AGE OF MARINE MOLLUSKS FROM THE LOWER MIOCENE POLLACK FARM SITE, DELAWARE, DETERMINED BY ^{87}SR/^{86}SR GEOCHRONOLOGY[1]

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ABSTRACT

Analyses of ^{87}Sr/^{86}Sr ratios in the shells of marine bivalve mollusks from the Pollack Farm Site in Kent County, Delaware, indicate that the fossils represent an early Miocene assemblage which lived about 17.9 ± 0.5 Ma. Faunal similarities, as well as Sr-isotopic data, support a correlation between the fossils at the Pollack Site and portions of the Kirkwood Formation to the north (New Jersey) and to the south the Fairhaven Member of the Calvert Formation (Maryland), the Pungo River Formation (North Carolina), and the Chipola Formation (Florida). A strong marine-nonmarine link with terrestrial vertebrates of the Hemingfordian North American Land Mammal Age is also suggested.

INTRODUCTION

The U. S. Atlantic Coastal Plain boasts a rich Neogene stratigraphic record which has attracted the attention of stratigraphers and paleontologists for nearly two centuries. Despite this long history of investigation, correlation and age determinations of particular deposits often have proven difficult because of poor and sporadic exposures combined with a lack of age-diagnostic index taxa (planktic micro- and nannofossils) in these predominantly shallow-water deposits. We believe that strontium (Sr)-isotope chronostratigraphy represents a powerful tool for correlating shallow-marine units of the Atlantic and Gulf Coastal Plains with one another as well as to deep-sea reference sections and the geomagnetic polarity time scale (Jones et al., 1993; Miller and Sugarman, 1995). Sr-isotope stratigraphy is one of the few techniques that offers promise of worldwide correlation because the Sr-isotopic composition of seawater is constant at any point in time owing to rapid ocean mixing and the relatively long residence time of Sr in the oceans. As a result, it is independent of ocean basin, latitude, or water depth—attributes particularly relevant for correlating and dating the shallow-water sequences of the Coastal Plains.

Within the last decade, ^{87}Sr/^{86}Sr chronostratigraphy has emerged as an important geochronologic technique in marine sedimentary systems. Investigations of well dated marine carbonates throughout the Phanerozoic have demonstrated significant and regular variations in the ^{87}Sr/^{86}Sr ratio of seawater throughout geologic time (Burke et al., 1982; Veizer, 1989). During intervals characterized by rapid Sr-isotopic change with respect to time, the ^{87}Sr/^{86}Sr ratio allows rather precise relative and absolute age determinations of unaltered marine carbonates and phosphates. Fortunately for geologists interested in Atlantic Coastal Plain stratigraphy, the Sr-isotopic ratio of seawater increased, often rapidly, through much of the Cenozoic (Elderfield, 1986; Hess et al., 1986). In fact, the best temporal resolution is offered for the early Miocene, between about 23 and 16 Ma, when the seawater Sr-isotope curve was steepest (Hodell and Woodruff, 1994). Refinements to the global seawater Sr-isotope curve for particular segments of the Paleogene and the Neogene (e.g., Miller et al., 1988, 1991; Hess et al., 1989; Capo and DePaolo, 1990; Hodell et al., 1991; Hodell and Woodruff, 1994; Oslick et al., 1994) indicate that high-resolution chronostratigraphy is possible for strata deposited from the latest Eocene through the middle Miocene, as well as from the late Pliocene through the Pleistocene. In this investigation we apply Sr-isotope geochronologic techniques to marine mollusk shells collected from the Pollack Farm Site, located in Kent County between Dover and Smyrna, Delaware (see Benson [1998], Ramsey [1998], and Ward [1998] for details of location and geologic setting), to help resolve chronostratigraphic uncertainties and provide a better temporal framework for stratigraphic and paleontologic interpretations.

