High-resolution stable isotope records from the Upper Cretaceous rocks of Italy and Spain: Glacial episodes in a greenhouse planet

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ABSTRACT

High-resolution δ13C and δ18O records from upper Albian to lower Santonian pelagic carbonates of the Contessa Quarry section in Italy exhibit large positive oxygen isotopic excursions of ~1‰ in the lower Cenomanian and upper Turonian–Coniacian strata. Within the uncertainties of biostratigraphic correlation, these positive excursions appear to correspond to times of large sea-level regressions in global sequence stratigraphic sea-level curves. Several lines of evidence suggest that the major δ18O excursions in Contessa reflect episodes of global cooling and not differential diagenesis. Numerical models of oxygen isotope exchange during diagenesis show that a high contrast in the degree of alteration would be required to produce these signals as artifacts of diagenesis, and lithological data provide no evidence for such large contrasts in the degree of alteration. Furthermore, although precise correlation with a section in the south of Spain is hampered by stratigraphic complexities, the general sequence of major positive δ18O excursions is reproduced. It is unlikely that differential diagenesis would produce similar artifacts in multiple sites. One explanation for the link between episodes of global cooling and sea-level falls is that global cooling events led to polar ice-sheet accumulation, lowering sea level. Although ice-free conditions in Cretaceous time and the potential for periodic episodes of glaciation.

INTRODUCTION

The longstanding view of Cretaceous time as a period of warm and equable climate presents a paradox in light of sequence stratigraphic evidence for rapid sea-level changes. Sequence stratigraphic sea-level curves for Cretaceous time infer multiple episodes of sea level falling and rising 50 to 100 m in <1 m.y. (Haq et al., 1987), while the warm Cretaceous climate is thought to have precluded the development of continental ice sheets, the only accepted mechanism for large global sea-level changes on such short time scales (Lisiecki et al., 1984; Schlanger, 1986). Paleontological evidence for Cretaceous warmth includes the poleward expansion of floral provinces and coral reefs by as much as 15° (Habicht, 1979; Vakhrameev, 1975), along with high-latitude occurrences of dinosaurs (Colbert, 1973) and diverse floral assemblages (Krassilov, 1981). Warm climates may have resulted from an enhanced greenhouse effect, as extensive Cretaceous volcanism and more rapid sea-floor spreading rates likely resulted in increased mantle outgassing of CO2 (Berner et al., 1983; Arthur et al., 1985). These data, typically with resolution of 1–20 m.y., document the overall warmth of the Cretaceous Period. Only recently has higher resolution paleoceanographic work begun to explore climatic variability over time scales of several million years and less (e.g., Jenkyns et al., 1994; Weisert and Lini, 1991, Kemper, 1987).

In this study we used high-resolution stable isotope data to investigate the variability of Cretaceous climate and its relation to eustatic sea-level changes. In particular, we investigate whether the amplitude of climatic variability in the Cretaceous may have been sufficient to facilitate periodic formation of polar ice sheets during brief episodes of climatic cooling, which in turn may have caused the large rapid Cretaceous sea-level changes identified in the sequence-stratigraphic curve. We focus on the upper Albian to lower Santonian strata, believed to record the warmest time interval of the past 200 m.y., when the potential for polar ice caps may have been the most remote. Pelagic carbonate sediments from the Contessa Quarry section in Italy are ideal for high-resolution stable isotopic study because they accumulated continuously in a deep open-ocean setting, they are lithologically homogeneous, and tight biostratigraphic control facilitates correlation with the sequence-stratigraphic sea-level curve of Haq et al. (1987). Using data from the Contessa section, we show that eustatic sea-level regressions correlate with large positive δ18O excursions, which may record episodes of global cooling associated with ice ages. However, we also investigate the possibility that oxygen isotopic excursions result from differential diagenesis. Using numerical models of diagenesis, we assess the likelihood that differential alteration is responsible for the observed signals. Evaluating the reproducibility of the major isotopic variations in a second section from the south of Spain provides additional information on the role of diagenesis in generating the signals, as it is unlikely that diagenesis would produce the same artifacts in two different sites. We reevaluate the strength of evidence for ice-free conditions in Cretaceous time and the potential for periodic episodes of glaciation.

