

# The relationship between wet bulk density and carbonate content in sediments from the Eastern Equatorial Pacific



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## ABSTRACT

Sediment cores collected from the Eastern Equatorial Pacific Ocean display a clear positive second-order relationship between wet bulk density (WBD) and carbonate content. This has long interested the paleoceanography community because detailed Gamma Ray Attenuation Porosity Evaluator (GRAPE) measurements, which approximate WBD, might be used to determine records of carbonate content at very high temporal resolution. Although general causes for the relationship are known, they have not been presented and discussed systematically on the basis of first principles. In this study, we measure the mass and carbonate content of 50 sediment samples with known WBD from Site U1338, before and after rinsing with de-ionized water; we also determine the mass related proportion of coarse (>63 μm) material. Samples exhibit clear relationships between WBD, carbonate content, mass loss upon rinsing, and grain size. We develop a series of mathematical expressions to describe these relationships, and solve them numerically. As noted by previous workers, the second-order relationship between WBD and carbonate content results from the mixing of biogenic carbonate and biogenic silica, which have different grain densities and different porosities. However, at high carbonate content, a wide range in WBD occurs because samples with greater amounts of coarse carbonate have higher porosity. Moreover compaction impacts carbonate particles more than biogenic silica particles. As such, a single two-component equation cannot be used to determine carbonate content accurately across depth intervals where both the porosity and type of carbonate vary. Instead, the WBD-carbonate relationship is described by an infinite series of curves, each which represents mixing of multiple sediment components with different densities and porosities. Dissolved ions also precipitate from pore space during sample drying, which adds mass to the sediment. Without rinsing samples, simple empirical relationships between WBD and carbonate content are further skewed by salt dilution.

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## 1. Introduction

The Eastern Equatorial Pacific Ocean (EEP) generally refers to a large area between 140° W and the coasts of Central and South America, and between about ten degrees north and south latitude. The region is characterized by major differences in Sea Surface Temperature (SST) and primary productivity, with steep zonal and meridional gradients related to wind-driven currents and upwelling of cold, nutrient-rich water (Kessler, 2006; Pennington et al., 2006). Moreover, these gradients can change significantly from one year to another (Barber and Chavez, 1986; Trenberth and Caron, 2000; Kessler, 2006; Pennington et al., 2006).

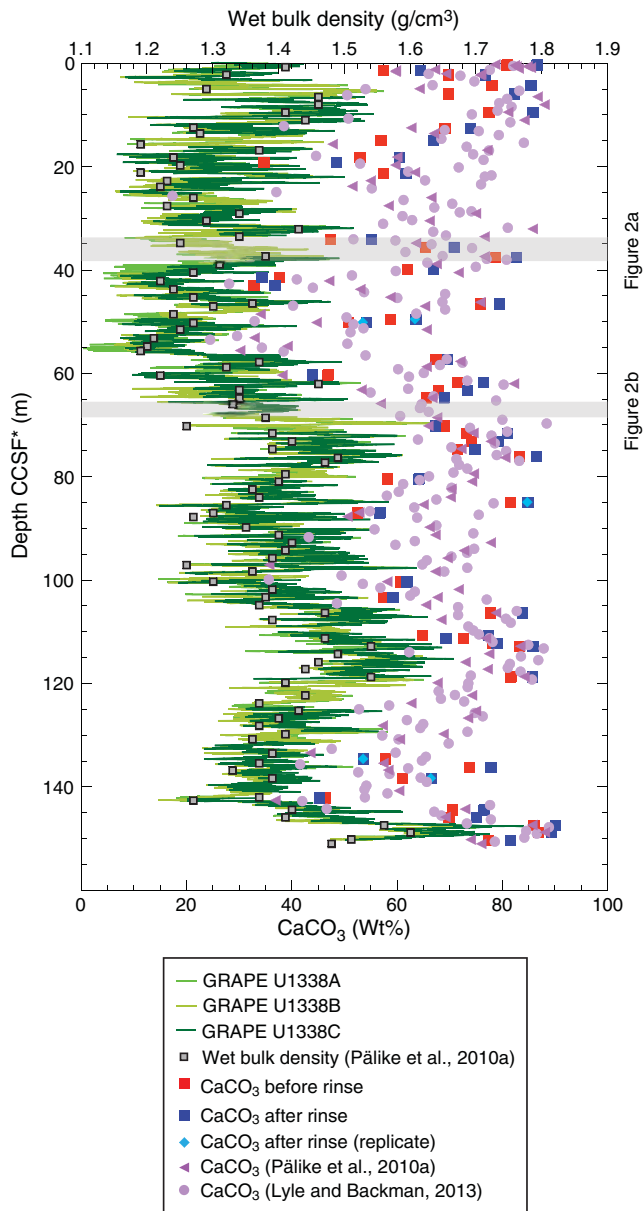
The EEP has long interested the paleoceanographic community (Arrhenius, 1952; Ravelo, 2010). This interest reflects the significance of this region to global primary productivity (Chavez and Barber, 1987; Fiedler et al., 1991; Pennington et al., 2006) and to Earth's