Several recent studies have successfully incorporated-isotopic analyses to help unravel age relationships for strata of the Gulf and Atlantic Coastal Plains. These include: Pliocene-Pleistocene of Florida (Webb et al., 1989; Jones et al., 1991; Jones et al., 1995); Oligocene and Miocene of Florida (Bryant et al., 1992; Compton et al., 1993; Jones et al., 1993; Sugarman et al., 1997); Paleogene of Alabama, Mississippi, and Louisiana (Denison, et al., 1993b); Cretaceous to Pleistocene of North Carolina (Denison et al., 1993a); and the Miocene of New Jersey (Sugarman et al., 1993; Miller and Sugarman, 1995; Miller et al., 1997). These studies demonstrate the clear potential for ^{87}Sr/^{86}Sr isotopic analyses to provide independent age information for shallow-marine strata. We apply these same techniques to mollusks from the Pollack Farm Site where we are interested in resolving the age relations of this richly fossiliferous, shallow-marine deposit which also contains the remains of terrestrial vertebrates. Such sites are particularly significant to paleontologists as they present opportunities to improve marine-nonmarine correlations (Tedford and Hunter, 1984).

Acknowledgments

We thank Laura Stanley for assistance with preparation of samples for Sr-isotopic analyses and Ann Heatherington for help with mass spectrometry. K.G. Miller and P.J. Sugarman provided thoughtful reviews of the manuscript. This paper represents Florida Museum of Natural History Contribution to Paleontology no. 448.

[1] *In* Benson. R.N., ed., 1998, Geology and paleontology of the lower Miocene Pollack Farm Fossil Site, Delaware: Delaware Geological Survey Special Publication No. 21, p. 21–25.
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MATERIALS AND METHODS

Five valves from articulated specimens of marine bivalve mollusks were selected from four individuals collected by L.W. Ward in November 1991 and by L.W. Ward and D.S. Jones on 15 June 1992. The specimens came from the main shelly unit, the approximately 3.0 m-thick Bed b of Ward (1998) which is the lower shell bed at the site as described by Ramsey (1998). Three individuals (Table 1, A-C) of *Mercenaria ducatelli* (Conrad), with aragonitic shells, and one *Crassostrea virginica* (Gmelin) (Table 1, D), with a calcitic shell, were used.

Table 1.

$^{87}Sr/^{86}Sr$ ratios, within-run error, and age estimates for marine mollusk samples from the Pollack Site, Kent County, Delaware. Columns 1 and 2 are based on the time scale of Berggren et al. (1985) whereas column 3 is based on Cande and Kent (1992) which is essentially the same time scale as Berggren et al. (1995) over this interval.

Specimen	$^{87}Sr/^{86}Sr$	Age (Ma) 1	2	3
A. *Mercenaria ducatelli*	0.708479±6	+++	+++	+++
A'. *Mercenaria ducatelli*	0.708618±6	17.8	18.0	17.8
B. *Mercenaria ducatelli*	0.708599±5	18.1	18.3	18.1
C. *Mercenaria ducatelli*	0.708619±11	17.8	18.0	17.8
D. *Crassostrea virginica*	0.708604±9	18.1	18.3	18.0
mean	0.708610	18.0	18.2	17.9

1 - Hodell et al. (1991); 2 - Miller et al. (1991); 3 - Oslick et al. (1994).
+++ - Sample diagenetically altered (see text).

Each specimen was examined microscopically for evidence of alteration or recrystallization. In addition, X-ray diffraction (XRD) and analysis of Sr/Ca ratios by atomic absorption spectrophotometry were performed on specimens of *Mercenaria ducatelli* to assess potential diagenetic effects which, in all but one case, were found to be minimal (Stanley, 1992). Scanning electron microscope (SEM) examination of the exterior shell surface of the right valve of specimen A revealed destruction and overgrowth of original shell microstructure. XRD analysis of powdered shell material indicated the presence of both calcite and aragonite, suggesting partial diagenetic alteration of this shell. SEM inspection and XRD analyses of the opposing (left) valve of this specimen indicated pristine microstructure without calcite. Both right and left valves were analyzed for comparative purposes (Table 1 - specimens A, A').

