

6. CARBON-ISOTOPE STRATIGRAPHY AND PALEOCEANOGRAPHIC SIGNIFICANCE OF THE LOWER CRETACEOUS SHALLOW-WATER CARBONATES OF RESOLUTION GUYOT, MID-PACIFIC MOUNTAINS¹

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ABSTRACT

Matching of Lower Cretaceous carbon-isotope curves derived from pelagic sediments of the Tethyan-Atlantic sector with that obtained from peritidal carbonates of Resolution Guyot (Site 866, Mid-Pacific Mountains) provides constraints in positioning the Hauterivian/Barremian, Barremian/Aptian, and Aptian/Albian stage boundaries. A negative excursion in the earliest Barremian of the reference sections suggests that the Hauterivian/Barremian boundary on Resolution Guyot should lie in the interval 1425 to 1500 mbsf. A major positive isotopic excursion, whose onset is positioned just below the base of a major oolitic sand package, is ascribed to the *blowi* Zone (late early Aptian), a time of regional deep-marine organic-carbon burial (Selli Level) in the Pacific, Atlantic, and European regions. A finely laminated organic-carbon-rich level (14.2% total organic carbon) in the shallow-water packstone-wackestones is exactly coincident with the beginning of the isotopic excursion and can be considered an equivalent to the Selli Level deposited in water of very modest depth. The Barremian/Aptian stage boundary must be located below strata attributed to the *blowi* Zone, and should lie close to 900 mbsf. Decay of the excursion is complete by about 500 mbsf, a level which should be near to the Aptian/Albian boundary.

INTRODUCTION

In an attempt to add some stratigraphic refinement to the dating of the Cretaceous shallow-water section penetrated on Resolution Guyot (Site 866, Mid-Pacific Mountains; Fig. 1), a considerable number of carbon- and oxygen-isotope analyses were undertaken in the hope that the signatures might be comparable with those already generated from well-dated pelagic sections. Dating of these peritidal sediments by standard biostratigraphic means presents problems as planktonic foraminifers and nannofossils are exceedingly scarce and poorly preserved. Benthic microfossils are more abundant, but are known to be environmentally sensitive and, in many cases, have poorly defined ranges established half a world away in southern Europe.

METHODS

Samples were collected throughout the core, care being taken to avoid clay-rich or grossly dolomitized lithologies wherever possible. Lithologic samples, plus a few separated rudist shells, were then broken and crushed to obtain sufficient material for analysis. Samples were cleaned using 10% H₂O₂ followed by acetone and then dried at 60°C. They were then reacted with purified orthophosphoric acid at 90°C and analyzed on-line using a VG Isocarb device and Prism mass spectrometer at Oxford University. Normal corrections were applied, and the results are reported, using the usual δ notation, in per mil (‰) deviation from the PDB (PeeDee belemnite) standard. Calibration to PDB was performed through a laboratory standard calibrated against NBS19 and Cambridge Carrara marble. Reproducibility of replicate analyses of standards was generally better than 0.1‰ for both carbon- and oxygen-isotope ratios. Analyses from different positions within limestone specimens typically differed by less than 0.3‰ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Samples that are enriched in ^{13}C or ^{18}O relative to the average are described as having positive values, whereas those that are relatively depleted in these isotopes are referred to as having negative values.

BACKGROUND

Carbon-isotope curves from Hauterivian through Aptian deep-sea carbonates have been reported from a number of Atlantic deep-sea drilling sites, and from southern France, Italy, and Switzerland in the Tethyan region (Arthur et al., 1979; Létolle et al., 1979; Weissert et al., 1985; Clauser et al., 1988; Weissert and Bréhéret, 1991; Weissert and Lini, 1991). They show relatively consistent trends. Most diagnostic is a negative followed by a pronounced positive $\delta^{13}\text{C}$ excursion in the early Aptian, followed by a small fall, subsequent rise, and decay across the Aptian/Albian boundary; the excursion itself is thus characterized by a two-pronged outline. The isotopic curves are calibrated against a stratigraphic framework, derived from planktonic foraminifers, which is still in a state of flux. Current work, however, suggests that the onset of the positive excursion is dated as *blowi* Zone (late early Aptian), a time of regional carbon-burial in Europe and across the Pacific Ocean (Coccioni et al., 1987; Bréhéret, 1988; Sliter, 1989; Arthur et al., 1990; Bralower et al., 1993). The subsequent fall lies in the *algerianus* Zone, as does the subsequent rise; the relatively positive values of the *trocoidea* Zone then decrease irregularly into the *bejaouaensis* Zone, to reach background levels by Aptian/Albian boundary time.

