Magnetic record of Milankovitch rhythms in lithologically noncyclic marine carbonates

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ABSTRACT

Rock magnetic variations record cyclicity within lithologically homogeneous basinal lime mudstones of the Lower Cretaceous San Angel Limestone, northeastern Mexico. Variations in ferromagnetic mineral concentrations, as measured by anhysteretic remanent magnetization (ARM), occur at frequencies consistent with Milankovitch orbital rhythms. Magnetic mineral compositions, grain-size distributions, and grain shapes from digested samples are congruent with far-traveled atmospheric dust. Prevailing winds and the proximity of the Cretaceous basin to an African eolian source support the encoding of orbitally modulated changes in wind intensity or source-area aridity. ARM measurements offer great potential to calibrate the pace of depositional processes in carbonates and to investigate high-frequency orbitally driven climate change in basinal strata throughout geologic time.

Keywords: rock magnetics, Milankovitch theory, carbonates, anhysteretic remanent magnetization, paleoclimate.

INTRODUCTION

Outer shelf to deep-ocean sedimentary rocks are excellent recorders of paleoenvironmental change because of their ubiquity, temporal stability, and continuity, but the absence of detailed chronologies leaves many of these data underutilized. Some marine successions display climatically controlled lithologic or biologic variations characterized by visually obvious changes in rock type, color, bioturbation, sedimentary structures, and/or organic matter, that are unraveled by time-series analyses of the varying characteristics (see discussions in Shackleton et al., 1999; Hinnov, 2000; D'Argenio et al., 2004). Many deeper marine carbonate successions, however, lack obvious lithologic or biogenic variations that can be measured from outcrop or core, but still may contain important paleoenvironmental records beneath a monotonous veneer.

Rock magnetics provide a high-resolution tool for detecting environmental change from decadal to orbital time scales (Maher and Thompson, 1999). Within marine carbonates, changes in magnetic mineral concentration can be externally driven and reflect changes in detrital influx, variations in carbonate content (dilution), or diagenesis (von Dobeneck and Schmieder, 1999). Magnetic susceptibility (MS), a commonly measured bulk-rock property, integrates the concentration of diamagnetic, paramagnetic, and ferromagnetic grains. MS is often used as a proxy for varying carbonate content and has been interpreted to reflect changes in climate (e.g., Mayer and Appel, 1999; Kashiyama et al., 2003). In carbonates, MS is dominated by calcite, muting variation in paramagnetic and ferromagnetic concentrations, which are known climate proxies. Anhysteretic remanent magnetization (ARM), a measurement of the concentration of fine-grained (<20 μm) ferromagnetic minerals, is insensitive to carbonate concentration and thus can elucidate climate change in carbonate rocks. We used ARM to identify and track orbital-scale climatic change in visually noncyclic carbonates. Identification of Milankovitch cycles (Milankovitch, 1941) allows precise stratigraphic correlation and accumulation rate determination.

GEOLOGIC SETTING

In northeastern Mexico, platform and shelf deposits accumulated from the Late Jurassic to middle Cretaceous with the opening of the Gulf of Mexico (Longoria, 1998). The units were deformed during the Late Cretaceous–Tertiary Sevier-Laramide orogeny and crop out within large-scale décollement folds within the Sierra Madre Oriental fold belt (Humphrey, 1956). At Cerro de la Silla anticline, a 2-km-thick Mesozoic succession is exposed in La Boca Canyon (Fig. 1). Here, the San Angel

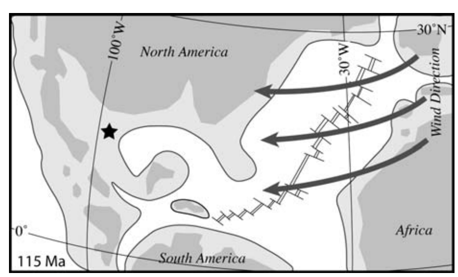

Figure 1. Paleogeographic reconstruction of Atlantic during middle Cretaceous. Star denotes field site in northeastern Mexico, shallow marine (light gray) and land (dark gray). Arrows denote trade winds from African continent at 115 Ma. Figure modified from Scotese et al. (1989).

