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Data report: bulk sediment calcium carbonate and organic matter from IODP Expedition 359 Site U1471 (0–21 m CCSF)[1]

Christine Buchwalter,[2] Carlos A. Alvarez Zarikian,[3] and Chang Liu[3]

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[2] Texas A&M University, Department of Geology & Geophysics, USA.
[3] International Ocean Discovery Program and Department of Oceanography, Texas A&M University, USA. Correspondence author: **zarikian@iodp.tamu.edu**

Abstract

During International Ocean Discovery Program (IODP) Expedition 359, Site U1471 was cored in the Maldives Inner Sea, where the sediments consist of hemipelagic carbonate drifts containing a mixture of components exported from the atolls and pelagic origin (periplatform ooze). The cores from this site provide a complete and uninterrupted record of the sedimentary and paleoceanographic changes in the Maldives Inner Sea from the Miocene through the Pleistocene. Here, we present the bulk sediment total organic carbon, total nitrogen, and calcium carbonate contents for the uppermost 21 m of the composite splice of Site U1471.

1. Introduction

This data report presents the total organic carbon (TOC), total nitrogen (TN), and calcium carbonate ($CaCO_3$) contents in bulk sediments for the uppermost 21 m of the composite splice of International Ocean Discovery Program (IODP) Site U1471. Site U1471 (4°45.98′N, 073°08.11′E) was cored during Expedition 359 at a water depth of 419 m in a semicentral position in the Maldives Inner Sea, southeast of Goidhoo atoll, in an area where the seafloor is essentially flat (**Betzler et al.**, 2017a; **Betzler et al.**, 2017b). The Maldives Inner Sea is a small basin surrounded by atolls that lie near or slightly above sea level in the elongated and isolated tropical archipelago of the Maldives. The maximum water depth in the inner sea is 550 m. The external slopes of the Maldives carbonate platform margin toward the ocean are very steep and rapidly reach bathyal and abyssal depths of the Indian Ocean (Lüdmann et al., 2013; **Betzler et al.**, 2017a; **Betzler et al.**, 2017b). Far away and isolated from India and Asia, the Maldives has grown to a ~3 km thick carbonate sedimentary succession that embodies an almost complete Cenozoic sedimentary record with minimal terrigenous input (Aubert and Droxler, 1992; Purdy and Bertram, 1993; Lüdmann et al., 2013; Lindhorst et al., 2019).

Five holes were drilled at Site U1471 with the aim of recovering sedimentary sections suitable for building a complete and uninterrupted composite record of paleoceanographic changes in the Maldives and monsoon cyclicity from the middle Miocene to the present (Betzler et al., 2016; **Betzler et al.**, 2017b). Holes U1471A–U1471D were cored to 685.1, 6.7, 178.8, and 58.0 meters below seafloor (mbsf), respectively. Hole U1471E was drilled without recovery to 596 mbsf and then rotary cored to 1003.7 mbsf to reach the base of the drift deposits. A core composite depth below seafloor (CCSF) depth scale or "splice" of Site U1471 was constructed during Expedition 359 by stratigraphically correlating the sediment core physical and magnetic properties across all holes.

A preliminary age model was established based on planktonic foraminifer and calcareous nannofossil biostratigraphic markers. The shipboard age model estimated an age of 14 Ma (middle Miocene) at the base of the record at 1003.7 mbsf in Hole U1471E (**Betzler et al.**, 2017b).

The sediments at Site U1471 consist of unlithified brownish gray planktonic foraminifer–rich, fine- to medium-grained packstone to wackestone. Besides planktonic foraminifers, common sedimentary components include well-preserved benthic foraminifers, ostracods, calcareous nannofossils, pteropods, echinoderm spines, sponge spicules, and mollusk fragments (**Betzler et al.**, 2017b and this study).

2. Methods

2.1. Sedimentary inorganic and organic carbon content

A total of 151 sediment samples taken at 15 cm intervals from the seafloor to 21 m CCSF at Site U1471 were analyzed for bulk sediment geochemistry at the IODP Gulf Coast Repository at Texas A&M University in College Station, Texas (USA).

First, the core samples were freeze-dried for at least 24 h and then subsampled, and the aliquots were crushed using an agate pestle and mortar. The powders were then analyzed for total carbon (TC), total inorganic carbon (TIC), and TN.