Included in the Pacific sites that register the carbon-burial event is Site 463, located on the flanks of Resolution Guyot (Fig. 2), which contains a lower Aptian record of organic-rich shales (Selli Level) dated as *blowi* Zone (Sliter, 1989): total organic carbon (TOC) values locally rise to more than 7% (Dean et al., 1984). Other locations include Magellan Rise (Site 167), Shatsky Rise (Site 305), and the Manihiki Plateau (Site 317). Given that the positive $\delta^{13}\text{C}$ excursion is interpreted as directly related to removal of isotopically light carbon (^{12}C), from the oceanic reservoir consequent upon its burial as organic matter (e.g., Scholle and Arthur, 1980; Weissert, 1989), it follows that the isotopic anomaly should have been registered by Pacific Ocean waters.

Most Mesozoic carbon-isotope stratigraphy has been undertaken on pelagic carbonates (Scholle and Arthur, 1980; Jenkyns and Clayton, 1986; Schlanger et al., 1987; Weissert and Lini, 1991; Lini et al., 1992). However, the coupling of the ocean-atmosphere system with respect to CO₂ (e.g., Sundquist, 1985) implies that any terrestrial organic matter synthesized should also register important disturbances in the global carbon-isotopic reservoir. Thus, shallow-water carbonates subjected to

¹ Winterer, E.L., Sager, W.W., Firth, J.V., and Sinton, J.M. (Eds.), 1995. *Proc. ODP, Sci. Results*, 143: College Station, TX (Ocean Drilling Program).

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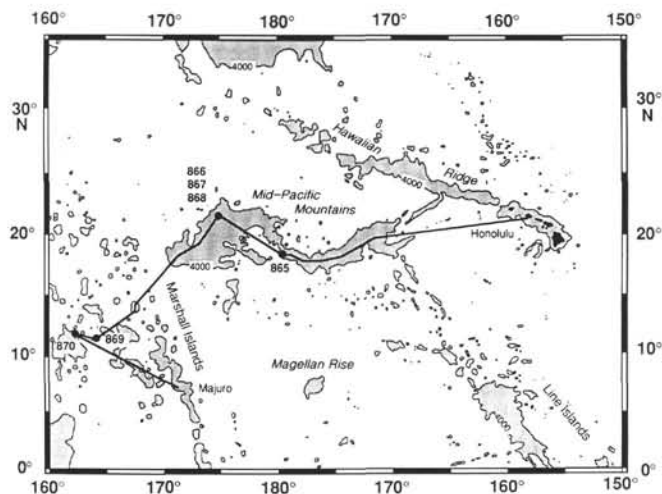


Figure 1. Map of portion of the Pacific Ocean, illustrating location of drill sites cored on Leg 143. Site 866 is the deep site drilled on Resolution Guyot.

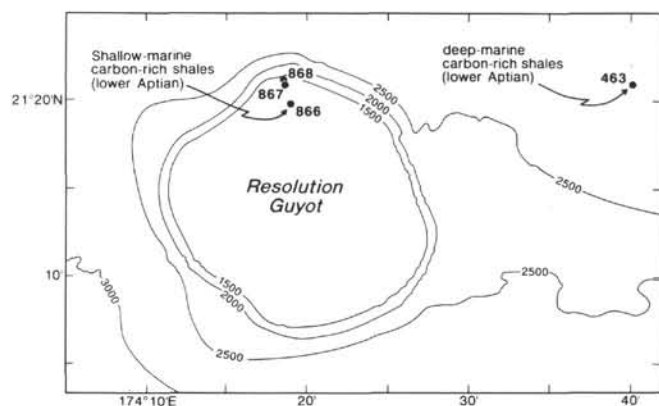


Figure 2. Detail of Resolution Guyot, also showing location of the adjacent deep-water Site 463, drilled during DSDP Leg 62. Depths in meters. Carbon-rich shales (Selli Level) of early Aptian age (*blowi* Zone) occur in both the shallow-water (Site 866) and deep-water sites.

