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

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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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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 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.

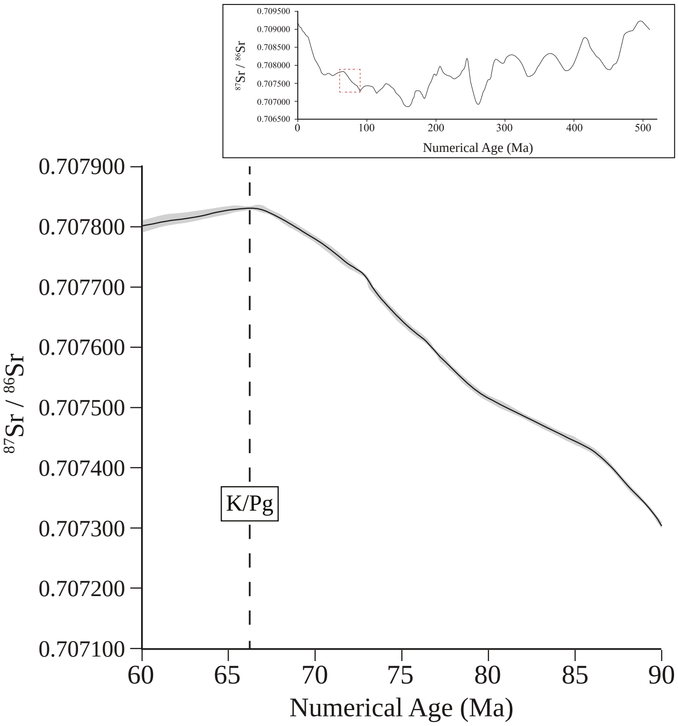

Fig. 1. LOWESS curve of strontium isotope ratio to numerical age for the Phanerozoic Eon (inset) and Late Cretaceous time period that is the focus of the current study. Gray area in Late Cretaceous graph indicates range of uncertainty in the curve. Figures modified from McArthur et al. (2012). K/Pg =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

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

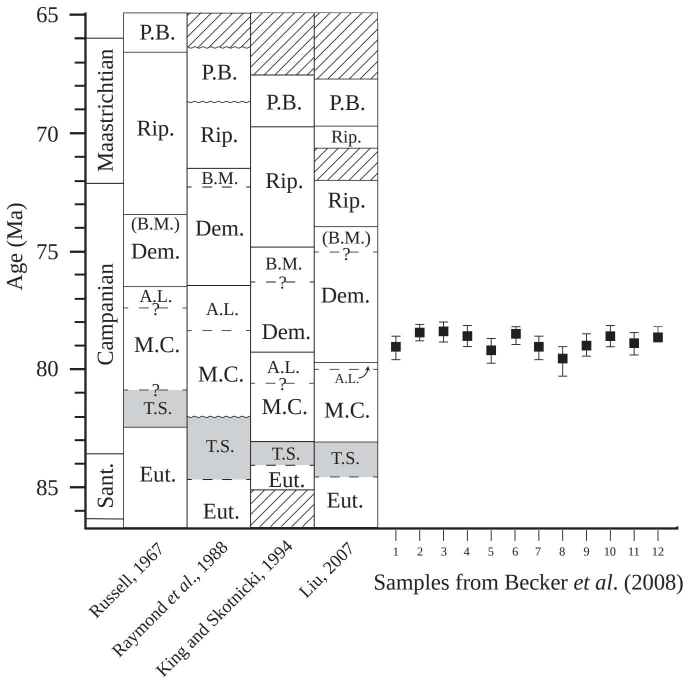

Fig. 2. Results of Becker et al. (2008) updated with look-up table Version 5 (McArthur et al., 2012) plotted against several published stratigraphic columns of Upper Cretaceous formations of Alabama. Note that the numerical ages of the samples are younger than any accepted age of the Tombigbee Sand (Shaded area) in Greene County, Alabama from which the specimens were collected. All Becker et al. (2008) samples were from *Scapanorhynchus texanus*. **Eut.** – Eutaw Formation; **T.S.** – Tombigbee Sand Member of Eutaw Formation; **M.C.** – Mooreville Chalk; **A.L.** – Arcola Limestone Member of Mooreville Chalk; **Dem.** – Demopolis Chalk; **B.M.** – Bluffport Marl Member of Demopolis Chalk; **Rip.** – Ripley Formation; **P.B.** – Prairie Bluff Chalk. Dashed lines indicate member divisions of geologic formations analyzed in this study, unnamed members are not indicated. A question mark indicates that the precise division between members was not indicated by the cited authors. Formational divisions are the work of the cited authors.

