Orbital time scale and new C-isotope record for Cenomanian-Turonian boundary stratotype

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ABSTRACT

Previous time scales for the Cenomanian-Turonian boundary (CTB) interval containing Oceanic Anoxic Event II (OAE II) vary by a factor of three. In this paper we present a new orbital time scale for the CTB stratotype established independently of radiometric, biostratigraphic, or geochemical data sets, update revisions of CTB biostratigraphic zonation, and provide a new detailed carbon isotopic record for the CTB study interval. The orbital time scale allows an independent assessment of basal biozone ages relative to the new CTB date of 93.55 Ma (GTS04). The $\delta^{13}C_{org}$ data document the abrupt onset of OAE II, significant variability in $\delta^{13}C_{org}$ values, and values enriched to almost −22‰. These new data underscore the difficulty in defining OAE II termination. Using the new isotope curve and time scale, estimates of OAE II duration can be determined and exported to other sites based on integration of well-established chemostratigraphic and biostratigraphic datums. The new data will allow more accurate calculations of biogeochemical and paleobiologic rates across the CTB.

Keywords: orbital time scale, Oceanic Anoxic Event II, Cenomanian-Turonian stratotype.

INTRODUCTION

The Cenomanian-Turonian boundary (CTB) interval is a widely distributed and well-preserved example of geologically rapid environmental and biotic change during an ancient greenhouse climate. The interval is characterized by major perturbations in oceanographic conditions (Oceanic Anoxic Event II or OAE II; Schlanger and Jenkyns, 1976), biogeochemical cycles (global organic carbon burial episode causing positive shift in $\delta^{13}C$ of organic carbon and carbonate: Arthur et al., 1985, 1988; Schlanger et al., 1987; Hayes et al., 1989) and macro- and microfaunas (extinctions among molluscs, planktic forams and nanoplankton: Leckie, 1985; Elder, 1989; Premoli-Silva et al., 1999; Leckie et al., 2002; Erba, 2004). Its distinctive chemostratigraphic signature offers a unique opportunity to improve understanding of sedimentological, geochemical, and paleobiological processes over large areas of the Cretaceous world. One of the key limitations in reconstructing such processes for geologically rapid but comparatively ancient events, however, is the quality of the available temporal framework. Efforts to develop a CTB time scale, and to estimate the duration of OAE II, have resulted in a significant range of values (≥320 k.y. to ≤ 960 k.y.). Such differences have important implications for the calculation of geochemical burial fluxes and rates of biotic change, and thus significantly impact interpretations of OAE II and the CTB biotic record. The purpose of this paper is to establish a comprehensive chronstratigraphic framework for the CTB stratotype in central Colorado and present a new high-resolution carbon isotope record for the CTB event in the stratotype area.

GEOLOGICAL BACKGROUND

An optimal site for development of a CTB time scale occurs in the Bridge Creek Limestone Member of the Greenhorn Formation in central Colorado. This interval and location are characterized by: 1) a reasonably conformable section (99% complete on Milankovitch time scales: Meyers and Sageman, 2004) represented by detailed sedimentological, geochemical, and paleontological data sets (e.g., Pratt et al., 1985; Elder, 1989; Dean and Arthur, 1998; Tsikos et al., 2004; Keller et al., 2004; Bowman and Bralower, 2005); 2) a well-developed macro- and microfossil biostratigraphic framework correlated to other regions of the world (e.g., Kennedy and Cobban, 1991; Cobban, 1993; Caron et al., 2005; Keller and Pardo, 2004); 3) a radiometric time scale based on ^{40}Ar-^{39}Ar dating of volcanic ash beds (bentonites) intercalated within the CTB section and confirmed by two independent labs (Obradovich, 1993; Kowallis et al., 1995); and 4) rhythmically bedded hemipelagic strata with an orbital signature quantified by advanced Fourier techniques (Sageman et al., 1997, Meyers et al., 2001). Although many of these attributes characterize CTB sections around the globe, only the central Western Interior includes all of them, strongly supporting the designation by Kennedy and Cobban (1991) and Kennedy et al. (2000) of a CTB stratotype in central Colorado.