meteoric-water diagenesis, and the systematic addition of soil-derived CO_2 , could well display reproducible and meaningful carbon-isotopic trends (see Hudson, 1977; Scholle and Halley, 1985; Marshall, 1992). Such geochemical stratigraphy has proven effective as a correlation tool in Cretaceous shallow-water carbonates from the Arabian Platform (Wagner, 1990); and the recognition of well-defined signals in Tertiary continental paleosols, correlatable with those in the deep-marine realm, points in this direction (Koch et al., 1992). Isotopic signals in Precambrian shallow-water carbonates are also proving to be of stratigraphic use (Brasier, 1993).

RESULTS AND DISCUSSION

Isotope Stratigraphy

The carbon- and oxygen-isotope stratigraphy for Site 866 is illustrated in Figure 3. Given the presence of intertidal-supratidal fabrics, implying the likely action of meteoric-water diagenesis, the oxygen-isotope data can probably be discounted as containing little useful paleoceanographic information (see Marshall, 1992). The overall pattern is of values becoming more negative with depth, a common trend with carbonates that may be related to the increasing impact of burial diagenesis (Scholle and Halley, 1985). It is notable that overall correlation is poor between the carbon- and oxygen-isotope values (Fig. 4),

which suggests that meteoric-water diagenesis has been unimportant enough or conservative enough to at least maintain the integrity of the carbon-isotope signal. Indeed, the carbon- and oxygen-isotope values from Resolution Guyot are comparable with those found in pelagic carbonates (Corfield et al., 1991; Lini et al., 1992), equally implying that soil-derived CO_2 has not significantly affected the composition of the shallow-water facies, as seems to be the case with most marine limestones in the geological record (e.g., Hudson, 1975, 1977; Marshall, 1992). Obviously set apart, however, are the four anomalously high $\delta^{18}\text{O}$ values that occur exclusively in the white sucrosic dolomites of Subunit VIIB and are clearly lithology-dependent. Values for $\delta^{18}\text{O}$ of this magnitude are known from Holocene evaporative sabkha dolomites from Abu Dhabi and Qatar (McKenzie, 1981; Major et al., 1992), but comparable isotopic ratios are also recorded from Pleistocene and Holocene dolomites thought to have formed by normal marine and mixed marine/meteoric waters (Ward and Halley, 1985; Carballo et al., 1987; Humphrey, 1988). It is difficult, therefore, to remark on the nature of the fluids that replaced the original grainstones; they may well have had the composition of normal seawater. Relative enrichment in $\delta^{18}\text{O}$ could be purely a function of the dolomite mineralogy (e.g., Land, 1980). The strontium-isotope studies of Flood and Chivas (this volume) indicate that these dolomites are of Tertiary age and, hence, late diagenetic, unlike other dolomites from Site 866.

Smoothed carbon-isotope data, with values from the sucrosic dolomites omitted, are given in Figure 5, with a stratigraphically calibrated isotope curve from the Cretaceous of the Southern Alps (Italy/Switzerland) for comparison. The identification of the Hauterivian in the section from Resolution Guyot is tentative. Reference to carbon-isotope data from the Southern Alps, however, suggests that the basal 100 to 200 m of the section may be attributed to the uppermost part of the stage. Particularly diagnostic is a pronounced negative excursion slightly above the Hauterivian/Barremian boundary. Absolute-age data from the basement of Site 866 (Pringle and Duncan, this volume) are consistent with this interpretation. Precise matching of the two curves within the Barremian is difficult and is not useful for fixing stage boundaries.