SITE SELECTION

Criteria for Extraction of Paleoclimate Information Using Stable Isotopes

The utility of oxygen isotopic variations in investigating Cretaceous climatic variability depends heavily on the characteristics of the section in which the isotopic measurements are made. As for most paleoclimatic studies, the section must be stratigraphically continuous through the interval studied, uninterrupted by faults, slumps, or folds, and without hiatuses. The section must also have good biostratigraphic control at relatively high resolution in order to correlate multiple sections and relate the oxygen isotopic data to the se-
quences stratigraphic sea-level curve. Biostratigraphy also enables the application of a numerical time scale to investigate the frequency and duration of climatic variations. To be suitable for oxygen isotopic study, the section must have relatively homogeneous lithology. Sharp contrasts in lithology may produce more complicated and less readily quantifiable diagenetic effects. For oxygen isotope study, the section should also represent exclusively pelagic sedimentation in a relatively deep environment, free of turbidites and neritic communities (which induce lithologic heterogeneity). More important, the section should also have remained a submerged environment of pelagic accumulation during syndepositional sea-level falls. In shallow sections, meteoric cements of more negative composition may precipitate when unconsolidated sediments are exposed by sea-level falls, drastically altering the isotopic record of climate change. Finally, the section should preserve primary variations in the isotopic composition of carbonates. Although unaltered carbonates of Cretaceous age are not likely to exist in any environment, in the past decade a number of studies have led to a quantitative understanding of the effects of early burial diagenesis on the elemental and stable isotopic composition of carbonates (e.g., Richter and DePaolo, 1987, 1988; Richter and Liang, 1993; Richter, 1996; Schrag et al., 1992, 1995). The consequences of diagenesis are best understood in sections that achieved most of their recrystallization and lithification in the sea-floor burial environment. During diagenesis, primary calcite dissolves and is replaced by secondary calcite, which forms in isotopic equilibrium with the sediment pore fluids; for the sea-floor burial environment, the equilibrium composition of secondary calcite can be predicted. Although recrystallization may shift the mean $^{18}$O value of carbonate by several per mil, making interpretations of absolute temperature meaningless, high-frequency variations will be preserved, although partially attenuated, as long as recrystallization rates are relatively uniform over moderate length scales (Schrag et al., 1992, 1995). Consequently, records of high-frequency changes in temperature and the $^{18}$O of seawater can be extracted from recrystallized carbonates, unless the oxygen of the carbonate has been completely exchanged with a fluid. The most difficult sediments for extraction of paleoclimatic information may be those that have undergone only minimal sea-floor burial diagenesis and lithification. Such sediments of high diagenetic potential (very susceptible to recrystallization), once exposed to surface conditions, may undergo more extreme alteration because even small amounts of recrystallization in meteoric or soil water environments may produce a large isotopic shift. This problem is evident in isotopic data collected from the Los Canutos section in Spain (Stoll, unpublished data), a section composed almost exclusively of nanofossils with negligible cement (R. Aguado, personal commun.). Portions of these highly reactive chalks have apparently exchanged heavily with soil waters and have highly variable carbon isotope compositions ranging from $-3\%$ to $+2.5\%$. Pee Dee belemnite. In contrast, lithified Cretaceous sediments 40 m upsection have carbon isotope values of $+1.5\%$ to $+2.5\%$, consistent with values in other sites of similar age.

**Previous Stable Isotopic Study of Upper Cretaceous Sections**

The most detailed published stable isotope study of Upper Cretaceous sediments is that of Jenkyns et al. (1994) on the carbon and oxygen isotope stratigraphy of the English Chalk and Bottacione section in Italy. The Bottacone section fulfills the criteria as an ideal section for application of oxygen isotopes to investigate climate, although the average sampling resolution of 1 m in Jenkyn’s study may not sufficiently define the most rapid climate variations. Unfortunately, in Jenkyn’s study, only the carbon isotope record of the Bottacone record is utilized, to document the potential of $^{13}$C variations as a correlative tool. Interpretation of climatic variations is derived exclusively from the oxygen isotope record of the English Chalk, which fails to meet several of the criteria described here. The chalk was deposited in a very shallow environment characterized by shallow benthic communities such as echinoderms, bivalves, and brachiopods, and sponge beds. The presence of erosion surfaces and hardgrounds may have resulted from subaerial exposure or lapses of sedimentation during sea-level lowstands. Episodic exposure of sediments during Cretaceous sea-level falls may also have subjected them to alteration by meteoric waters, resulting in localized precipitation of isotopically light cements. H. Jenkyns (1999, personal commun.) noted that lighter oxygen isotopic ratios in the English Chalk correspond with lowstands identified by sequence stratigraphy. The high reactivity of the exposed sediments may also make them susceptible to recent alteration by meteoric waters.

**Contessa Quarry Section, Italy**

The upper Albian to Santonian sequence of the Contessa Quarry section fulfills all of the aforementioned criteria as an ideal section for isotopic study. The Contessa Quarry and dirt road below the quarry, near the town of Gubbio in the Italian Apennines (Fig. 1), splendidly expose the upper Albian to Santonian Scaglia Blanca and Scaglia Rossa Formations. This exposure is free of faults or slumps and no hiatuses have been identified by detailed biostratigraphy. The section is carbonate rich, with CaCO$_3$ averaging 80%–90% over the studied interval (Arthur, 1979); silica is the dominant noncarbonate component in these sections. The average sedimentation rate for the section is 12 m/my., uncorrected for compaction. The sediments were deposited at depths of 1500–2500 m (Kuht, 1990) in an open Tethyan ocean setting and are free of turbidites. With the exception of the meter-thick organic-rich black shale of the Bonarelli Horizon and occasional centimeter-thick lenses of chert, the lithology is remarkably homogeneous thick- to thin-bedded limestones. Detailed lithological descriptions were given by Premoli-Silva and Sliter (1994) and Arthur (1977, 1979); the generalized lithology is presented along with the biostratigraphy in Figure 2. Numerous workers, beginning with Renz (1936), have studied the biostratigraphy of the sequence.

**Figure 1. Location of studied Contessa Quarry section near Gubbio, Italy, and Santa Ines section near Caravaca, Spain.**
The most recent detailed biostratigraphic study is the planktonic foraminiferal study of Premoli-Silva and Sliter (1994) on the Bottacione section ~4 km from the Contessa Quarry. We apply this biostratigraphic scheme to the Contessa section by translating the depths of biostratigraphic boundaries using the base of the Bonarelli horizon as a reference level. High-resolution biostratigraphy is facilitated by the small average sampling interval (0.75 m) in the Premoli-Silva and Sliter (1994) study.

