Cretaceous Research 62 (2016) 1–12

Contents lists available at ScienceDirect

Cretaceous Research

journal homepage: www.elsevier.com/locate/CretRes

Strontium isotope age-dating of fossil shark tooth enameloid from the Upper Cretaceous Strata of Alabama and Mississippi, USA

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ARTICLE INFO

Article history:
Received 27 September 2015
Received in revised form
4 January 2016
Accepted in revised form 27 January 2016
Available online 11 February 2016

Keywords:
Biogeochemistry
Gulf Coastal Plain
Mississippi Embayment
Paleontology
Stratigraphic correlation
Stratigraphy

ABSTRACT

Cretaceous strata in Alabama and Mississippi (USA) represent one of the most complete records of shallow marine deposition worldwide for the Upper Cretaceous. The age assignment of these strata in the eastern Gulf Coastal Plain is difficult due to the comparative lack of radiometrically datable beds and sometimes conflicting results of biostratigraphy using different taxonomic groups. Numerical age dating using strontium isotope ratios ($^{87}Sr/^{86}Sr$) preserved in diagenetically resistant fossil shark tooth enameloid had been proposed by previous researchers as a solution to dating some geologic units. Here we apply this methodology to the whole Upper Cretaceous, using teeth of two fossil shark genera (*Scapanorhynchus* and *Squalicorax*) collected from variable facies. Shark teeth collected from a bentonite mine in Monroe County, Mississippi, were also analyzed and compared with the radiometric date of the bentonite layer. Results indicate a strong correlation between stratigraphic position of the fossil teeth and numerical age determination based on $^{87}Sr/^{86}Sr$ content. Furthermore, this method is equally effective for both of the fossil shark genera analyzed in the study. Because of the nearly uniform distribution of strontium in ocean water, numerical age dating using strontium isotope ratios preserved in fossil shark tooth enameloid can be a useful method to employ in the correlation of marine geological strata on both regional and global scales.

1. Introduction

The Upper Cretaceous strata of the eastern Gulf Coastal Plain of the United States represent a nearly continuous record of marine depositional cycles, spanning approximately 21 million years in age (Mancini and Puckett, 2003; Liu, 2007). At least three major eustatic transgressive–regressive cycles are recorded in these units, which are important markers for stratigraphic correlation on a regional and global scale (Mancini and Puckett, 2005; Mancini et al., 2008). Precise age dating of these strata in Alabama and Mississippi has primarily depended on biostratigraphic methods using foraminifera (Cushman, 1946; Smith, 1997), coccolithophores (Cepek and Hay, 1969; Hester and Risatti, 1972), ostracodes (Puckett, 1994), bivalves (Stephenson, 1933; Stephenson and Monroe, 1938), or ammonites (Cobban and Kennedy, 1995). Additionally, correlative sequence stratigraphy has been used in conjunction with biostratigraphy for age assignment of these strata (Mancini and Tew, 1997; Mancini and Puckett, 2005; Liu, 2007). In many cases, this dependence on relative dating methods has produced equivocal results leading to considerable variation in the reported age of Cretaceous units in this region (Russell, 1967; Raymond et al., 1988; King and Skotnicki, 1994; Mancini and Soens, 1994; Dockery, 1996; Mancini and Puckett, 2005; Liu, 2007). The variation in reported age is further exacerbated by the lack of radiometrically dateable strata over wide geographic areas in the Mississippi Embayment, although isolated, locally-prominent bentonite beds with suitable minerals do exist (Munyan, 1940; Stephenson and Monroe, 1940; Monroe, 1941; Merrill, 1983). A more definitive method is needed to refine the numerical ages of Upper Cretaceous strata in the region so that age determination is not solely dependent on biostratigraphic relative dating.