Both curves show, as their most striking feature, a significant (2–3‰ in the case of Resolution Guyot) drop followed by (i.e., up-section) a positive excursion where values rise to levels between 4.0 and 5.5‰ from a background of 2 to 3‰. Although the high carbon-isotope ratios are independent of lithology in the guyot section, the zone of relatively positive values is largely confined to the package of oolitic grainstone (Unit V) sandwiched between cyclic packstone-wackestones. A figure greater than 7‰ is attained from a rudist shell within these coarse-grained deposits (Fig. 4). The excursion does, however, commence in cyclic packstone-wackestones below the oolite, and the second highest value ($\delta^{13}\text{C} = 5.3\text{‰}$) occurs in the packstone-wackestones stratigraphically overlying the oolite. Above this point, there is a gradual, but irregular, decay in values within the same facies. If, as seems likely, the oolitic facies represent an increase in water depth relative to the underlying wackestones and algal laminites, then the common association between regional deepening, carbon-burial events, and positive $\delta^{13}\text{C}$ excursions is being maintained (e.g., Arthur et al., 1987; Weissert and Lini, 1991; Jenkyns et al., 1994). The generation of oolites within parts of a carbonate-platform system can be viewed as a response to a rise in relative sea level (Jenkyns and Strasser, this volume).

The exact contours of the curve are such that, following the pronounced dip, there is an extremely abrupt increase in values to form a two-pronged peak, which is followed by steep fall. Aptian $\delta^{13}\text{C}$ profiles published for European and Atlantic sections for both carbonate (Fig. 5) and organic carbon (Weissert, 1989; Weissert and Lini, 1991) have remarkably similar shapes and suggest that the basal part of the oolitic package (Unit V) and at least the top 50 m of the underlying cyclic packstone-wackestones (Subunit VIA) should be attributed to the *blowi* Zone (lower Aptian). The Barremian/Aptian boundary (base of *similis* Zone) thus must lie somewhere in the region of 900 mbsf. Background $\delta^{13}\text{C}$ values (i.e., 2–3‰) are re-established