We collected 1100 samples at intervals of 10 cm through the Cenomanian and Turonian and at 20 cm intervals in the upper Albian and Coniacian-Santonian strata for isotopic study. Recent quarrying provided fresh exposure and efforts were made to obtain the freshest material possible, away from veins and fractures and beneath the surface weathering rind.

Santa Ines Section, Spain

The Cenomanian to Santonian sequence of the Santa Ines section fulfills many of the criteria for ideal extraction of isotopic climate records, but stratigraphic complexities make the Santa Ines section less ideal for paleoclimate study than the Contessa section. We use this section to verify the major features seen in the isotopic data from the Contessa section. Cenomanian to Santonian sediments of the Capas Blancas and Capas Rojas Formations are exposed on steep slopes behind the Cortijo de Santa Ines ranch near the town of Caravaca in the Spanish Betic Cordillera (Fig. 1). Like the Contessa section, the Santa Ines section represents continuous pelagic carbonate-rich sedimentation in a deep setting (1500–2500 m; Kuhnt, 1990) in an open Tethyan ocean environment. The Santa Ines section is relatively uniform lithologically, consisting of nodular, thin- and thick-bedded limestones with occasional chert bands from the uppermost Cenomanian through the Coniacian strata (Fig. 3), but is much less siliceous than the Contessa section. The average sedimentation rate for the section is 10 m/m.y., uncorrected for compaction. Ferromanganese nodules are prevalent in the Cenomanian and early Turonian rocks, and siliciclastic turbidites are present at the base of the section. The section is much more poorly exposed than the Contessa Quarry and stratigraphically more complex. In several places, slumps and faults result in displacements of as much as a few meters in the section. No major hiatuses have been identified biostratigraphically. The resolution of biostratigraphy available for this site is much lower than for the Contessa section, with an average sampling distance of 8 m over the sampled interval. In addition, because of overgrowth and changing land use, we were unable to resample in the exact location where biostratigraphic data were collected. The section we sampled is ~75 m south of the biostratigraphic section. We relate the biostratigraphy to our section by correlating the stratigraphically highest chert layer, which induces a maximum uncertainty of 8 m due to a covered interval of 8 m thickness above the last chert in the section used for biostratigraphy. Samples were collected at intervals of 0.3–0.5 m in the Cenomanian strata, as exposure permitted; a
Figure 3. Generalized lithologic columns, biostratigraphy, and stable isotopic records from the Santa Ines section. Biostratigraphy is from Aguado (1994); ages of biostratigraphic zone boundaries are those of Haq et al. (1987). δ18O data represent a five-point running mean. Thickness of biostratigraphic boundaries reflects uncertainty given as the square root of the average biostratigraphic sampling interval. Lithologic symbols and abbreviations as in Figure 2.

METHODS

We measured stable isotopes of bulk carbonate, which facilitates rapid analysis of a large number of samples and requires very little sample material. Although less-altered microfossil components (e.g., foraminifera) are often selected in attempt to circumvent complications of diageneric, alteration in foraminifera separates may be nearly as extreme as in bulk sediments (Barerra et al., 1987). Furthermore, it is more difficult to quantify the extent of diagenetic alteration in foraminiferal tests than in bulk carbonate because the recrystallization rate cannot be calculated directly, as done by Richter (1996) for bulk carbonate. Analysis of bulk carbonate also facilitates rapid analysis of a large number of samples and requires very little sample material.

One concern often raised about the use of bulk carbonate is that different species show a range of vital effects, and as a result, bulk carbonate δ18O records may not perfectly record the temperature and δ18O of seawater where microfossil components are changing. However, changes in species composition, dissolution intensity, and relative abundance of nannofossils do not appear to obscure significant trends in the temperature and δ18O of seawater in bulk carbonate records. Comparisons of bulk carbonate and single species foraminiferal δ18O records have demonstrated that δ18O values of bulk carbonate accurately record changes in sea-surface temperature and δ18O of seawater over glacial cycles (Shackleton et al., 1993; Schrag et al., 1995). In the Contessa sediments, calcareous nannofossils contribute 90% of the carbonate (Arthur and Fisher, 1977). Different species of modern calcareous nannofossils are characterized by different vital effects on oxygen isotope fractionation (Dudley et al., 1980). However, in polycpecific assemblages of calcareous nannofossils, oxygen isotopic variations parallel those of monospecific planktonic foraminiferal in the surface ocean photic zone. assemblages during Pleistocene time (Steinmetz and Anderson, 1984; Anderson and Steinmetz, 1981; Anderson and Cole, 1975) and for most of Cenozoic time (Margolis et al., 1975) despite changes in the abundance of the dominant taxon.

Isotopic data were collected on a gas source mass spectrometer at Princeton University and Harvard University. Approximately 2 mg of bulk sediment was loaded into a stainless steel capsule and placed in a drying oven for 48 hr at 50 °C. Samples were dissolved on line in a common acid bath of orthophosphoric acid at 90 °C. Precision (1 σ) averages 0.07‰ for oxygen and 0.05‰ for carbon.

STABLE ISOTOPIC DATA

The carbon and oxygen isotopic results for the Contessa section are shown in Figure 2. The carbon isotopic record is characterized by maximum δ13C values in a broad positive excursion during late Cenomanian and early Turonian time, as well as multiple positive δ13C excursions of 0.5‰–1.5‰, lasting 0.5–2 m.y. The pattern of carbon isotopic variation is observed in a number of Cretaceous sections (e.g., Jenkyns et al., 1994; Gale et al., 1993) and its reproducibility in Contessa is further confirmation of the completeness of the Contessa section.