TC and TN contents were determined by a ThermoElectron Corporation FlashEA 1112 carbon-hydrogen-nitrogen-sulfur (CHNS) elemental analyzer equipped with a ThermoElectron packed column CHNS/NCS gas chromatograph (GC) and a thermal conductivity detector (TCD) using the dry, homogeneous sample powder. About 10–15 mg of sediments were weighed into a tin foil cup. Vanadium oxide was then mixed with the sediment as a catalyst to yield the sulfur peak in the CHNS analyzer's chromatography. Afterward, the tin cup was wrapped compactly and then combusted under 950°C in a stream of oxygen. The reaction gases were passed through a reduction chamber to reduce nitrogen oxides to nitrogen and were then separated by the GC before detection by the TCD. All measurement results were calculated into content in percentage by weight using a linear regression line created by measuring a certified sediment standard (Buffalo River sediments). Five standards with masses of 3, 5, 10, 15, and 20 mg were weighed into tin cups, and a linear regression curve was created based on their known absolute elemental contents corresponding to each of the elemental peak areas from the chromatography. In addition, a check standard was run every 10 samples to check the accuracy and reproducibility of the measurements.

TIC was determined using a UIC, Inc., Model 5011 CO_2 coulometer. Approximately 10–18 mg of powdered sediments were weighed on a microbalance, loaded into a glass tube, and acidified with 2 M HCl. A weighed amount (~10 mg) of a standard of pure $CaCO_3$ was measured three times before the samples' measurement sequence as a calibration and then once every 10 samples as a check to confirm accuracy of the instrument.

The liberated CO_2 from the reaction between samples and HCl was titrated, and the corresponding change in light transmittance in the coulometric cell was monitored using a photometric detector. The weight percent of $CaCO_3$ was calculated from the inorganic carbon content using the following equation:

$$CaCO_3\ (\text{wt\%}) = \text{coulometer reading (TIC; µg)} \times 8.333/\text{sample mass (mg)}.$$

This equation assumes that all carbonate present is $CaCO_3$. TOC content was calculated by subtracting inorganic carbon from TC. The C/N ratio was calculated by dividing TOC by TN.

3. Results

3.1. Calcium carbonate and organic matter

The TOC, TN, and $CaCO_3$ contents and C/N ratio data are presented in Tables **T1** and **T2** and illustrated in Figure **F1**. The results are plotted against the CCSF depth scale (in meters) and compared to the sediment color spectral reflectance (L*) and red-green-blue (RGB) green channel data extracted from the digital section image taken during Expedition 359 to provide a stratigraphic context because these high-resolution parameters can be used to estimate sediment composition. In this case, they can be related to the $CaCO_3$ content, which is linked to biogenic carbonate productivity variations during glacial/interglacial intervals (Giosan et al., 2002). In the Maldives Inner Sea, glacial sediments have less abundant carbonate deposition and lower L* and RGB green values, whereas interglacial sediments have higher L* and RGB green values due to a higher carbonate deposition (**Betzler et al.**, 2017b).

The sediment $CaCO_3$ content ranges 73.5–95.6 wt%, with an average of 88.7 wt%. The standard deviation per sample replicates ranges 0–8.2, with an average of 1.1. The data reproducibility ranges 0%–3.6% and averages 0.91%. The $CaCO_3$ record shows a cyclic pattern with alternations of higher and lower $CaCO_3$ values that follow the trends in the L* and RGB green curves, with higher $CaCO_3$ content associated with higher spectral values. Higher $CaCO_3$ is linked to increased biogenic carbonate production in the Maldives during interglacial periods (**Betzler et al.**, 2017b; Kunkelova et al., 2018; Alvarez Zarikian et al., 2022). Conversely, lower $CaCO_3$ content coincides with intervals of lower spectral values, which are linked to glacial/stadial periods in the Maldives.