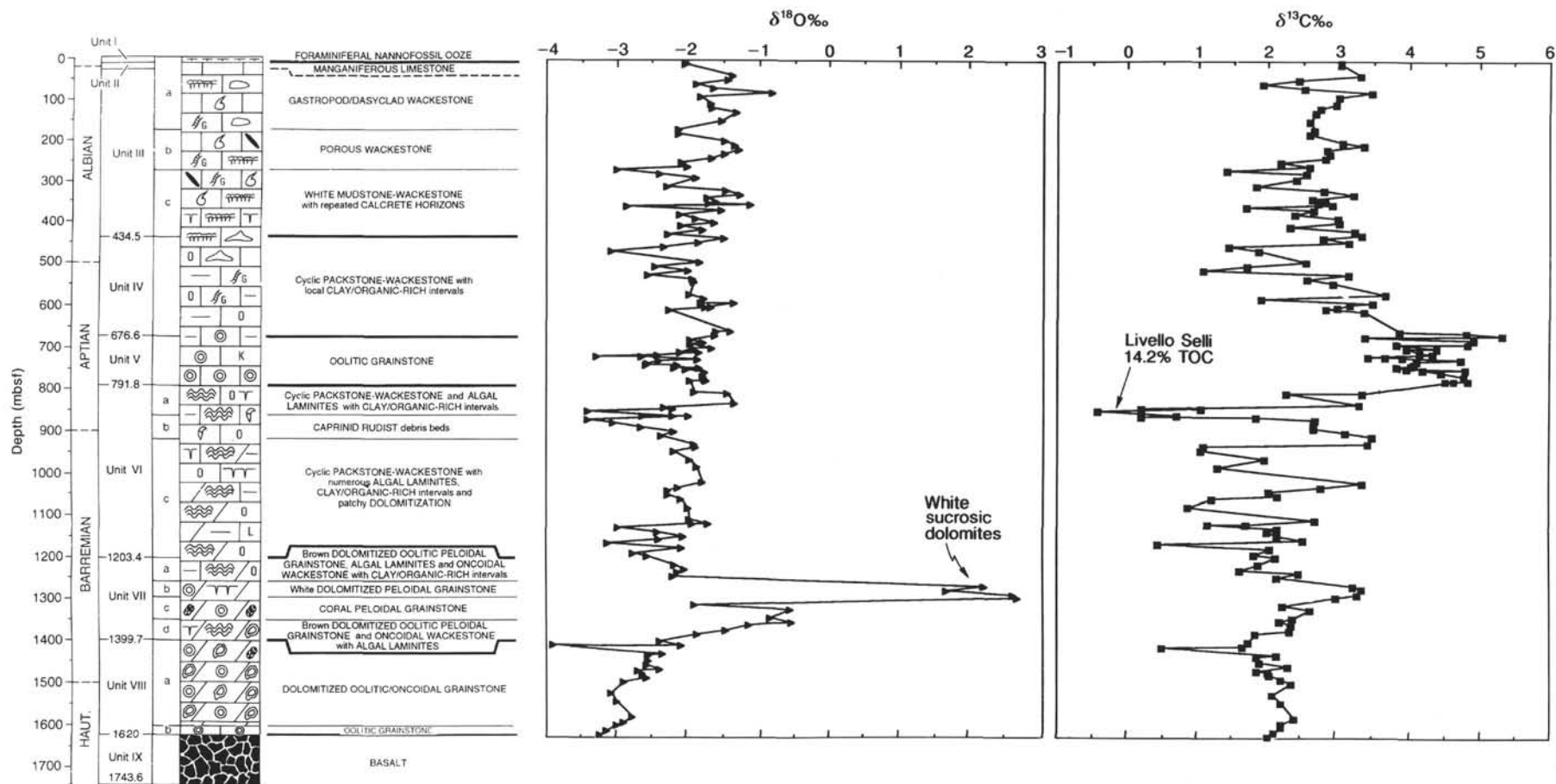


Figure 3. Carbon- and oxygen-isotope stratigraphy (right) compared with lithostratigraphy (left) of Cretaceous carbonates from Resolution Guyot. This data set is derived from analysis of bulk samples only; single rudist shells have been excluded as they can show anomalously high $\delta^{13}\text{C}$ values, which may result from vital effects (Fig. 4). The cluster of heavy $\delta^{18}\text{O}$ values reflects the presence of late diagenetic replacement sucrosic dolomite.

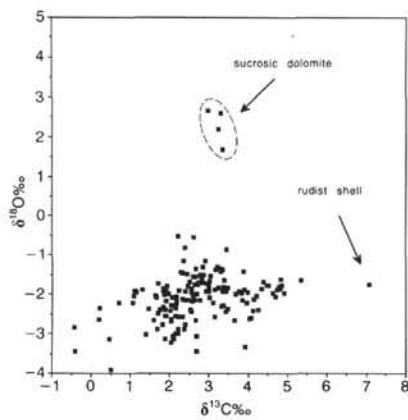


Figure 4. Cross-plot of carbon- and oxygen-isotope values from Resolution Guyot, including shell material. The sucrosic dolomites with their high $\delta^{18}\text{O}$ values are notable, as is a single rudist shell with a $\delta^{13}\text{C}$ value greater than 7‰. Correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is poor, and the isotopic ratios of bulk shallow-water carbonate are little different from those of Cretaceous pelagic limestones (Corfield et al., 1991; Lini et al., 1992).

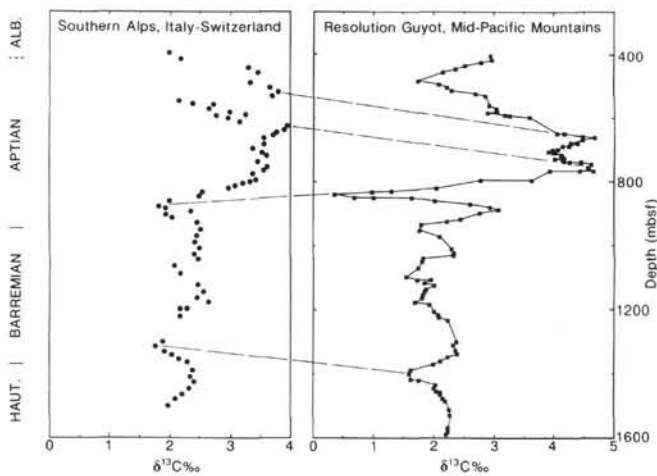


Figure 5. Comparison between smoothed (five-point moving average) carbon-isotope curve from the shallow-water carbonates of Resolution Guyot (right) and reference curve from the Southern Alps (Weissert and Lini, 1991). Original data for Resolution Guyot are as in Figure 3, except that isotopic ratios from the white sucrosic dolomites have been omitted, as the strontium-isotope data of Flood et al. (this volume) show them to be of Tertiary age. Other partially dolomitized samples, whose isotopic values are in no way exceptional, are included. Matching of the curves, as indicated, has led to erection of the suggested stratigraphy for Site 866 (Fig. 3).