Scapanorhynchus texanus can be used for accurate strontium isotope age dating; and 3) To compare strontium isotope derived age dates with a radiometric date from the same collection locality to gauge the relative accuracy of this method.

1.3. *Geology of study area*

The fossil shark teeth used in this study (Fig. 3, Table 1) were collected by Alabama Museum of Natural History staff from outcropping Upper Cretaceous marine formations in western Alabama, and by the third author (GP) at one additional site in eastern Mississippi (Fig. 4). These formations were deposited along the southeastern portion of the Mississippi Embayment during the Late Cretaceous, in depositional environments ranging from subtidal to outer shelf (Cagle, 1985; King, 1990; King and Skotnicki, 1990; Kiernan, 2002). The reported age of these deposits ranges from late Coniacian for the lower Eutaw Formation through the mid to late Maastrichtian of the Prairie Bluff Chalk (Mancini et al., 2008). Although the sequence of strata is nearly continuous, a few hiatuses are present in the stratigraphic column (Mancini and Puckett, 2005; Liu, 2007) (Fig. 2).

Eutaw Formation – The Eutaw Formation is subdivided into the lower unnamed member and the upper Tombigbee Sand Member. The lower unnamed member is a fine to medium-grained, cross-bedded, largely unfossiliferous, micaceous, glauconitic sandstone approximately 52 m thick (Mancini and Soens, 1994). The Tombigbee Sand Member disconformably overlies the lower unnamed member and attains a maximum thickness of approximately 30 m in western Alabama (Stephenson and Monroe, 1940; Liu, 2007), although other studies report a maximum thickness of approximately 6 m in the same region (Kiernan, 2002). The Tombigbee Sand is composed of massive fine-grained sandstone to coarse-grained siltstone, that is glauconitic, micaceous, calcareous, locally bentonitic, highly fossiliferous, and bioturbated (Raymond et al., 1988; Mancini and Soens, 1994). The macrofaunal assemblage, shark tooth lag deposits, and abrasion evident on many fossils suggest that reworking of specimens is a possibility in the Tombigbee Sand (Manning, 2006). The Tombigbee Sand is porous and supports an aquifer used locally in the region (Davis, 1987).

Mooreville Chalk – The Mooreville Chalk is divided into the lower unnamed member and the upper Arcola Limestone Member. The contact of the lower unnamed member of the Mooreville Chalk with the underlying Tombigbee Sand Member of the Eutaw Formation is gradational, but it is indicated by a layer of phosphatic pebbles and invertebrate steinkerns (Mancini and Soens, 1994). Other researchers have suggested an arbitrary contact where the sand content reaches 50% (Liu, 2007). The lower unnamed member is approximately 79 m thick in western Alabama and increases to 180 m in central Alabama (Raymond et al., 1988). Lithologically, the lower member is composed of calcareous, glauconitic, and micaceous sandstone near the base that fines upward into clay-rich, chalky marlstone (Raymond et al., 1988; Kiernan, 2002). The vertebrate fauna of the lower unnamed member of the Mooreville Chalk is well-known and very diverse (Zangerl, 1948; Thurmond and Jones, 1981; Kiernan, 2002). The Arcola Limestone Member is approximately 3 m thick in the study area, and it is composed of two to four beds of impure limestone separated by marlstone interbeds (Raymond et al., 1988).

Demopolis Chalk – The Demopolis Chalk is subdivided into the lower unnamed member and the upper Bluffport Marl Member. The lower unnamed member of the Demopolis Chalk conformably overlies the Arcola Limestone Member of the Mooreville Chalk and is approximately 132 m thick within the study area (Raymond et al., 1988). Near its base in the shallower-water facies, the lower unnamed member is lithologically similar to the Mooreville Chalk that underlies the Arcola Limestone Member, being composed of clay-rich marlstones, but upsection becomes a more pure chalk (Puckett, 1996; Kiernan, 2002; Mancini and Puckett, 2005). This reduction of terrigenous clastics in the deeper-water facies suggests a transgressive maximum of the epeiric sea during the Late Cretaceous in Alabama (Liu, 2007). The overlying Bluffport Marl Member ranges from 15 m to 20 m in thickness in western and central Alabama (Raymond et al., 1988), but the depositional environment is still considered to be outer shelf (Cagle, 1985), despite the increase in siliciclastic content. The Demopolis Chalk possesses a relatively rich and diverse vertebrate fauna (Derstler, 1988), although it is not as fossiliferous as the Mooreville Chalk.