The oxygen isotopic record is characterized by a long-term decrease from late Albian to middle Turonian time. Several positive excursions of 0.75‰–1.5‰ over 0.5–1 m.y. are superimposed on pervasive higher frequency, lower amplitude variations. A plot of smoothed δ18O records shows these excursions more clearly (Fig. 2). A large 1.5 m.y. positive excursion is seen in the lower Cenomanian record. The middle Cenomanian through middle Turonian interval is one of relatively stable δ18O ratios, followed by a pair of prominent positive δ18O excursions of ~1‰ in the upper Turonian–Coniacian interval. Several smaller excursions of 0.5‰ follow in the lower Santonian interval.

The δ18O record is compared with the sea-level curve of Haq et al. (1987) in Figure 4. The two records appear to exhibit similar patterns of variations, although precise correlation of the records is uncertain due to complications of biostratigraphy. In particular, there is uncertainty about how well the facies defining onlap and offlap records can be correlated to planktonic foraminiferal zonations. In general, positive δ18O excursions appear to correspond to sea-level regressions in the Haq curve, and periods of more stable δ18O ratios correspond to more constant sea level. The δ18O excursion at the top of the R. brotzeni zone and bottom of the R. cushmani zone may correspond to the large sea-level fall at the bottom of the R. cushmani zone in the sea-level curve. The up-
per *R. cushmani* through upper *H. helvetica* zones, which contain no major regression events, contains no major excursions in the $\delta^{18}$O record. The largest $\delta^{18}$O excursions in the *M. sigali* and lower *D. concavata* zones may correspond to the largest sea-level regressions in the upper *H. helvetica* and *M. sigali* zones. Smaller sea-level falls during the *R. breggiensis* to *R. reicheli* zones may have counterparts in the oxygen isotope curve, but these signals are difficult to identify because this time interval is characterized by lower isotopic sampling resolution and smaller excursions are more difficult to separate from the longer term trends in the $\delta^{18}$O record. Early Santonian time, a second period of more constant sea level in the Haq curve, is characterized by higher amplitudes and more rapid $\delta^{18}$O fluctuations than the late Cenomanian period of stable sea levels.

We do not observe any strong correlation between our carbon isotopic record and the sequence stratigraphic sea-level curve, or between the carbon isotopic record and oxygen isotopic records of Contessa where there is no uncertainty due to correlation (Fig. 2). Although the early Cenomanian oxygen isotopic excursion corresponds to lower carbon isotopic values, the late Turonian to earliest Santonian excursions correspond to positive $\delta^{13}$C excursions.

The carbon and oxygen isotopic results for the Santa Ines section are shown in Figure 3. Like the Contessa record, the Santa Ines record also contains several positive carbon and oxygen isotopic excursions. In both the Contessa and Santa Ines records, the largest $\delta^{13}$C excursions are in the upper Cenomanian and uppermost Turonian strata. It is likely that the other major $\delta^{13}$C excursions are also reproducible in the two sections, but that the relationships are more difficult to recognize due to stratigraphic complexities and imprecision in the biostratigraphy of the Santa Ines section. The $\delta^{13}$C excursions over 100 k.y. are likely to be globally synchronous steady-state variations (e.g., Kump, 1991), and their reproducibility in numerous European and North American sites has been documented (e.g., Jenkyns et al., 1994; Gale et al., 1993). In the case of oxygen isotopic variations, it is impossible to evaluate the reproducibility of oxygen isotopic records between the Santa Ines and Contessa sites without a more detailed correlation of the two sites, which we undertake in a subsequent section.

**DISCUSSION**

**Relation of Stable Isotopic Excursions and Sea-Level Changes**

Despite uncertainties in the precise correlation of isotopic excursions and sea-level changes, the correspondence between the sea-level curve of Haq et al. (1987) and the oxygen isotopic record of Contessa is compelling. In particular, the correlation of regression events in the sea-level curve with positive oxygen isotopic excursions may indicate a link between climate and sea-level changes, possibly through control of sea level by buildup of continental ice sheets during episodes of climatic cooling. Apparent diachronies between sea-level changes and isotopic excursions in the Contessa record are generally half a biozone or less and likely result from problems in biostratigraphic correlation. The difficulties of correlation are underscored by a comparison of independently derived sea-level curves from the U.S. Western Interior (Weimer, 1984) and British region (Hancock, 1990). Although both curves are generally quite similar to that of Haq et al. (1987), the timing of events is often slightly diachronous because of problems with biostratigraphic boundaries. For example, the middle Turonian sea-level peak is half a biozone earlier in the Haq et al. record than in the British record, which Hancock (1990) attributed to problems with biostratigraphy. Furthermore, the dependence of the global sea-level curve on biostratigraphic correlation of multiple records of regional sea-level variations means that the global sea-level curve may not be capable of resolving sea-level events of very short duration (several hundreds of thousands of years) and may smooth over shorter composite sea-level events.