at about 500 mbsf within cyclic packstone-wackestones, and this level should lie close to the Aptian/Albian boundary.

Over the Aptian interval, the carbon-isotope profile from Resolution Guyot, with its highly diagnostic two-pronged positive excursion, can be used to produce a more detailed zonation of the shallow-water carbonates by comparison to curves from the Tethyan region. The success of such an exercise, however, hinges on use of a reference curve whose $\delta^{13}\text{C}$ values are uncompromised by diagenesis and whose stratigraphic foundation, in this case utilizing the ranges of planktonic foraminifers, is fixed unambiguously. Neither is indisputably the case, and hence, two slightly differing zonations are offered in Figures 6 and 7.

A final point to discuss is the amplitude of the early Aptian excursion in the shallow-water carbonates from Resolution Guyot. From most negative to most positive, there is a shift of approximately 4‰,

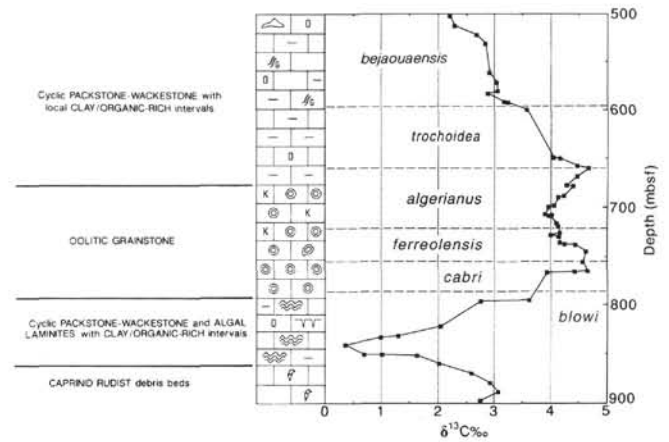


Figure 6. Tentative hypothetical planktonic foraminiferal zonation of shallow-water carbonates from Resolution Guyot, generated by using carbon-isotope profiles from the Southern Alps of Italy/Switzerland and Atlantic DSDP sites as a reference curves (Weissert and Lini, 1991). Definition of the base of the *blowi* Zone is poorly constrained in standard biostratigraphy owing to the considerable range of the index species.

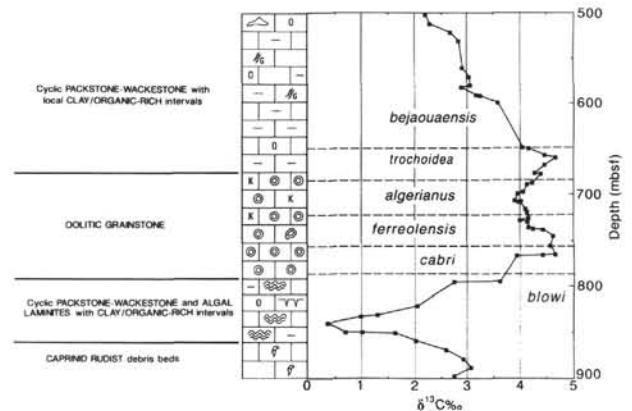


Figure 7. Tentative hypothetical planktonic foraminiferal zonation of shallow-water carbonates from Resolution Guyot, generated by using the carbon-isotope profile from the Vocontian Trough of southern France as a reference curve (Weissert and Bréhéret, 1991). Definition of the base of the *blowi* Zone is poorly constrained in standard biostratigraphy owing to the considerable range of the index species.