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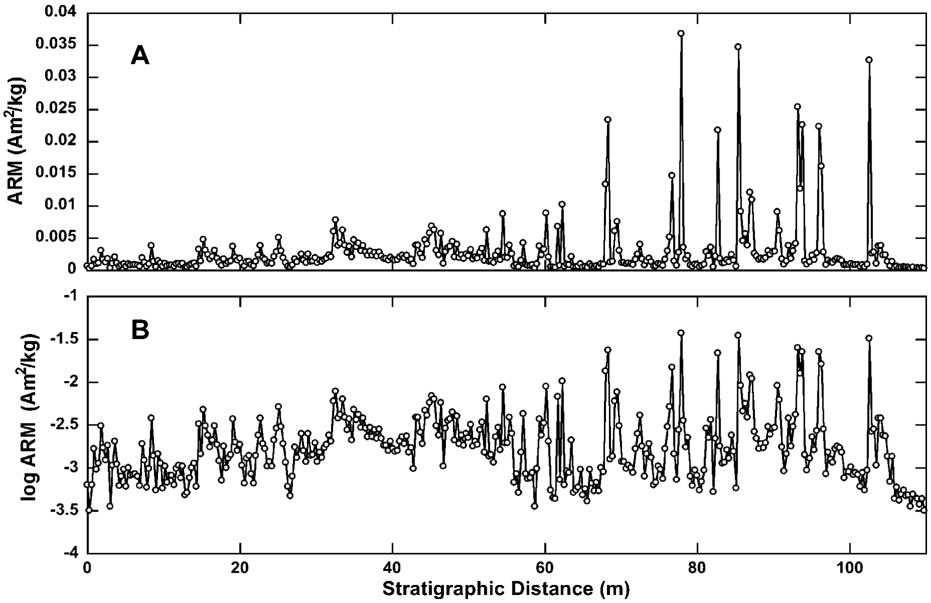

Figure 2. A: Anhysteretic remanent magnetization (ARM) data for homogeneous basinal deposits of San Angel Limestone, La Boca Canyon, Mexico. B: Log-transformed ARM values used in time-frequency analysis to stabilize section variance.

Limestone conformably overlies the Barremian La Casita Formation and conformably underlies the Aptian La Peña Formation. The San Angel Limestone is composed of thick-bedded lime mudstones with rare chert nodules, nannofossils, and planktonic foraminifera (Bralower et al., 1999). The San Angel Limestone accumulated just prior to the globally correlated ocean anoxic event 1a (e.g., Bralower et al., 1999) and was chosen because of the occurrence of well-documented Milankovitch cycles in the coeval nearshore upper Cupido Formation. (e.g., Goldhammer et al., 1991).

MAGNETIC METHODS AND RESULTS

To test for orbitally influenced climate changes in the San Angel Limestone, 110 m were described and sampled at 30 cm intervals to capture a precession index signal. We collected 367 unoriented samples, hand crushed them to granule-size pieces, and weighed them in 8 cm^3 paleomagnetic boxes. ARM was acquired in a peak alternating field of 100 mT and a DC field of 0.1 mT on Lehigh University's superconducting rock magnetometer. Mass normalized ARM measurements vary periodically between 3.7×10^{-2} and 3.1×10^{-4} Am^2/kg (Fig. 2A). Variations in ARM are due to differences in ferromagnetic mineral content, of either detrital (e.g., riverine, eolian) or diagenetic origin (e.g., chemical or thermal remagnetization, microbial mediated sulfate precipitation, bacterial magnetosomes). Each of these possibilities results in characteristic magnetic mineralogies, grain sizes, and shapes. Ferromagnetic and paramagnetic mineralogies were identified in eight samples on the Magnetic Properties Measurement System (MPMS) at the Institute of Rock Magnetism. The magnetic moment of samples, acquired in a 2.5 T field at 20 K, was measured at 5 K increments while heated from 20 K to 300 K in a 0 T field. A second 2.5 T field application at 300 K was followed by cooling back to 20 K in the presence of a 0 T field. Magnetic grain size of the ferromagnetic grains and relative proportions of diamagnetic and ferromagnetic grains in 13 samples were determined using a vibrating sample magnetometer where the field varied between 1.0 and −1.0 T. Magnetic hysteresis parameters for 13 samples reveal contributions from a diamagnetic component. After removing the diamagnetic contribution, hysteresis loops indicate the presence of a single low-coercivity ferromagnetic mineral population. An analysis of the ratio of saturation remanence to saturation magnetization versus magnetic coercivity reveals a dominance of pseudo–single domain size grains (0.1–20 μm). Low-temperature MPMS experiments reveal a sharp transition at 100 K, upon cooling from 300 K to 20 K, interpreted to be the Verwey transition, indicating the presence of fine magnetite in 7 of the 8 samples.