Absolute time scales for the CTB interval and duration estimates for OAE II have been based on radiometric dates and cyclostratigraphic analysis of rhythmic bedding features related to astronomical phenomena. Using these methods, previous studies have produced estimates of OAE II duration that vary by a factor of three. There are several reasons for the disparities. The most significant is the stratigraphic definition of OAE II, originally based on the occurrence of black shale facies and a distinctive carbon isotope excursion (Schlanger and Jenkyns, 1979; Tsikos et al., 2004). Although the C-isotope excursion is now the most widely accepted means of discriminating the event (because patterns of organic enrichment vary spatially), the excursion itself also differs in its geographic expression (e.g., Hasegawa et al., 2002; Tsikos et al., 2004; Keller and Pardo, 2004; Keller et al., 2004; Bowman and Bralower, 2005; Kolonic et al., 2005).

Additional reasons for time scale disparities concern the nature of available radiometric data, as well as assumptions and/or methods used in the development of orbital time scales for the CTB interval (e.g., Kauffman, 1995; Gale, 1995; Kuhnt et al., 1997). In this study, Obradovich's (1993) ^{39}Ar-^{40}Ar dates from CTB bentonites of the Western Interior (see also Kowallis et al., 1995) provided an in situ temporal framework. Although the 2004 Geologic Time Scale (Gradstein et al., 2004) recalculates Obradovich's (1993) dates using a new calibration age for the ^{39}Ar-^{40}Ar monitor mineral (Renne et al., 1998) to arrive at a revised age for the CTB (93.55 Ma: Fig. 1), this revision does not change duration estimates based on Obradovich (1993). To address the problems associated with assessment of orbital periodicity an evolutive spectral analysis technique was used (Meyers et al., 2001). This method corrects for variations in sedimentation rate and avoids a priori assumptions that any given orbital period is dominant.

NEW CTB C-ISOTOPE RECORD AND ORBITAL TIME SCALE

The stratigraphic succession of the CTB stratotype and point is excellently preserved in the USGS #1 Portland core. The marker bed designations of Cobban and Scott (1972) for limestones and Elder (1985) for bentonites (Fig. 1) provide a bed-for-bed correlation to the

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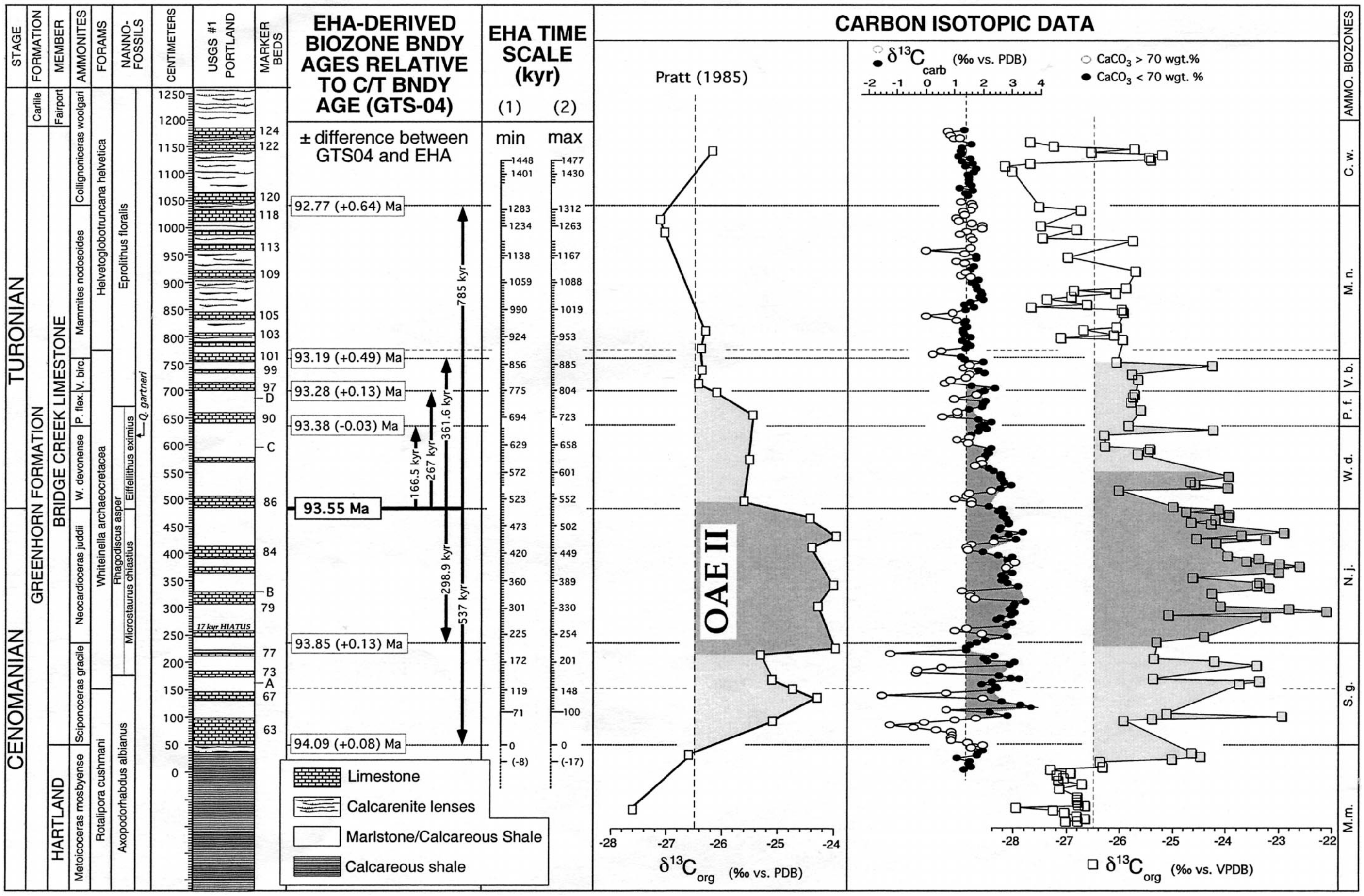