A potential solution to the problem of age dating these Cretaceous marine strata in the eastern Mississippi Embayment is through the use of stable strontium isotope ratios ($^{87}Sr/^{86}Sr$) preserved in fossil shark teeth (Schmitz et al., 1997; Becker et al., 2008), a dating method that was first proposed by Wickman (1948). Strontium is a trace element dissolved in seawater which has a

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http://dx.doi.org/10.1016/j.cretres.2016.01.011
0195-6671/

more or less uniform global distribution due to the long residence time for strontium in seawater of $\approx 10^6$ years, and the comparatively fast mixing time of seawater by ocean currents of $\approx 10^3$ years (McArthur et al., 2012). Changes in the $^{87}Sr/^{86}Sr$ ratio occur over long periods of time due to input and removal of strontium in the ocean by geologic processes, and there are two primary pathways through which $^{87}Sr/^{86}Sr$ ratios in seawater are altered: 1) input of weathered silicate continental crust and dissolved marine carbonate deposits via freshwater rivers, and 2) hydrothermal circulation at mid-ocean ridges (McArthur, 1994; Shields, 2007). A portion of ^{87}Sr is generated by the radioactive decay of ^{87}Rb, which is often present in potassium-bearing silicate rocks (Faure and Mensing, 2005). Because of this ^{87}Sr enrichment of silicate rocks, large-scale orogenic events that increase continental crust weathering gradually raise the $^{87}Sr/^{86}Sr$ ratio in seawater, whereas hydrothermal circulation at mid-ocean ridges tends to reduce the ratio through precipitation of anhydrite (McArthur, 1994).

Strontium becomes incorporated in calcium carbonate and apatite crystals through a substitution with calcium, due to their similar ionic radius and oxidation state (Faure and Mensing, 2005). The $^{87}Sr/^{86}Sr$ ratio preserved in calcium-bearing minerals at the time of their formation (both biotic and abiotic) is the same as that present in the surrounding seawater (Veizer, 1989) and, provided there is no diagenetic alteration of the crystals, maintains a record of the oceanic $^{87}Sr/^{86}Sr$ ratio in the geologic past (DePaolo and Ingram, 1985; McArthur, 1994). Preserved $^{87}Sr/^{86}Sr$ ratios have been collected globally (McArthur et al., 1994; Veizer et al., 1997; Veizer et al., 1999; McArthur et al., 2012) and, when combined with the biostratigraphy of containing strata and absolute age dating of appropriate adjacent strata, produce accurate, high-resolution numeric ages. Databases of $^{87}Sr/^{86}Sr$ numeric ages are combined and the LOWESS (Locally Weighted Scatterplot Smoothing) statistical method (Cleveland, 1981) is applied to produce a continuous strontium isotope curve representing the Phanerozoic Eon that can allow the easy conversion of most $^{87}Sr/^{86}Sr$ ratios into numeric ages (McArthur et al., 2001; McArthur et al., 2012). The peaks and valleys (maxima and minima) of the strontium isotope curve are troublesome in that certain $^{87}Sr/^{86}Sr$ ratios result in two different ages over a narrow span of time. However, the Late Cretaceous portion of the curve relevant to the present study area is represented by a steady increase in the $^{87}Sr/^{86}Sr$ ratio until the Cretaceous/Paleogene (K/Pg) boundary, after which the ratio begins to decrease (Fig. 1) (McArthur et al., 2001).

1.1. Previous work

The use of $^{87}Sr/^{86}Sr$ ratios preserved in fossil shark tooth enameloid for numeric age dating in the Mississippi Embayment was first proposed by Schmitz et al. (1997) and later by Becker et al. (2008), who refined the sampling method. Schmitz et al. (1997) analyzed fossil shark teeth from the Paleogene Tuscahoma and Bashi formations in Mississippi, noting that the $^{87}Sr/^{86}Sr$ ratio of the outer enameloid was well-preserved in comparison with the dentine (osteodentine and orthodentine) found in the tooth interior. Their hypothesis for this difference in ratios was that the dentine had diagenetically recrystallized during fossilization and lost its original $^{87}Sr/^{86}Sr$ signal whereas the enamel, with its larger and coarser bioapatite crystals, was more resistant to diagenetic recrystallization and retained its original $^{87}Sr/^{86}Sr$ ratio.