The lack of any systematic correlation between carbon isotopes and the sea-level curve is not...
likely to result from uncertainties in biostratigraphic correlation, but may reflect the complexity of numerous factors controlling the carbon isotopic ratio of seawater. Previous workers suggested that a buildup of ice sheets might also be responsible for a general correlation between sea-level lowstands and negative carbon isotopic excursions observed in pelagic sections from the Aptian of northern Italy (Weissert and Lini, 1991). However, the interpretation of positive carbon isotopic excursions as times of accelerated carbon cycling, increased atmospheric pCO₂, and warm climates, and negative excursions as times of decelerated carbon cycling, low pCO₂, and cooler climates, which may include ice ages, is probably oversimplified. Furthermore, in Cenozoic time, the opposite relationship is observed. Jenkyns et al. (1994) presented a detailed review of the issue, concluding that while there may be some links between sea level and the fraction of carbon burial in organic form, the mechanisms for such links are complicated and may be more closely tied to rates of transgressions than sea level per se. The relationship between climate and sea-level changes and the kinds of carbon cycle variations recorded by carbon isotopes require a more sophisticated analysis and probably more detailed modeling of the carbon cycle before it can be used to enhance our understanding of climate changes in Cretaceous time. Consequently, we focus on the oxygen isotopic record, which records climatic information directly, as the primary tool for investigating Cretaceous climate variations.

The correlation of sea-level regressions and positive δ¹⁸O excursions is what we would expect to see if sea-level regressions were caused by the buildup of continental ice sheets during episodes of climatic cooling. Alternatively, the isotopic excursions may record episodes of cooling without ice ages, in which case the correlation with sea-level regressions is merely coincidence, as there is no other reasonable mechanism for linking sea level and global climate on this time scale. A third possibility is that the positive isotopic excursions were caused by differential alteration of the sediments during diagenesis, and that the correlation with the sea-level curve is largely coincidence.

If the oxygen isotope variations do reflect primary climatic variations, it is not possible to distinguish whether ice-sheet buildup accompanied apparent episodes of global cooling in Cretaceous time on the basis of the oxygen isotopic evidence alone. It is likely that oxygen isotopic excursions are primarily due to large temperature changes and not large ice-volume effects. The ice-volume effect would have been minimal because with overall warmer Cretaceous temperatures, the isotopic composition of ice would have been less depleted than in Quaternary time, producing a smaller change in the δ¹⁸O of seawater for a given volume of ice. In addition, any Cretaceous ice-volume changes were probably smaller than late Cenozoic ice-volume changes. Consequently, the argument for Cretaceous ice ages rests on the assertion that it would be an unlikely coincidence that both multiple episodes of extreme cooling and large sea-level regressions, as well as time periods of relative climatic and sea-level stasis, would independently coincide for a 12 m.y. time interval. It would seem more likely that periodic ice ages would provide a mechanistic link between global cooling and sea-level regressions.

Fortunately, we can investigate more rigorously the possibility that the observed oxygen isotopic excursions are not records of primary climatic variations, but artifacts of differential alteration of sediments during diagenesis. We use two approaches to evaluate whether the positive δ¹⁸O excursions in the Contessa record represent primary climatic variations or whether they are likely due to differential diagenesis. In the first approach, we numerically model the consequences of diagenesis in the sediments to assess whether it is reasonable for the largest positive δ¹⁸O excursions to be produced through differential alteration of the sediments. Second, we test whether major isotopic excursions are reproduced at the Santa Ines site, as differential alteration is unlikely to be the same in multiple sites of differing sediment character and burial histories.

**Diagenetic Effects on Oxygen Isotopes in Deep-Sea Sediments**

Exchange of oxygen isotopes between carbonates and pore fluids can potentially alter the δ¹⁸O of carbonates during diagenesis. Following burial, primary calcite dissolves and is replaced by secondary calcite, which forms in equilibrium with the temperature and oxygen isotopic composition of sediment pore fluids. The δ¹⁸O of pore fluids is lower than that of seawater due to low-temperature alteration of the underlying basement rock. With increasing depth, the geothermal gradient elevates sediment temperatures above sea-surface temperatures recorded by planktonic carbonates. Consequently, the δ¹⁸O of secondary calcite is frequently more negative than the primary calcite. However, in low-latitude sites, bottom water and shallow pore-fluid temperatures are cooler than surface-water temperatures, and secondary calcite formed in the first few hundred meters of burial may have a δ¹⁸O higher than the primary calcite. In either circumstance, the extent to which the δ¹⁸O of primary carbonate is altered depends on the extent of carbonate recrystallization.

Carbonate recrystallization in deep-sea sediments does not proceed at a constant rate with progressive burial. Models of strontium exchange and transport in deep-sea sediments and pore fluids show that rates of bulk carbonate recrystallization decrease exponentially by 1–2 orders of magnitude within 10–20 m.y. following burial (Richter and DePaolo, 1987, 1988; Richter and Liang, 1993; Richter, 1996). These results also indicate that at different sites, carbonate sediments of the same age may recrystallize at different rates. The origin of different rates between sites presumably results from differences in the reactivity of the sediments but has not been rigorously evaluated.

As long as sediments from the same section are comparably reactive and follow the same trend of decreasing carbonate recrystallization rate with time, all will contain approximately the same amount of secondary calcite (the difference in amount of secondary calcite added between 86 and 98 Ma is minimal). Consequently, although the mean δ¹⁸O will have shifted, primary variations will be preserved, although partly attenuated. We demonstrate this scenario in the following section with a numerical simulation of the consequences of burial diagenesis on the oxygen isotope record of Contessa sediments.