climate evolution (Lyle et al., 2008; Brierley and Fedorov, 2010). It also relates to the fact that sediment cores collected within the region contain major changes in physical properties and composition that occur over short stratigraphic distances and that can be traced over hundreds of kilometers along the equatorial region (Herbert and Mayer, 1991; Farrell et al., 1995; Piasias et al., 1995; Bloomer and Mayer, 1997; Lyle and Wilson, 2006). Notably, a clear positive relationship exists between wet bulk density (WBD) and carbonate content has been repeatedly demonstrated from the EEP region (Luz and Shackleton, 1975; Lyle and Dymond, 1976; Johnson et al., 1977; Kominz et al., 1977; Mayer, 1979; Denis-Clocchiatti, 1982; Curry and Lohmann, 1986; Chuey et al., 1987; Curry et al., 1990; Herbert and Mayer, 1991; Mayer, 1991; Piasias et al., 1995; Weber et al., 1997; Weber, 1998). Intervals of low WBD correspond to low carbonate content, and vice versa (Figs. 1, 2).

The general cause for the density-carbonate relationship in EEP sediment cores is known (Lyle and Dymond, 1976; Kominz et al., 1977; Mayer, 1991; Herbert and Mayer, 1991; Weber et al., 1997; Weber, 1998). The WBD of a sample represents the additive volumes of

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**Fig. 1.** Shipboard GRAPE measurements, wet bulk density (WBD) and carbonate content for the upper 151 m at Site U1338. GRAPE and WBD data come from shipboard measurements (Pälike et al., 2010a). Carbonate content data come from shipboard measurements (Pälike et al., 2010a), other work at Site U1338 (Lyle and Backman, 2013) and this study. The depth scale is in corrected meters composite depth (Wilkens et al., 2013). Note that discrete WBD data and GRAPE measurements from the same depth have similar values.

porosity holding seawater ( $1.024\text{--}1.028\text{ g/cm}^3$ ) and grains with different compositions (Fig. 3). Primary components of sediment in the EEP are carbonate (mainly calcareous nannofossil and foraminifera tests), biogenic silica (mostly diatom tests) and clays, with the first two especially important near the Equator (Pisias et al., 1995). Carbonate, biogenic silica and clays have grain densities of  $2.6\text{--}2.7\text{ g/cm}^3$ ,  $2.1\text{--}2.3\text{ g/cm}^3$ , and  $2.6\text{--}2.7\text{ g/cm}^3$ , respectively (Becking and Moore, 1959; Hamilton, 1974; Herbert and Mayer, 1991; Weber et al., 1997). Because intervals with high biogenic silica content typically have higher porosity, sediment with low carbonate content and high biogenic silica content has lower WBD.