Figure 1. Chronology and C-isotope data for CTB stratotype documented in USGS #1 Portland core. Lithostratigraphy is shown with marker bed designations of Cobban and Scott (1972) for limestones and Elder (1985) for bentonites. Biozonation schemes include ammonites (Kennedy and Cobban, 1991; Cobban, 1993), planktic foraminifera (Leckie, 1985; Caron et al., 2005) and nanofossils (Bralower and Bergen, 1998); dotted lines mark ammonite biozones, dashed lines constrain *W. archaeocretacea* biozone; note FO datum for *Q. gartneri* (Tsikos et al., 2004). Two variants of orbital time scale based on EHA are shown; tick marks on radiometric and EHA time scale axes indicate spatial resolution of time control (see text for explanation). Biozone boundary ages are calculated using EHA time scale relative to CTB date from GTS-2004 (Gradstein et al., 2004); EHA-based biozone ages older than GTS2004 ages have positive differences. Carbon isotopic data compares $\delta^{13}C_{org}$ of Pratt (1985) from PU-79 core with new C-isotope data from #1 Portland core (open ovals—$\delta^{13}C_{carb}$ in limestones; solid ovals—$\delta^{13}C_{carb}$ in marlstones/shales; squares—$\delta^{13}C_{org}$ in marlstone/shale or limestone). PU-79 isotope record was correlated to #1 Portland stratigraphy using marker beds. Dashed line for background isotope values is average of data points above *P. flexuosum* and below *S. gracile* biozones.

well-known outcrop section at Rock Canyon. Bentonites A-D are indicated in Figure 1, but their thicknesses were removed for time scale construction—the geochemical data have been adjusted accordingly. Published macro- and microfossil biozones are also illustrated in Figure 1 (see figure caption for citations). Additional key biostratigraphic datums include the FO for *Quadrum gartneri*, which is placed in bed 89 (Tsikos et al., 2004), and the FO defining the base of the *Helvetoglobotruncana helvetica* zone, which is placed in the shale above marker limestone bed 101 (Caron et al., 2005). Keller and Pardo (2004) proposed a lower FO for *H. helvetica* (bed 89), but this range was not confirmed in earlier work (Eicher and Diner, 1985), nor could it be repeated by Caron et al. (2005) in their study of the Rock Canyon section. The latter authors hypothesize that the *H. helvetica* FO may be diachronous due to ecological effects and suggest it should not be used as a datum.