Differential alteration of sediments within the section may result in a potentially more problematic consequence of diagenesis, the creation of high-frequency δ¹⁸O variations where none existed in the primary sediment. Such differential alteration would require variation in the character or reactivity of the sediments, so that for a given age, some sediments recrystallize more rapidly, and hence to a greater extent, than adjacent sediments. Schlanger and Douglass (1974) suggested that the reactivity, or diagenetic potential, of carbonate sediments is likely to be controlled by the relative contributions of different nanofossil and microfossil assemblages as well as by the amount of dissolution the sediment had undergone prior to burial. These lithological factors are known to vary between sites, and may explain the different average recrystallization rates measured by Richter (1996). It is also possible that these factors vary over short length scales within a single site, causing variation in recrystallization rates. In the following section we use a numerical model of diagenesis to investigate whether it is likely that the major δ¹⁸O excursions in the Contessa record resulted from differential diagenesis due to lithological variations.

**Modeling Diagenesis in Contessa Sediments**

We develop a numerical model that simulates oxygen isotope exchange during deposition and compaction of sediment on the sea floor, based on models described by Schrag et al. (1992, 1995). The model includes time-varying sedimentation rates based on the biostратigraphy and numerical
primary sediment dissolving and reprecipitating (Richter and DePaolo, 1987, 1988; Richter and form R = a + β ε -age, where R is the fraction of primary sediment dissolving and reprecipitating per million years, and α, β, and γ are constants (Richter and DePaolo, 1987, 1988; Richter and Liang, 1993; Richter, 1996). Hereafter, we refer to the recrystallization/age relation defined by α, β, and γ as the recrystallization rate trajectory of the sediments. We use a range of recrystallization rate trajectories calculated by Richter (1996). For our first exercise, in which we assume that all Contessa sediments follow the same recrystallization trajectory, we run a simulation using both his lowest rate (α = 0.001, β = 0.016, and γ = 8.5) and a simulation using his highest rate (α = 0.004, β = 0.067, and γ = 2.1). For the second exercise, in which sediments follow different recrystallization trajectories, the slowest recrystallizing sediments follow the lowest rate of Richter (1996) and the rate of the most rapidly recrystallizing sediments is a fit parameter used to induce oxygen isotopic excursions comparable to those in the Contessa record.

The model calculates the δ18O value and amount of secondary calcite that precipitates during sediment burial. Measured δ18O values can then be corrected to give primary δ18O values from the conservation relationship: δ18Oprimary - δ18Osecondary = (δ18Omeasured - δ18Osecondary) / (1 - xsecondary).

In the first set of simulations, we demonstrate the effect of homogeneous diagenesis on the Contessa sediments by assuming that all sediments follow the same recrystallization rate trajectory (Fig. 5). Note that to simplify the figure, we have decreased the number of data points plotted and that the smoother record is not a result of diagenetic effects. Correcting the Contessa record for the model-calculated addition of secondary carbonates yields primary oxygen isotopic values that are more negative than the measured values, because secondary calcite is isotopically heavier than measured values. Secondary calcites are heavier than primary calcites because Contessa sediments are not deeply buried (700 m at most), and are almost always recrystallizing in pore waters that are cooler than the tropical sea-surface temperatures in which the primary calcite was precipitated. The δ18O of pore waters in which the Contessa sediments recrystallize are only slightly more negative than seawater because a thick sequence of carbonates separates these sediments from the underlying basement rock where low δ18O pore waters are produced. More rapid rates of recrystallization produce greater amounts of relatively heavy secondary calcite and thus imply even lighter primary oxygen isotope values. A higher geothermal gradient would imply lighter secondary carbonate and thus slightly heavier primary compositions. For example, a 10 ºC/km increase in the geothermal gradient results in primary δ18O values 0.25‰ higher for the faster recrystallization rates. In addition to changing the absolute values, correcting the isotopic record for the effects of diagenesis also increases the amplitude of isotopic excursions. The largest excursion in the measured record is 1.25‰; correcting for the slowest recrystallization rate trajectory amplifies the excursion to 1.5‰, while correcting for the fastest recrystallization rate trajectory amplifies the excursion to 1.9‰. Calculated primary δ18O values for Contessa sediments range from ~3‰ to ~5‰. Pe Dee belemnite; these values are not unreasonable for tropical sea-surface temperatures of 25–35 ºC, assuming “ice free” seawater δ18O of ~1‰.

In the second exercise, we investigate whether lithological variations in the Contessa sediments may have caused sediments to follow different recrystallization rate trajectories, leading to differential alteration and artifacts in the δ18O record. Rather than allowing recrystallization rate trajectories to vary with a single lithological characteristic (e.g., percent CaCO3) and comparing the result to measured isotopic excursions, we solve for the variations in recrystallization rate trajectories that would be required to produce the major excursions in the Contessa δ18O record entirely as a consequence of differential diagenesis, assuming that the primary δ18O record was relatively featureless. We then see if the pattern of required variation in recrystallization rate trajectories is similar to the variation in any lithological factor and assess whether the magnitude of required variation is reasonable. This latter approach makes more efficient use of the model and provides a more complete answer to the question of whether the observed δ18O excursions are likely the result of differential diagenesis. Because the model solves the diagenesis problems in the inverse direction—by calculating the amount and composition of secondary calcite and subtracting it from the measured δ18O to estimate the primary δ18O—we are in fact seeking the amount of variation in recrystallization rate trajectories required to eliminate the major excursions from the model-calculated primary δ18O record. We accomplish this by allowing each meter of sediment to follow a different recrystallization rate trajectory, so that after the ~100 m.y. of the simulation the sediments have altered to varying extents.