To better understand the magnetic remanence, isothermal remanences (IRMs) were imparted using three orthogonal fields on a sample that displayed high ferromagnetic mineral concentrations (X—0.1 T, Y—0.6 T, and Z—1.2 T). The sample was progressively thermally demagnetized in 50 °C to 10 °C steps from 100 °C to 600 °C (e.g., Lowrie, 1990). Demagnetization results reveal that the 0.6 T IRM has a Curie temperature of 580 °C, indicative of fine-grained magnetite, and results show a small contribution from a high-coercivity (1.2 T) magnetization, which is not detectable by ARM measurements, and therefore does not affect our results. Demagnetization results also indicated that the low-coercivity magnetization (0.1 T) has an unblocking temperature at 350 °C, consistent with a sulfide mineral, possibly greigite, common in marine environments. However, ratios of the saturation isothermal remanent magnetization to magnetic susceptibility ranging from 4940 to 9390 for 4 samples with relatively high ARM values are well below those expected for greigite (∼70,700) (e.g., Peters and Dekkers, 2003).

Scanning electron microscope (SEM) images of magnetic grains collected from HCl-insoluble residues were used to characterize ferromagnetic grain morphology and size. SEM and energy-dispersive X-ray analysis (SEM/EDX) of an ∼100 μm view revealed an average grain size of 3.3 μm. Some grains are coated with quartz cement, suggesting a detrital rather than diagenetic origin. Sulfide minerals were not observed, nor were grain textures indicative of bacterial magnetosomes (e.g., Bazylinski, 1996).

TIME-SERIES ANALYSIS

Time-frequency analysis of the ARM data series was used to explore the astronomical theory of climate change and to determine if variations in the magnetic data contained periodicities consistent with those for the Early Cretaceous (e.g., Park and Herbert, 1987; Grippo et al., 2004). Cyclic components suggestive of orbital forcing have been tracked as far back as the early Mesozoic (case studies in De Boer and Smith, 1994; Shackleton et al., 1999; D'Argenio et al., 2004). Eccentricity frequencies are thought to have remained constant through geologic time, whereas obliquity and precession frequencies are dynamic and time variable. In particular, tidal friction in the Earth-Moon system may have slowed Earth's rotation rate over time, effectively slowing the precession rate and thus lengthening the effective periods of obliquity and precession (e.g., Berger and Loutre, 1994). In the Early Cretaceous, these orbital frequencies were ∼10% shorter than the present. The ARM values were log-transformed in order to stabilize the variance between the bottom and top of the section (Fig. 2B) and analyzed using the multitaper method provided in the program Analyseries 1.2 (Paillard et al., 1996). The multitaper window was set to 2π to maximize spectral estimator resolution while maintaining suitable confidence levels. A linear trend was estimated and removed, the data were normalized to unit variance, and then linearly interpolated and resampled every 0.1 m. The