Carbon Isotope Data

Rock samples were taken at 5-cm spacing through the study interval in the #1 Portland core. Each sample was crushed to 200 mesh and represents homogenization of a 1-cm thick core segment. Isotopic measurements of whole-rock carbonate ($\delta^{13}C_{carb}$) were conducted on a Finnigan MAT 252 with automated common acid bath at 90°C. Sample splits were acidified (buffered acetic acid), washed in deionized water and repeatedly centrifuged, freeze dried, and analyzed by EA-irms on a Finnigan Delta +XP to produce $\delta^{13}C_{org}$ values (analyses performed at Stable Isotope Biogeochemistry Lab, Penn State University). All values are reported in per mil notation relative to VPDB (NBS 19 standard). The $\delta^{13}C_{org}$ data set has fewer values because some samples contained insufficient organic carbon for analysis. Randomly selected samples were run in duplicate or triplicate to test for sample variability; the reported data are averages. Analytical precision was within 0.1‰ (raw data available in the GSA Repository[1]).

To aid interpretation of the isotopic data, the curves are shaded. The core of the excursion, termed the plateau by Tsikos et al. (2004), is shaded dark. A lighter gray shades the excursion below the plateau, which corresponds to the ‘‘A’’ peak of Pratt (1985), as well as the post-plateau zone of relatively enriched values. Using a ‘‘return to back-

[1]GSA Data Repository item 2006026, raw isotope data, is available online at www.geosociety.org/pubs/ft2006.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

ground'' reference line defined by the average of values overlying the *P. flexuosum* biozone, $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ records show positive excursions of up to 2‰ and 4‰, respectively. The onset of the $\delta^{13}C_{org}$ excursion is very rapid. It predates the base the Bridge Creek Limestone by 30 cm and appears to precede the onset of the $\delta^{13}C_{carb}$ excursion. However, a clear signal of diagenetic alteration is reflected in the comparatively depleted $\delta^{13}C_{carb}$ values of many limestone beds, and may obscure the onset of the $\delta^{13}C_{carb}$ excursion (see also Bowman and Bralower, 2005). A one-to-one comparison of $\delta^{13}C_{org}$ in the new curve and the Pratt (1985) curve shows excellent correlation, but the higher resolution data capture significantly greater variability and a number of the new $\delta^{13}C_{org}$ values are much more enriched than the Pratt (1985) data. Based on the occurrence of enriched $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ values, the expression of OAE II in the Western Interior could extend as high as the *V. birchbyi* biozone. A conservative estimate corresponding to the end of the ''plateau'' would be placed just below the middle of the *W. devonense* zone (Fig. 1).

Orbital Time Scale

Empirical identification of specific orbital periods and construction of an orbital time scale for the CTB interval (Meyers et al., 2001) were accomplished as follows: 1) a high-resolution pixel (grayscale) data series from the #1 Portland core with sampling frequency sufficient to assess the full range of potential orbital periods was used (spatial resolution $<$ 1mm; pixel record available upon request); 2) the pixel data were analyzed for frequency content with the multi-taper method (MTM) of Thomson (1982). This Fourier technique offers superior evaluation of short, noisy geological time series, including a statistical test for the relative significance level of individual harmonic components. 3) Spatial bedding frequencies between bentonites A and B were converted to periodicities using sedimentation rates calculated from the average ^{40}Ar-^{39}Ar ages of Obradovich (1993) and Kowallis et al. (1995) (note that recalibration of ages does not change durations between bentonites). The orbital signature was calibrated by recalculation of the temporal frequencies following adjustment of the strongest signal in the time series (81 k.y. based on Obradovich's [1993] dates; 98 k.y. based on Kowallis et al.'s [1995] dates) to the calculated value for the closest Late Cretaceous eccentricity period (95 k.y.; Berger et al., 1992). This calibration resulted in the other dominant measured orbital periods matching predicted values within errors of 1% to 7%. 4) Stratigraphic variability in spatial bedding frequencies throughout the study interval was quantified using an evolutive application of the MTM (Evolutive Harmonic Analysis or EHA; Meyers et al., 2001).