In Figure 6, we plot the variation in the amount of secondary calcite that would be required to produce the major positive δ18O excursions purely as a consequence of differential diagenesis. The amount of secondary calcite produced must vary by a factor of three. If we fix the minimum amount of secondary calcite by using the lowest recrystallization rate trajectory of Richter (1996), the amount of secondary calcite varies from 19% to 59% of the total carbonate. The positive excursions could also be eliminated by a similar contrast at higher recrystallization rates, for example a range of 30%–90% secondary calcite. However, the primary isotopic composition re-
The required contrast in recrystallization rates within the Contessa section is larger than that observed between different DSDP sites measured by Richter (1996). Variations between the maximum and minimum recrystallization rate trajectories for different carbonate-rich deep sea sites measured by Richter (1996) yield only a factor of two variation in the amount of secondary carbonate after 100 m.y. (Fig. 6).

One would expect that a significant change in lithology would have been required in order to cause such large contrasts in the extent of sediment alteration. However, the required pattern of variations in the degree of alteration does not coincide with lithologic variations in the Contessa sediments (Fig. 6; data from Premoli-Silva and Sliter, 1994; Arthur, 1979). Variations in the CaCO₃ content of Contessa sediments are minimal (except at the Bonarelli horizon) and do not coincide with either episode of enhanced alteration. Although there are variations in the abundance of planktonic foraminifera, large planktonic foraminifera, benthic foraminifera, and radiolarians, there is no consistent change in any one of these variables over either interval of enhanced alteration. Intervals of positive oxygen isotopic excursions do not correspond to episodes of primary dissolution of foraminifera (Fig. 6) or to changes in the bedding thickness. Thus the available sedimentary data do not provide evidence for large contrasts in lithology and the degree of alteration of Contessa sediments. This does not rule out the possibility that there may be contrasts in the degree of alteration, but contrasts of the magnitude required to produce the oxygen excursions as diagenetic artifacts seem highly unlikely.

Reproducibility of Oxygen Isotope Variations

Assessing whether the Contessa oxygen isotopic excursions are reproduced in the Santa Ines section in Spain is a second approach to examine the probability that the positive excursions are diagenetic in origin. In order to compare the oxygen isotopic records from the Contessa and Santa Ines sections, we must first correlate them with an uncertainty better than the time scale of the events we are interested in comparing. The stratigraphic complexity and lower biostratigraphic sampling resolution make it difficult to correlate the Santa Ines section with the Contessa Quarry section. Biostratigraphy has traditionally been the foundation for correlation between sites but has a precision limited by the consistency of microfossil zone assignments by different workers, and by the actual synchrony of microfossil first and last appearances as well as the biostratigraphic sampling resolution. Correlation based on δ¹³C variations may be more precise when geochemical sampling resolution is very high, because signals lasting 10⁵ yr are likely to be globally synchronous steady-state variations (e.g., Kump, 1991), and there is no subjectivity involved in their quantification. However, δ¹³C excursions are not unique, and can only be used for finer scale correlation within an existing biostratigraphic framework. Our approach is to combine these methods by matching δ¹³C excursions that are biostratigraphically closest in age. We check this approach by confirming that the apparent diachrony of microfossil events does not exceed the uncertainty inherent in biostratigraphic correlation or the uncertainty in the position of bioevents in our section (due to biostratigraphic sampling resolution and uncertainty translating the biostratigraphy to our new section).

The isotopic data from Santa Ines are plotted as a function of depth in Figure 3. When compared with the isotopic data from the Contessa Quarry (plotted in Fig. 2), a number of similarities emerge. Both the Santa Ines and Contessa records show maximum δ¹³C values in a large positive excursion during late Cenomanian time. In addition, both records contain multiple positive δ¹³C excursions of 0.5‰–1.5‰, lasting 0.5–2 m.y.; the general pattern of peaks and shoulders in these smaller excursions is also reproduced in both records. Our proposed correlation of the δ¹³C records is shown in Figure 7A. Although the correlated records are similar, there are differences in the relative amplitudes of peaks and degree of peak separation between the records. The
Figure 6. (Left) Variation in amount of secondary calcite produced from varying recrystallization rate trajectories in the sediments, expressed as percent of total calcite that has recrystallized. Thick line is variation in amount of secondary calcite required to produce major positive $\delta^{18}O$ excursions through differential diagenesis. Thin line is variation in amount of secondary calcite when recrystallization rate trajectories vary between maximum and minimum of Richter (1996). (Center and right) Variation in CaCO$_3\%$ (Arthur, 1979) and foraminiferal and radiolarian excursions through differential diagenesis. Thin line is variation in amount of secondary calcite when recrystallization rate trajectories vary between maximum and minimum of Richter (1996). (Center and right) Variation in CaCO$_3\%$ (Arthur, 1979) and foraminiferal and radiolarian abundance and dissolution events (Premoli-Silva and Sliter, 1994). Abundance data represent a five-point running mean below the Bonarelli horizon and a three-point running mean above it. R—rare, F—few, C—common, A—abundant, AA—very abundant. Large planktonic foraminifera $\leq 250$ $\mu$m. Abbreviations as in Figure 2.

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complexities that may have eliminated small portions of the section.