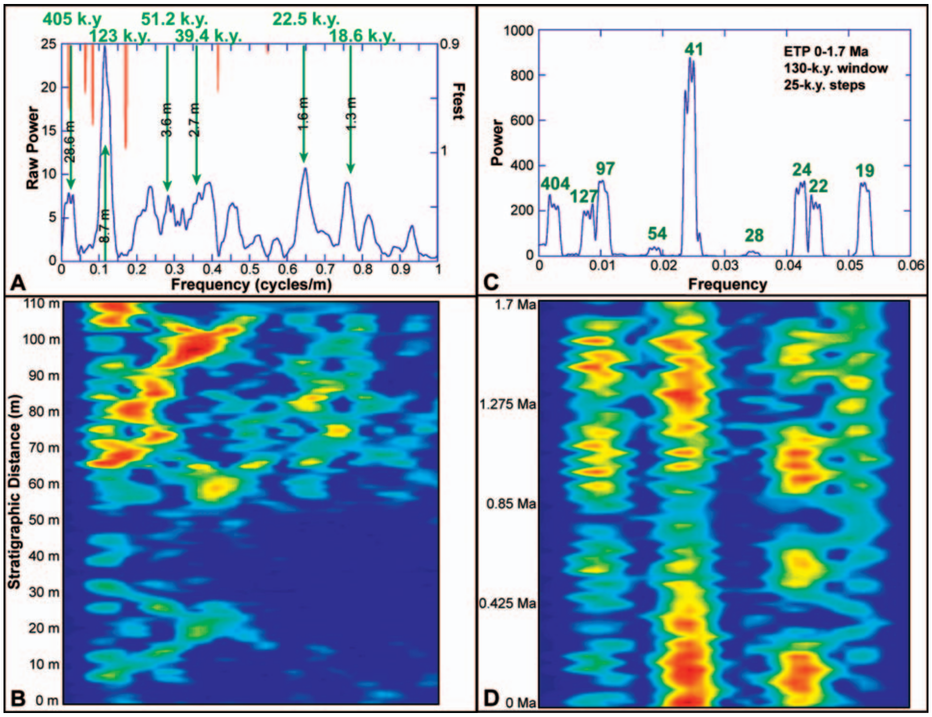

Figure 3. Time-frequency analysis of log-transformed anhysteretic remanent magnetization (ARM) series from San Angel Limestone records variations in ferromagnetic mineral concentrations consistent with Cretaceous orbital periodicities. A: 2π multitapered power spectrum of log-transformed ARM series. B: Spectrogram of ARM data over a moving 9 m window at 0.5 m steps shows stability of ARM frequencies. "Doublet" patterns in interpreted precession index band are similar to those of orbital models (e.g., D). C: 2π multitapered power spectrum of Earth's orbital parameters (Laskar et al., 2004) (e.g., Imbrie et al., 1984). D: Spectrogram of orbital parameters taken over moving 130 k.y. window at 5 k.y. steps, illustrating "doublet" pattern of precession index.

ARM data were analyzed using the harmonic F-test to investigate sinusoidal components with >90% significant contribution to the spectral power.

The significant peak at the lowest frequency on the spectral plot was interpreted as the Cretaceous long eccentricity (Laskar et al., 2004) (Fig. 3A). Assignment of the 405-k.y.-long eccentricity period at 0.035 cycles/m calibrates the other spectral peaks to the 123 k.y. eccentricity band at 0.115 cycles/m, the 51.2 k.y. and 39.4 k.y. obliquity band at 0.278 cycles/m and 0.370 cycles/m, respectively, and the 22.5 k.y. and 18.6 k.y. precession index band at 0.625 cycles/m and 0.769 cycles/m, respectively. The calibration results in an average sediment accumulation rate of 7 cm/k.y. for the1.6 m.y record.

Spectrogram analysis corroborates the assignment of the orbital frequencies, highlights the stability of the eccentricity periodicities throughout the measured section, and reveals an increase in strength and stability of the interpreted precession index components in the upper 50 m of the section (Fig. 3B). The ''doublet'' pattern in the ARM spectrogram in the precession index band mimics a similar pattern in frequency modulation of the precession index (Fig. 3D). On the other hand, where the nominal obliquity variation is predicted to be sustained by a predominantly single-frequency signal with a long-term (1.3 m.y.) amplitude modulation, the ARM spectrogram shows only sporadic occurrence of power in the obliquity band, at 20 m, 60 m, and 100 m (i.e., every 570 k.y.). In addition, the interpreted eccentricity components maintain constant strength, although there is a power shift to higher frequencies in the upper 20 m of the section that could explain some of the power in the obliquity band and indicate a slowing of accumulation.