Sample powders, drilled from the outer shell layer of each valve, were analyzed for strontium isotopic composition ($^{87}Sr/^{86}Sr$) in the Department of Geology at the University of Florida using standard techniques of dissolution, centrifugation, evaporation, cation exchange chemistry, and mass spectrometry (Hodell et al., 1991). Five separate analyses, including one "duplicate" (same individual mollusk, opposite valve) were made. $^{87}Sr/^{86}Sr$ analyses were normalized to $^{86}Sr/^{88}Sr = 0.1194$. The NBS standard $SrCO_3$ (SRM-987) was measured at 0.710244 during the course of this study with a long-term analytical precision (2σ) of $\pm 2 \times 10^{-5}$. The ratios reported in Table 1 are corrected to SRM-987 = 0.710235 so that they may be directly correlated to the Sr-isotope seawater curve of Hodell et al. (1991) and Hodell and Woodruff (1994). Corrections to SRM-987 = 0.710252 and = 0.710255 permit comparisons with seawater Sr-isotope reference curves developed by Miller et al. (1991) and Oslick et al. (1994), respectively.

Measured Sr-isotope ratios were converted to estimates of absolute age using the regression equations of Hodell et al. (1991), Miller et al. (1991), and Oslick et al. (1994). Discrepancies between age estimates arising from these three different equations are relatively small for the early Miocene, within the error of the various age estimates. Detailed discussions of errors associated with Sr-isotopic ages can be found in Hodell et al. (1991) and Miller et al. (1991). For the time interval considered here, errors about single sample Sr-isotopic age estimates typically fall into the range of ±0.5 to no more than ±1.0 Ma at the 95% level of confidence.

RESULTS: AGE ESTIMATES

The results of the Sr-isotopic analyses are reported in Table 1. Values for $^{87}Sr/^{86}Sr$ range from 0.70848 (right valve of specimen A with calcitic alteration) to 0.70862. Excluding specimen A (right valve), the ratios of the other samples cluster tightly about the mean ratio value (0.70861), falling well within the range of long-term analytical precision (2σ) $= \pm 2 \times 10^{-5}$. There is very little heterogeneity among the unaltered samples at the site.

As indicated in Table 1, the $^{87}Sr/^{86}Sr$ of the right valve of specimen A (0.70848) was significantly lower than the others. Because the right valve of this shell revealed evidence of secondary calcite overgrowth and replacement near the shell exterior, and because its $^{87}Sr/^{86}Sr$ was substantially lower than that of the left (unaltered) valve, as well as the other specimens, this ratio was not included in age determinations.

The $^{87}Sr/^{86}Sr$ values for specimens A'-D all gave ages in the range 17.8-18.3 Ma. Errors associated with these ages are on the order of ± 0.5-1.0 m. y. (Hodell, 1991; Miller et al., 1991; Oslick et al., 1994). When all four sample measurements (A'-D) were pooled, and an age calculated for the mean $^{87}Sr/^{86}Sr$, the resulting age was 17.9 to 18.2 Ma, depending on which seawater Sr-isotope reference curve was used (Table 1).

DISCUSSION: COMPARISON WITH OTHER Sr-ISOTOPIC DATA

The early Miocene ocean was characterized by rapidly rising $^{87}Sr/^{86}Sr$, making this portion of the Neogene particularly suitable for Sr-isotopic geochronology (Hodell et al., 1991; Hodell and Woodruff, 1994; Oslick et al., 1994). Hence, the ages calculated here from the mollusk $^{87}Sr/^{86}Sr$ measurements serve to place the fossils recovered from the Pollack Site into a fairly narrow chronostratigraphic context (Fig. 1). The ratios presented in Table 1, with their associated age calculations, suggest that the shells in this deposit range in age from approximately 17.9 to 18.2 ± 0.5 Ma.