Ripley Formation – The Ripley Formation in western Alabama ranges from approximately 11 m near the Mississippi border to 76 m in central and eastern portions of Alabama. Lithologically, the Ripley Formation is composed of fine glauconitic sandstone, calcareous sand and clay upsection, and thin layers of fossiliferous sandstone (Raymond et al., 1988). The Ripley Formation contains a diverse, well-preserved invertebrate fauna but also has produced a number of significant vertebrate fossils. Like the Tombigbee Sand, sandier portions of the Ripley Formation are used as a regional aquifer (Davis, 1987). Reworking of fossils is a possibility given the nearshore depositional environment for portions of the formation (King and Skotnicki, 1990).

Prairie Bluff Chalk – The Prairie Bluff Chalk disconformably overlies the Ripley Formation in western Alabama. Bryan (1992) suggests that this unconformity represents subaerial exposure and erosion of the upper Ripley Formation. The Prairie Bluff Chalk attains

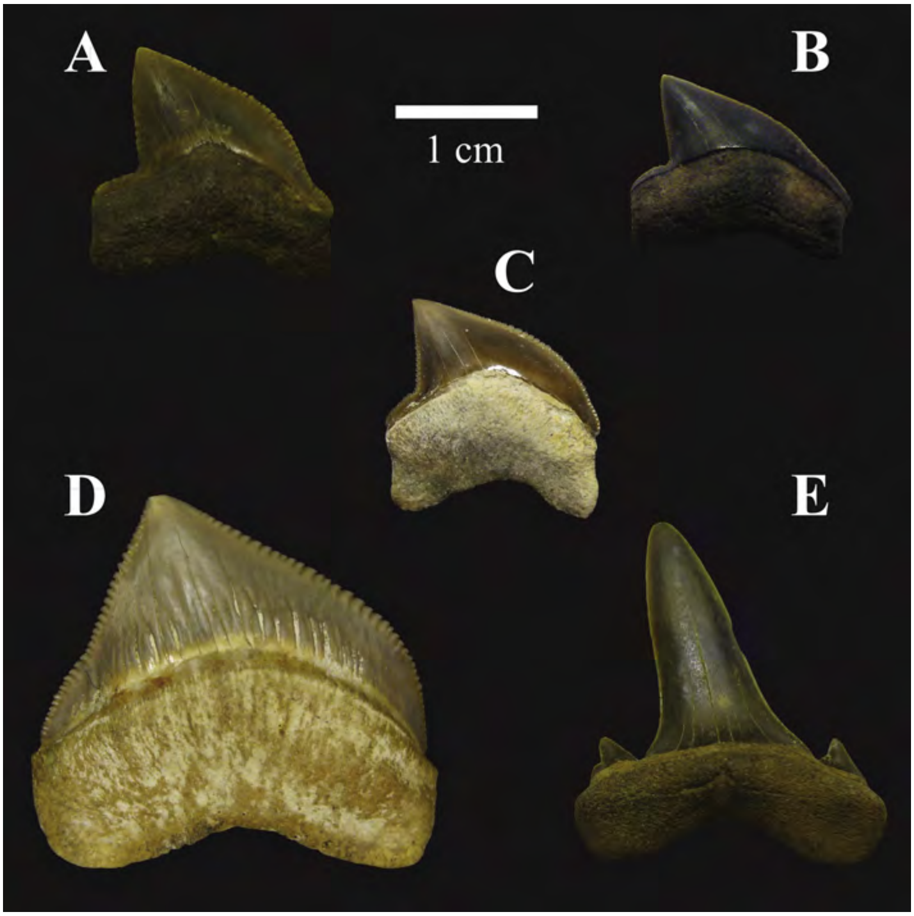

Fig. 3. Representative teeth of fossil shark taxa analyzed in this study. **A** – *Squalicorax* cf. *yangaensis* from the Tombigbee Sand Member of the Eutaw Formation in Greene County, AL (AGr-43), **B** – *Squalicorax lindstromi* from the Tombigbee Sand Member of the Eutaw Formation in Greene County, AL (AGr-43), **C** – *Squalicorax kaupi* from the Mooreville Chalk in Dallas County, AL (ADa-3UA), **D** – *Squalicorax pristodontus* from the Prairie Bluff Chalk in Lowndes County, AL (ALn-7), **E** – *Scapanorhynchus texanus* from the Tombigbee Sand Member of the Eutaw Formation in Greene County, AL (AGr-43). All teeth are in lingual view.