whereas the shift in the pelagic carbonates from the Tethyan sector is about half this figure. Synchronous positive $\delta^{13}\text{C}$ shifts of differing amplitude in organic matter (greater) and carbonate (lesser) have been recorded for several intervals in the Cretaceous, where they have been related to changes in carbon-isotope fractionation during algal photosynthesis, in turn dependent on a reduction of atmospheric carbon dioxide (Arthur et al., 1988; Lini et al., 1992). However, it is difficult to see how such a mechanism could impose an isotopic difference on lime mud or sand secreted on an oceanic carbonate bank, as opposed to pelagic ooze derived from calcareous planktonic microfossils and nanofossils. In addition, what is needed is an explanation for an increase in the relative amplitude of both the negative as well as the positive excursion in the early Aptian. Perhaps the simplest explanation is to assume that Resolution Guyot was close to the water masses, which, during the earliest Aptian, were characterized by a particularly negative carbon-isotope composition and, subsequently, by an unusually positive carbon-isotope composition. In terms of the latter, this could imply that the Pacific was a more important sink for organic carbon during the *blowi* Zone than was the Tethyan-Atlantic region.

Aptian Black Shales (Selli Level)

Within the cyclic packstone-wackestones of Subunit VIA (Interval 143-866A-89R-1, 92-1 cm), there is an intercalation of green to black millimeter-laminated, organic-carbon-rich clay (14.2% TOC). Similar, but less well-developed, black claystones occur in stratigraphic proximity to this level (Sections 143-866A-88R-1 and -91R-1). The onset of the isotopic excursion is located immediately below Core 143-866A-88R. Hence, these intercalations of black shale are dated as *blowi* Zone and are coeval with the deep-water equivalents cored on the flanks of Resolution Guyot at Site 463 and elsewhere in the Pacific Ocean: they are shallow-water equivalents of the Selli Level (Fig. 3). Interestingly, in both the shallow (Site 866) and deep-water (Site 463) settings, the organic matter has similar characteristics: a low hydrogen index and resembling Type III kerogen (Dean et al., 1981, 1984). In fact, in the case of the deep-water site, detailed geochemical work shows the material to be dominantly nonterrestrial in origin and comprising lipid-rich kerogen derived from aquatic marine algae and bacteria. The synchronous deposition of carbon-rich sediments in both pelagic and shallow-water carbonate environments has been previously documented for the Cenomanian/Turonian boundary event (oceanic anoxic event: OAE), which is also accompanied by a positive $\delta^{13}\text{C}$ excursion (Schlanger et al., 1987; Jenkyns 1991). The impact of increased productivity and/or anoxia also can clearly be experienced in very shallow-water environments.

CONCLUSIONS

The data presented here from Resolution Guyot, Mid-Pacific Mountains, show clearly that isotope stratigraphy is not uniquely the preserve of the pelagic domain and that meaningful signals can be deciphered from shallow-water carbonates. Meteoric-water diagenesis has apparently not operated in a random manner to destroy primary isotopic signals. These results indicate that carbon-isotope stratigraphy has considerable potential for cross-correlation between different facies domains and can add stratigraphic detail to poorly dated shallow-water carbonate sections. The overall signal in the oxygen isotopes, however, appears dominated by the effects of burial diagenesis and appears to contain little, if any, paleoenvironmental information.

The carbon-isotope profile can give stratigraphic refinement to stage level, but locally, where the curve is particularly diagnostic, allows identification of planktonic foraminiferal zones. Dating of a laminated carbon-rich horizon as *blowi* Zone (late early Aptian) from Resolution Guyot shows that this level is coeval with deep-water black shales from several Pacific sites and elsewhere. This indicates that the early Aptian oceanic anoxic event was registered in shallow-water carbonate environments of the Mid-Pacific Mountains.

ACKNOWLEDGMENTS

I am grateful to Julie Cartlidge in the Oxford Isotope Laboratory for generating the relevant data and to Elisabetta Erba and Helmut Weissert for supplying unpublished information on the Cretaceous stratigraphy of the Apennines and Southern Alps. Valuable reviews were furnished by Lee Kump, Will Sager, and Helmut Weissert.

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Date of initial receipt: 24 September 1993

Date of acceptance: 11 April 1994

Ms 143SR-213