Without additional samples from multiple specimens collected at successive stratigraphic horizons throughout the sequence, it is impossible to refine the age structure of the deposit. Stratigraphic condensation, which has been observed elsewhere in Coastal Plain shell beds, can result in mixtures of shells of different ages and different Sr-isotopic ratios (e.g., Webb et al., 1989; Jones et al., 1995), but this process does not appear to have played a major role here. However, it was interesting to discover a specimen of *Mercenaria ducatelli* in which one valve (sample A') appears to have faithfully record-

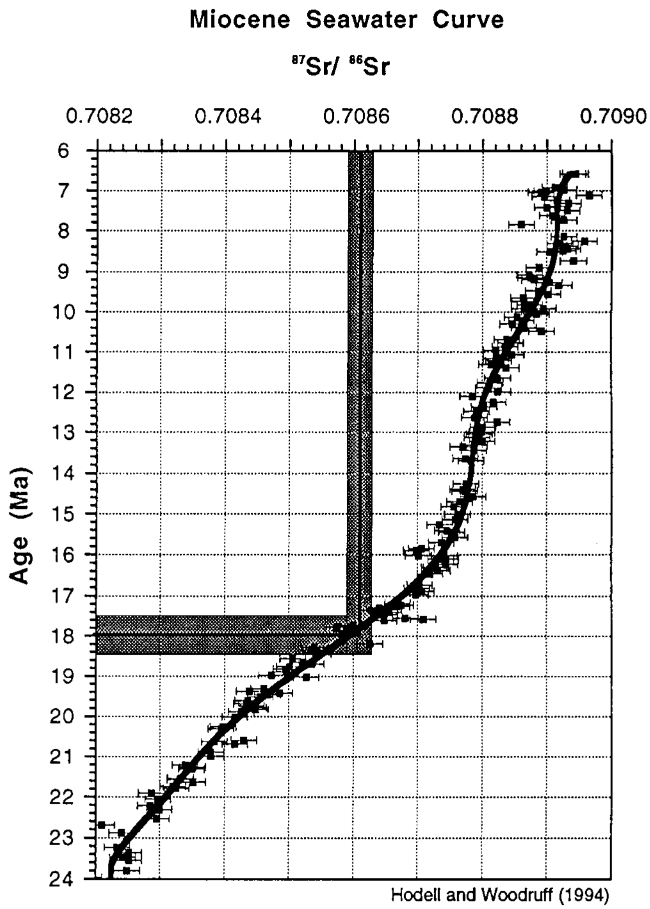

Figure 1. Composite Miocene seawater $^{87}Sr/^{86}Sr$ reference curve from Hodell and Woodruff (1994) showing the mean Sr-isotopic ratio determined from mollusk shells at the Pollack Site, 0.70861 ± 2 X 10-5 (2σ), and the corresponding age.

ed the $^{87}Sr/^{86}Sr$ of seawater at the time of deposition whereas the lower Sr-isotopic ratio in the other valve (sample A) appears to represent overprinting due to dissolution, replacement, and precipitation of secondary calcite. It remains unclear as to why the Sr-isotopic ratio in the altered, right valve should be lower and not higher than the other ratios at this site, derived from apparently unaltered $CaCO_3$. Perhaps diagenetic fluids with relatively lower $^{87}Sr/^{86}Sr$ could have arisen from older (deeper) sediments during compaction and dewatering. Whatever the explanation, it is increasingly clear that sample preservation state must be monitored closely in order to insure reliable results.

As Sr-isotopic techniques are employed in an ever-increasing number of Coastal Plain studies, it becomes easier to refine geochronologic assessments as well as compare deposits across broad geographic regions where biogeographic, paleoenvironmental, and/or lithologic changes might otherwise obscure temporal relations. For example, across the Delaware River, to the northeast, the Miocene Kirkwood Formation of southern New Jersey was the subject of recent Sr-isotopic investigations by Sugarman et al. (1993, 1997). These authors used mollusk shells obtained primarily from wells and boreholes for analyses of $^{87}Sr/^{86}Sr$ in order to help constrain the age of the Kirkwood. Sr-isotopic ratios helped define several sequences within this unit. The lowermost Miocene and lower Miocene Kirkwood sequences (Kw0, Kw1a and Kw1b) of Sugarman et al., 1993) correspond to East Coast Diatom Zone (ECDZ) 1 of Andrews (1988) and appear to be older than the Pollack Farm Site with ages of 23.6-18.4 Ma. After a major unconformity, the next youngest, or Kw2a sequence, covers the period 17.8 to 16.6 Ma ± 0.5 m.y. (Sugarman et al., 1997), corresponding to ECDZ 2 of Andrews (1988). Centering around 17.9 Ma ± 0.5 m.y., the mean Sr isotopic ages of specimens A'-D from the Pollack Site are younger than the Kirkwood 1 ages and seem to correspond most closely with the Kirkwood 2a ages. Thus, they appear to fall within the dated portions of the upper lower Miocene Kirkwood Formation of southern New Jersey.