High-resolution (<5 cm spacing) WBD records of marine and lacustrine sediments can be measured using the Gamma Ray Attenuation Porosity Evaluator (GRAPE) tool. This tool and its operating procedure

have been described in detail (Boyce, 1976), and GRAPE records are now routinely generated on many scientific drilling expeditions (e.g., Weber et al., 1997; Fortin et al., 2013). For drill sites in the EEP, the GRAPE records have been used to generate high-resolution carbonate and silica records pertinent to paleoceanography (Herbert and Mayer, 1991; Mayer, 1991; Hagelberg et al., 1992; Weber et al., 1997).

The relationship between bulk density and carbonate has been described empirically (Luz and Shackleton, 1975; Lyle and Dymond, 1976; Kominz et al., 1977; Herbert and Mayer, 1991; Mayer, 1991; Snoeckx and Rea, 1995; Weber et al., 1997). However, the relationship has not been verified and discussed from first principles, here referring to the fundamental coupling of volume and mass for porous media. Moreover, other than Lyle and Dymond (1976), the effects of compaction and salt precipitation from pore water generally have been omitted in discussions. In this study, we examine the WBD–carbonate relationship at IODP Site U1338 in the EEP. We measure the mass and carbonate content of sediment samples with known WBD before and after rinsing with de-ionized water. We also determine the relative proportion of coarse (>63  $\mu\text{m}$ ) particles. An appreciable mass loss and rise in carbonate content occurs in most samples upon rinsing, and these correlate to WBD. There is also a clear relationship between grain size and WBD. We present a model for these observations based upon first principles, and discuss the implications toward the generation of carbonate records in the EEP.

## 2. Site and samples

Integrated Ocean Drilling Program (IODP) Site U1338 is located at  $2^\circ 30.47'$  N latitude,  $117^\circ 58.18'$  W longitude, and a water depth of 4200 m below sea level (mbsl). The site comprises four holes: U1338A, U1338B, U1338C, and U1338D (Pälike et al., 2010a). When spliced together into a composite section, the holes provide a ~400 m thick, nearly continuous sediment sequence (Wilkens et al., 2013).

The sequence has been divided into three lithological units on the basis of the composition, physical properties and color reflectance of sediment (Pälike et al., 2010a). Lithological differences are principally related to variations in the amount of biogenic components. The two upper units, Unit I and Unit II, are of interest to this study. Unit I is approximately 50 m thick and accumulated from the middle Pliocene to the Holocene. It is composed of alternating, multicolored intervals of nannofossil ooze, diatom nannofossil ooze, and radiolarian nannofossil ooze. Unit II is approximately 194 m thick and accumulated from the late Miocene to the middle Pliocene. This unit comprises nannofossil ooze, diatom nannofossil ooze, nannofossil diatom ooze and radiolarian diatom ooze. In general, silica-rich intervals are more abundant in Unit II (Pälike et al., 2010a).

Discrete samples of sediment from Hole U1338A, nominally 1.5 m apart, were examined onboard for WBD (Figs. 1, 2; Pälike et al., 2010a). High-resolution GRAPE records, with measurements every 2.5 cm, exist at all four holes (Pälike et al., 2010a; Wilkens et al., 2013). These records have been “cleaned” in intervals showing sediment disturbance or incomplete recovery (Wilkens et al., 2013). At Site U1338 sediment disturbance through drilling was minimized in the upper ~240 m by using the advanced piston corer (APC; Pälike et al., 2010a). Moreover, there are shipboard and shore-based analyses of carbonate content on individual sediment samples. Over the upper 150 m of the sediment column, carbonates were measured in 105 samples from Hole U1338A (Pälike et al., 2010a), in 208 samples from Holes U1338A, U1338B and U1338C (Lyle and Backman, 2013), and 74 samples across two short intervals at Hole U1338B (Supplementary Table S1).

Shipboard inorganic geochemistry analyses on sediment from Holes U1338A and U1338B indicate that pore waters have a salinity very similar to that of seawater. Hence, at the site, pore water density is  $1.024\text{ g/cm}^3$ , which corresponds to a salinity of 35 g/L (Pälike et al., 2010a).

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