Correlated $\delta^{13}$C records from Santa Ines appear to reproduce several of the largest excursions observed in the Contessa record, although there are significant differences between the records (Fig. 8). The early Cenomanian positive excursion may be reproduced in the Santa Ines record. The middle Cenomanian through middle Turonian interval of both sections is one of more stable $\delta^{18}$O ratios, followed by several prominent positive $\delta^{18}$O excursions of ~1‰ in late Turonian–early Santonian time. Although the relative amplitudes of late Turonian–Santonian $\delta^{18}$O excursions differ, the general pattern of peaks and troughs is reproduced in both sections after late Turonian time. The apparently larger amplitude of the Santa Ines $\delta^{18}$O variations in the Santonian may be due to a longer term trend of increasing $\delta^{18}$O values. The most salient discrepancy in the records is the earlier onset of late Turonian $\delta^{18}$O excursions in the Santa Ines section. In the carbon isotope record, the 91–89.5 Ma interval is also a period of poor agreement, implying that stratigraphic complications such as nonlinear sedimentation rates or postdepositional displacements may be partially responsible for the discrepancy. Although there are some similarities between the Contessa and Santa Ines records, given the stratigraphic complications in the Santa Ines record, we would ideally like to reproduce the Contessa isotopic variations in an additional site.

Despite the stratigraphic complications of the Santa Ines section, the $\delta^{18}$O record from Santa Ines reproduces the major features of the Contessa $\delta^{18}$O record, suggesting that the major excursions reflect primary variations in the temperature and $\delta^{18}$O of seawater and are not artifacts of diagenesis. Furthermore, large $\delta^{18}$O variations do not occur throughout the section, resulting in a clear distinction between $\delta^{18}$O events and the lower amplitude, high-frequency background variability that may be in part due to diagenesis. Slight differences in the $\delta^{18}$O signals between the records may result from differences in the relative contribution of temperature and seawater $\delta^{18}$O changes or from different diagenetic histories. However, as emphasized previously, diagenesis is not likely to be responsible for the similar pattern of variation in the records, probably due to primary oceanographic signals.

Cretaceous Ice Sheets

Evidence suggests that the major $\delta^{18}$O excursions in Contessa reflect episodes of global cooling and not differential diagenesis. Although we have no way to directly prove that ice-sheet accumulation accompanied episodes of global cooling, it seems more likely that periodic ice ages provide a mechanism linking global cooling and sea-level regressions, and less likely that multiple episodes of extreme cooling and large sea-level falls independently coincided for 12 m.y. in Late Cretaceous time. The issue of ice-sheet accumulation during Cretaceous time is nonetheless difficult to reconcile with the current view of the Cretaceous Period as a time of continuous climactic warmth. We need to reexamine evidence for Cretaceous warmth and carefully assess whether it is compatible with periodic episodes of polar ice-sheet accumulation.

Numerous sources of climatically sensitive paleontologic data provide evidence for much warmer temperatures and reduced equator to pole temperature gradients during Cretaceous time. Floral provinces and coral reefs expanded poleward by as much as 15° (Habicht, 1979;
Vakhrameev, 1975), dinosaurs were found north of the Arctic circle (Colbert, 1973), and diverse floral assemblages characterize several high-latitude sites (Krasilov, 1981). Although some more recent evidence suggests that high-latitude temperatures may have been cooler and latitudinal gradients steeper than previously estimated (e.g., Pirrie et al., 1995; Sellwood et al., 1994; Parrish and Spicer, 1988), the mean Cretaceous climate is still generally thought to have precluded the existence of ice sheets.

Nonetheless, mean Cretaceous climate may not be the most appropriate context in which to consider the feasibility of ice sheets. Our proposed ice-sheet link between sea level and climatic variations does not require the persistence of ice sheets throughout Cretaceous time, only their periodic buildup and subsequent decay during interludes of climatic cooling. Paleontologic data for Cretaceous warmth are inherently of low resolution, and while they provide a general picture of the mean climatic state over periods of tens of millions of years, climatic excursions of a few million years or less could be easily missed or averaged out in these data sets. Furthermore, direct geological records of Cretaceous glaciation, such as tillites, would be generally inaccessible because any ice-sheet buildup would most likely have occurred on Antarctica, which was situated over the South Pole at the time. Thus, it is conceivable that climatic fluctuations may have permitted episodic formation of ice sheets even though mean Cretaceous climate did not support it.

Recent General Circulation Model (GCM) experiments for Late Cretaceous time (Bush and Philander, 1997) provide an additional perspective on the feasibility of Cretaceous ice sheets. The GCM model experiment run for mean Cretaceous climate conditions did not simulate ice accumulation because summer temperatures at the South Pole reached 8° in their model, which was sufficient to melt winter snow accumulations. However, it is possible that episodic coolings of 8° in this region over periods of several hundred thousand years could have permitted ice-sheet accumulation. Our oxygen isotopic records from the subtropics imply 4°–8° of cooling, assuming accumulation. Our oxygen isotopic records from thousand years could have permitted ice-sheet 8° in this region over periods of several hundred sufficient to melt winter snow accumulations. The GCM model experiment run for mean Cretaceous time (Bush and Philander, 1997) provide an additional perspective on the feasibility of Cretaceous ice sheets. The GCM model experiment run for mean Cretaceous climate conditions did not simulate ice accumulation because summer temperatures at the South Pole reached 8° in their model, which was sufficient to melt winter snow accumulations. However, it is possible that episodic coolings of 8° in this region over periods of several hundred thousand years could have permitted ice-sheet accumulation. Our oxygen isotopic records from the subtropics imply 4°–8° of cooling, assuming accumulation. Our oxygen isotopic records from thousand years could have permitted ice-sheet 8° in this region over periods of several hundred sufficient to melt winter snow accumulations.

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