Table T1. Calcium carbonate content, Site U1471 (0–21 m CCSF). **Download table in CSV format.**

Table T2. Total carbon, nitrogen, sulfur, inorganic carbon (IC), organic carbon, and $CaCO_3$ contents and C/N ratio data, Site U1471 (0–21 m CCSF). **Download table in CSV format.**

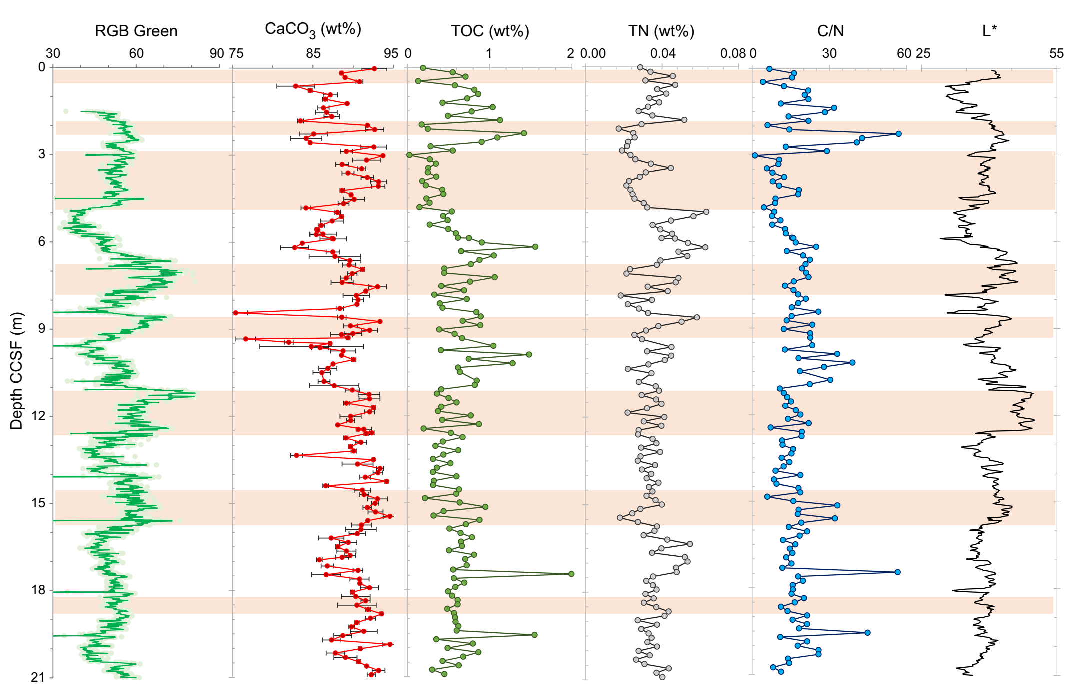

Figure F1. $CaCO_3$, TOC, and TN contents and C/N ratio of sediment samples from Site U1471 compared to sediment lightness (L*) and RGB green spectral channel of core section digital images. Orange bars = periods of high RGB green and L* values, which can be interpreted to represent interglacial or interstadial periods.

Table T3. Buffalo River N, C, and S standard data (measured by CHNS analyzer). **Download table in CSV format.**

Table T4. Pure $CaCO_3$ standard data (measured by coulometer). **Download table in CSV format.**

TOC values vary between 0.02 and 2.0 wt% and average 0.6 wt%. Values are below average from ~15 to 11 m CCSF and from ~5.5 to 3 m CCSF. Intervals of above average values are centered around 10, 6, and 3 m CCSF, where sediment color reflects lower values (Figure **F1**). Two sample outliers produced TOC peaks at 17.5 and 19.5 m CCSF. TN content is very low (0.02–0.06 wt%). The highest TN values generally coincide with intervals of a lighter sediment color. Two intervals of consistently low values are observed between 5.5 and 2 m CCSF. Sulfur content is below the detection limit for most of the record. C/N ratios range 1–56.8, with an average of 17.4, and for the most part follow TOC patterns. In general, C/N ratios of marine algae are lower than 10, and land plants' organic matter typically shows higher values (Schubert and Calvert, 2001; Meyers and Lallier-Vergès, 1999), which suggests that the Maldives Inner Sea receives significant eolian contribution of continental organic matter.

3.1.1. Data reproducibility

A check on the measurements on the Buffalo River sediment standard conducted in the CHNS analyzer showed a reproducibility of 4.92%, 1.05%, and 7.31% and an accuracy of 94.1%, 99.4%, and 102% for nitrogen (N), carbon (C), and sulfur (S), respectively (Table **T3**). The measurements of the pure $CaCO_3$ standard measured in the coulometer showed a reproducibility of 2.7% and accuracy of 99.4% (Table **T4**).

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