The EHA approach is critical for accurate construction of an orbital time scale because it allows the temporal significance of changes in sedimentation rate, as well as hiatuses, to be quantified (Meyers and Sageman, 2004). Tracking stratigraphic changes in the most statistically significant (95 k.y.) frequency using EHA allowed a high-resolution sedimentation history to be reconstructed. Numerical integration of the sedimentation rate curve produced the high-resolution time scale shown in Figure 1. The ticks on the EHA time scale designate points with at least an 80% significance level for the spectral estimate of the eccentricity tracking component (although this component generally has a significance better than 90%); temporal values are arbitrarily shown every 50 cm; the gaps in the ticks marks reflect intervals for which the significance level was less than 80%. The orbital time scale is an independent temporal estimate; radiometric data were used to calculate candidate sedimentation rates for conversion of prominent peaks in the MTM spectra to periodicities, but the time scale was determined by the spectral analysis procedure.

Due to the nature of the EHA moving window approach, the orbital time scale begins 60 cm above the base of the Bridge Creek Limestone Member. To estimate the duration of the OAE II interval from the base of the $\delta^{13}C_{org}$ excursion, two methods were used. These methods rely on slightly different assumptions resulting in time scales that are minimum (EHA-1) and maximum (EHA-2, Fig. 1) estimates. Each EHA time scale includes the 17 k.y. hiatus identified by EHA at 2.65 m (Meyers and Sageman, 2004). EHA-1 was calculated assuming that the sedimentation rate at 1.1 m (0.84 cm/k.y.) is characteristic of the lower 60 cm of the Bridge Creek Limestone and results in a duration of 71 k.y. for the basal portion of the member. EHA-2 is based on the observation that the basal limestone (bed 63 or ''LS 1'') separates into about 5 distinct beds at several localities in the basin (Sageman, 1991), suggesting it may represent a condensed eccentricity cycle. If true, the lower 60 cm of the Bridge Creek Limestone represents about 100 k.y. (EHA-2, Fig. 1). The $\delta^{13}C_{org}$ excursion begins about 30 cm below the Bridge Creek Limestone in the Portland core (Fig. 1). Radiometric dates from bentonites within a few meters of the base and top of the Hartland Shale (Obradovich, 1993) suggest an average sedimentation rate of 2.76 cm/k.y. for this interval. Using this value and a maximum error of $\pm$1 cm/k.y., the upper 30 cm of the Hartland Shale Member is estimated to represent $\sim$8 to 17 k.y.

CONCLUSIONS

The Western Interior stratotype will continue to be a key global reference point for studies of the CTB and OAE II because of its superior chronostratigraphic control. The new orbital time scale presented herein can be exported to other CTB sections using chemostratigraphic or biostratigraphic methods and it should complement efforts to constrain time in the CTB interval at other localities. At the stratotype, initiation of OAE II is abrupt and constitutes an excellent datum, but its termination is more gradual and thus harder to define. Using our minimum and maximum time scales, the duration of OAE II to the new ''end of plateau'' point in central Colorado (5.5 m) is 563 to 601 k.y. A less conservative estimate that includes all significantly enriched $\delta^{13}C_{org}$ values, and considers the protracted return of the $\delta^{13}C_{carb}$ curve to a ''background'' value of 1.4‰ (the average of values above 7.5 m), extends OAE II up to the *V. birchbyi* zone (7.5 m) and represents 847 to 885 k.y. The orbital time scale also allows estimates of biozone boundary ages relative to the CTB boundary age reported in the 2004 Geologic Time Scale (Gradstein et al., 2004). These biozone age estimates can be compared with those determined by radiometric interpolation methods such as spline fitting (Fig. 1). Predictably, they show increasing disparity with ages based on interpolation as the distance from dated bentonite horizons increases (upsection).

ACKNOWLEDGMENTS

Parts of this study were funded by the National Science Foundation (grant EAR-0001093). The authors gratefully acknowledge sample contributions from the #1 Portland core (U.S.G.S. Core Research Center, Denver) and the support of Dr. Walter Dean. Constructive reviews of the manuscript were provided by Wolfgang Kuhnt, Elisabetta Erba, and two anonymous reviewers, and are greatly appreciated.

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Manuscript received 16 July 2005
Revised manuscript received 24 October 2005
Manuscript accepted 25 October 2005

Printed in USA