Becker et al. (2008) obtained fossil shark teeth of *Scapanorhynchus texanus* (Roemer 1849) from the Tombigbee Sand Member of the Eutaw Formation in Alabama and a modern shark tooth of *Isurus oxyrinchus* to test the hypothesis of Schmitz et al. (1997). These authors developed a “scratch” method that restricted sampling to the outermost enameloid portion of the tooth and compared the results with sectioned portions of the tooth that

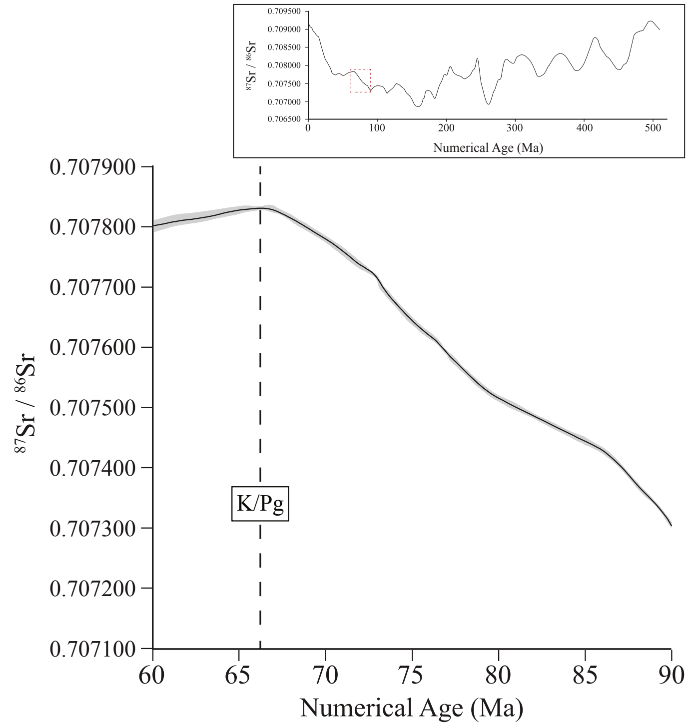

Fig. 1. LOWESS curve of strontium isotope ratio to numerical age for the Phanerozoic Eon (inset) and Late Cretaceous time period that is the focus of the current study. Gray area in Late Cretaceous graph indicates range of uncertainty in the curve. Figures modified from McArthur et al. (2012). K/Pg = Cretaceous/Paleogene boundary.

contained osteodentine and/or orthodentine. In the modern shark tooth, $^{87}Sr/^{86}Sr$ ratios of the enamel and dentine portions of the tooth were close to the isotopic composition of present-day seawater. In the fossil shark teeth, the $^{87}Sr/^{86}Sr$ ratio of the dentines was considerably higher than that of the enameloid, suggesting diagenetic alteration of the interior osteodentine and the resistance of the enameloid. Becker et al. (2008) converted the enameloid $^{87}Sr/^{86}Sr$ ratio of the fossil shark teeth to numeric age dates using the LOWESS strontium isotope curve and look-up table (Version 4b) initially developed by McArthur et al. (2001). The average age of the fossil shark teeth was 78.8 ± 0.4 Ma, which is within the Late Cretaceous and fits within the known stratigraphic range for *Scapanorhynchus texanus* reported by Becker et al. (2008). However, when compared to stratigraphic columns of Upper Cretaceous strata of Alabama, the numeric ages of specimens analyzed by Becker et al. (2008) are much too young for the currently accepted age of the Tombigbee Sand of late Santonian to earliest Campanian (Fig. 2). When the results of their study are updated to Version 5 of the look-up table (McArthur et al., 2012), which increases the age of the samples, they are still too young for the Tombigbee Sand as well as some of the overlying strata (Fig. 2). Possible reasons for this discrepancy are: 1) that the strontium ratio in the enameloid has been diagenetically altered through long-term leaching by groundwater, 2) enameloid contamination by underlying dentine during sampling, or 3) the Tombigbee Sand may be geologically younger than currently accepted.

1.2. Purpose of study

The study presented here has three primary objectives: 1) To determine if $^{87}Sr/^{86}Sr$ ratios can be used for accurate numeric age dating of Upper Cretaceous strata in Alabama (AL) and Mississippi (MS); 2) To determine whether Cretaceous fossil sharks other than