samples provided by the Integrated Ocean Drilling Program. We would like to thank the Co-Chief Scientists, Ryuji Tada and Richard W. Murray, and all Expedition 346 participants. Furthermore, we would like to express our gratitude to Chang Liu for a very helpful review and to Carlos Alvarez Zarikian and the Expedition Co-Chief Scientists for comments on the manuscript. This research was supported by a NERC IAPETUS Doctoral Training Partnership studentship (NE/L002590/1) and by a British Geological Survey CASE partnership (BUFI S270) and forms part of S. Felder's PhD research ("The mid-Pleistocene climate transition in the Japan Sea: insights of a combined paleoceanographic and -monsoon, multiproxy study using marine sediments of IODP Site U1427 from the shallow, southern Japan Sea"; Newcastle University, United Kingdom). Analyses were also supported by the NERC Isotope Geoscience Facility at the British Geological Survey under awards IP-16668-111 and IP-1486-1114. We are also grateful to UK IODP for supporting the participation of A.C.G. Henderson in Expedition 346 (NE/L002655/1) and for supporting S. Felder in her participation in the Expedition 346 second postcruise meeting in Melbourne, Australia.

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