DISCUSSION

Quasi-periodic variations in ARM, but not MS, data suggest concealment of paramagnetic and ferromagnetic mineral concentrations by calcite; thus, ARM is a better climate proxy than MS measurements in carbonates (Latta, 2005). The ARM spectral analysis supports the predictions for Cretaceous Milankovitch periodicity of Berger and Loutre (1994). The ARM series resolves long and short eccentricity, obliquity, and precession index components. The presence of a 123 k.y. cycle and absence of the predicted 95 k.y. cycle are probably due to the short duration of the series. The power spectrum of the Earth's orbital parameters over the past 1.7 m.y. (Fig. 3C) shows barely separable short eccentricity components. Given the documented variation in accumulation rates (Fig. 3B), the peak at 0.115 cycles/m may represent a mix of the two short eccentricity components in the ARM data. The sporadic appearance of power in the obliquity band is inconsistent with the predicted obliquity variation. Instead, these could be expressions of locally increased accumulation rates dilating several precession-scale cycles into the obliquity band, or decreased rates squeezing an eccentricity cycle into the obliquity band. The timing of the two peaks in the precession index band at 22.5 k.y. and 18.6 k.y. periods supports predictions for an ~10% faster precession rate in the Early Cretaceous and corroborates similar results from the Albian of Tethys (e.g., Park and Herbert, 1987).

The calculated accumulation rate (7 cm/k.y.) is twice as fast as the rates estimated by Clement et al. (2000) using magnetostratigraphy, which averages deposition in both the San Angel Limestone and the overlying La Peña Formation during chrons CM0–CM7. Our results highlight the ability of rock magnetic data to generate higher-resolution chronological records than traditional magnetostratigraphic studies.

Rock magnetic measurements and SEM analyses allow characterization of the ferromagnetic grains. Hysteresis parameters, low-temperature magnetic measurements, and thermal demagnetization of three orthogonal components of IRM indicate that the ARM is recording concentration variations of fine-grained magnetite. In a paleomagnetic study of the Lower Cretaceous in the Sierra Madre Oriental fold belt, Clement et al. (2000) recorded as many as three components of magnetic remanence; a high-unblocking-temperature component (350–560 °C) carried by primary, low-coercivity, magnetite grains, an intermediate-unblocking-temperature component (300–530 °C) carried by secondary, high-coercivity, sulfide minerals, and a low-unblocking-temperature component (<300 °C) indicative of a modern viscous magnetic overprint that is not related to growth of secondary magnetic minerals. ARM is insensitive to high-coercivity minerals and is not affected by a viscous magnetization overprint. Lowrie's (1990) experiments indicate that the magnetic sulfide only contributes a small percentage of the overall remanence (Latta, 2005). Thus, our ARMs are a direct measurement of the high-unblocking-temperature remanence-carrying magnetite grains, which we interpret to reflect a primary depositional signal.

SEM/EDX images of the magnetite grain shapes and detection of quartz coatings on many of the grains are consistent with weathered detritus and not diagenetic growth. Magnetite grain sizes, interpreted from rock magnetic data and measured by SEM (average 3.3 μm), are consistent with far-traveled atmospheric dust (e.g., Pye, 1987; Sun et al., 2002). North Atlantic Deep Sea Drilling Project cores (387, 391C, and 367) contain Lower Cretaceous eolian dust transported from northwestern Africa (e.g., Dean and Arthur, 1999). Chester et al. (1972) reported that 88% of atmospheric dust samples within modern equatorial Atlantic deposits contain particles <4 μm. Currently, Sahara dust is blown across the Atlantic to places throughout the Americas (e.g., Thompson et al., 1995; Goudie and Middleton, 2001).

CONCLUSIONS

Spectral analysis of ARM measurements of the basinal lime mudstones of the Lower Cretaceous San Angel Limestone in La Boca Canyon reveal Milankovitch cycles encoded as variations in ferromagnetic mineral concentrations. Data suggest a single population of magnetite grains that have sizes and shapes most consistent with that of far-transported atmospheric dust whose abundances fluctuate to changes in wind intensity or source-area aridity. ARM measurements are a powerful but underutilized tool for detecting paleoenvironmental change in carbonates. Variations in magnetic mineral composition and grain sizes can distinguish depositional and diagenetic processes related to climate change at orbital time scales, providing an additional paleoenvironmental proxy in otherwise homogeneous strata. Identification of orbitally controlled sedimentary cycles within deeper water carbonates allows for high-resolution stratigraphic correlations between proximal nearshore and basinal deposits, precise determinations of sediment accumulation rates, and the possibility of timing the durations of distinct paleoenvironmental and paleoecological events.

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