The molluscan assemblage at the Pollack Farm Site is analyzed by Ward (1998), and it has close affinities with the assemblage from the Kirkwood Formation at Shiloh, New Jersey. Most of the taxa named from Shiloh also occur in the Delaware pit.[5] Ward (1998) also notes similarities between the molluscan fauna of the Pollack Site and the beds at such localities to the south as Centerville, Church Hill, Sudlersville, and Wye Island, Maryland. The sediments in these equivalent beds fine to a silty clay on the western shore of the Chesapeake Bay, but are identifiable by the presence of the marker diatom, *Actinoptychus heliopelta*, on whose appearance Andrews (1988) based his ECDZ 1.[5] This species occurs throughout the Kirkwood, but only in one bed of the Calvert Formation, Bed 3A, which occupies the lower 3 m (10 ft) of the Fairhaven Member.[6] Sr-isotopic measurements on mollusk shells from sections along the southwestern shore of Chesapeake Bay (Jones et al., in prep.) indicate that the mollusks from the Pollack Farm Site are just slightly older (ca. 1 m.y.) than specimens recovered from Zone 4, Plum Point Marl Member of the Calvert Formation (Ward, 1992).

Ward (1998) also discusses faunal similarities between the mollusks of the Pollack Farm Site and those of the Pungo River Formation in North Carolina and the Chipola Formation exposed in the Florida Panhandle. The Chipola has been the subject of two recent geochronologic investigations using Sr isotopes to help constrain its age (Bryant et al., 1992; Jones et al., 1993). Samples from the Chipola Formation at the well known Alum Bluff exposure yielded $^{87}Sr/^{86}Sr$ age estimates of 18.3-18.9 Ma (Bryant et al., 1992). Samples collected from outcrops along Tenmile Creek in nearby Calhoun County gave nearly identical $^{87}Sr/^{86}Sr$ ages, 18.4-18.9 Ma (Jones et al., 1993). The close correspondence in Sr-isotopic ratios between mollusks of the

[5] Stratigraphic correlation of geophysical logs between the Pollack Farm Site and the Shiloh area of New Jersey by Benson (1998) shows that the Pollack shell beds are younger than the Shiloh beds and are absent at Shiloh by having been eroded. Also, Benson (1998) identified *Actinoptychus heliopelta* from a sandy silt overlying the main (lower) shell bed at the Pollack Farm Site and cites other studies in Delaware showing that this marker species identifying ECDZ 1 occurs within beds equivalent in age to the Kw2a sequence of New Jersey and, therefore, ranges stratigraphically higher than its New Jersey range as indicated by Sugarman et al. (1993).—ED.

[6] This applies to the occurrence of Bed 3A in outcrop. The ECDZ 1 diatom assemblage zone identified by the occurrence of *Actinoptychus heliopelta* occurs within almost the entire lower Miocene section of Delaware and New Jersey as indicated by Benson (1998) and Sugarman et al. (1993).—ED.

Chipola Formation and those of the Pollack Farm Site provides strong support for the contemporaneity of these two widely separated fossil faunas, reinforcing observations of faunal similarities.

From Sr-isotopic age determinations on four specimens, it is clear that the mollusks from the Pollack Farm Site represent an early Miocene assemblage that lived about 17.9 ± 0.5 Ma. Good correlations with other, well-dated, Coastal Plain mollusk faunas to the north and south support this assessment. Marine mollusks from Florida with identical $^{87}Sr/^{86}Sr$ ages have been successfully correlated with terrestrial vertebrates of the early Hemingfordian North American Land Mammal Age (Bryant et al., 1992). A similar marine-nonmarine link is strongly suggested for the Pollack Site as well.

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