Table 1
Sample numbers, Alabama Museum of Natural History (ALMNH) and Mississippi Museum of Natural Science (MMNS) specimen identification numbers, taxa, and locality data.

Sample #	Museum specimen #	Taxon	Geologic unit	Locality #	Site/Town	County	State
MS-1	MMNS RN 8584.3 09-128	*Squalicorax lindstromi*	Tombigbee Sand	MGS-162	Fowlkes Mine	Monroe	MS
MS-2	MMNS RN 7762 07-168	*Squalicorax lindstromi*	Tombigbee Sand	MGS-162	Fowlkes Mine	Monroe	MS
MS-3	MMNS RN 7330.1 07-30	*Squalicorax lindstromi*	Tombigbee Sand	MGS-162	Fowlkes Mine	Monroe	MS
MS-4	MMNS RN 7330.1 07-30	*Scapanorhynchus texanus*	Tombigbee Sand	MGS-162	Fowlkes Mine	Monroe	MS
MS-5	MMNS RN 8387.2 09-63	*Scapanorhynchus texanus*	Tombigbee Sand	MGS-162	Fowlkes Mine	Monroe	MS
MS-6	MMNS RN 8387.2 09-63	*Scapanorhynchus texanus*	Tombigbee Sand	MGS-162	Fowlkes Mine	Monroe	MS
AL-1	ALMNH Unnumbered Specimen	*Squalicorax* cf. *yangaensis*	Tombigbee Sand	AGr-43	Trussell's Creek	Greene	AL
AL-2	ALMNH Unnumbered Specimen	*Squalicorax* cf. *yangaensis*	Tombigbee Sand	AGr-43	Trussell's Creek	Greene	AL
AL-3	ALMNH Unnumbered Specimen	*Squalicorax lindstromi*	Tombigbee Sand	AGr-43	Trussell's Creek	Greene	AL
AL-4	ALMNH PV1994.0002.0054.002	*Squalicorax* cf. *yangaensis*	Tombigbee Sand	AGr-43	Trussell's Creek	Greene	AL
AL-5	ALMNH PV1990.0022	*Squalicorax kaupi*	Mooreville Chalk	ADa-3UA	Harrell Station	Dallas	AL
AL-6	ALMNH PV2000.0007.0001	*Squalicorax kaupi*	Mooreville Chalk	ADa-3UA	Harrell Station	Dallas	AL
AL-7	ALMNH PV2001.0005.0003	*Squalicorax kaupi*	Mooreville Chalk	ADa-3UA	Harrell Station	Dallas	AL
AL-8	ALMNH PV2002.0005.0004	*Scapanorhynchus texanus*	Mooreville Chalk	ADa-3DW	Harrell Station	Dallas	AL
AL-9	ALMNH PV1988.0020.0324	*Squalicorax pristodontus*	Demopolis (Lower Mbr.)	ADa-13	Safford	Dallas	AL
AL-10	ALMNH PV2005.0006.0403.001	*Squalicorax pristodontus*	Demopolis (Lower Mbr.)	Unnumbered	Boligee	Greene	AL
AL-11	ALMNH PV1993.0002.0032.001	*Squalicorax pristodontus*	Demopolis (Lower Mbr.)	ADa-24	Harrell Station	Dallas	AL
AL-12	ALMNH Unnumbered Specimen	*Squalicorax pristodontus*	Bluffport Marl	Unnumbered	Belmont	Sumter	AL
AL-13	ALMNH Unnumbered Specimen	*Squalicorax pristodontus*	Bluffport Marl	Unnumbered	Belmont	Sumter	AL
AL-14	ALMNH Unnumbered Specimen	*Squalicorax pristodontus*	Bluffport Marl	Unnumbered	Belmont	Sumter	AL
AL-15	ALMNH PV1993.0002.0097.001	*Squalicorax pristodontus*	Ripley	ALn-11	Braggs	Lowndes	AL
AL-16	ALMNH Unnumbered Specimen	*Squalicorax pristodontus*	Prairie Bluff Chalk	ALn-7	Braggs	Lowndes	AL
AL-17	ALMNH PV1991.0013.0008	*Squalicorax pristodontus*	Prairie Bluff Chalk	ALn-7	Braggs	Lowndes	AL
AL-18	ALMNH PV1990.0018.0001	*Squalicorax pristodontus*	Prairie Bluff Chalk	ALn-7	Braggs	Lowndes	AL

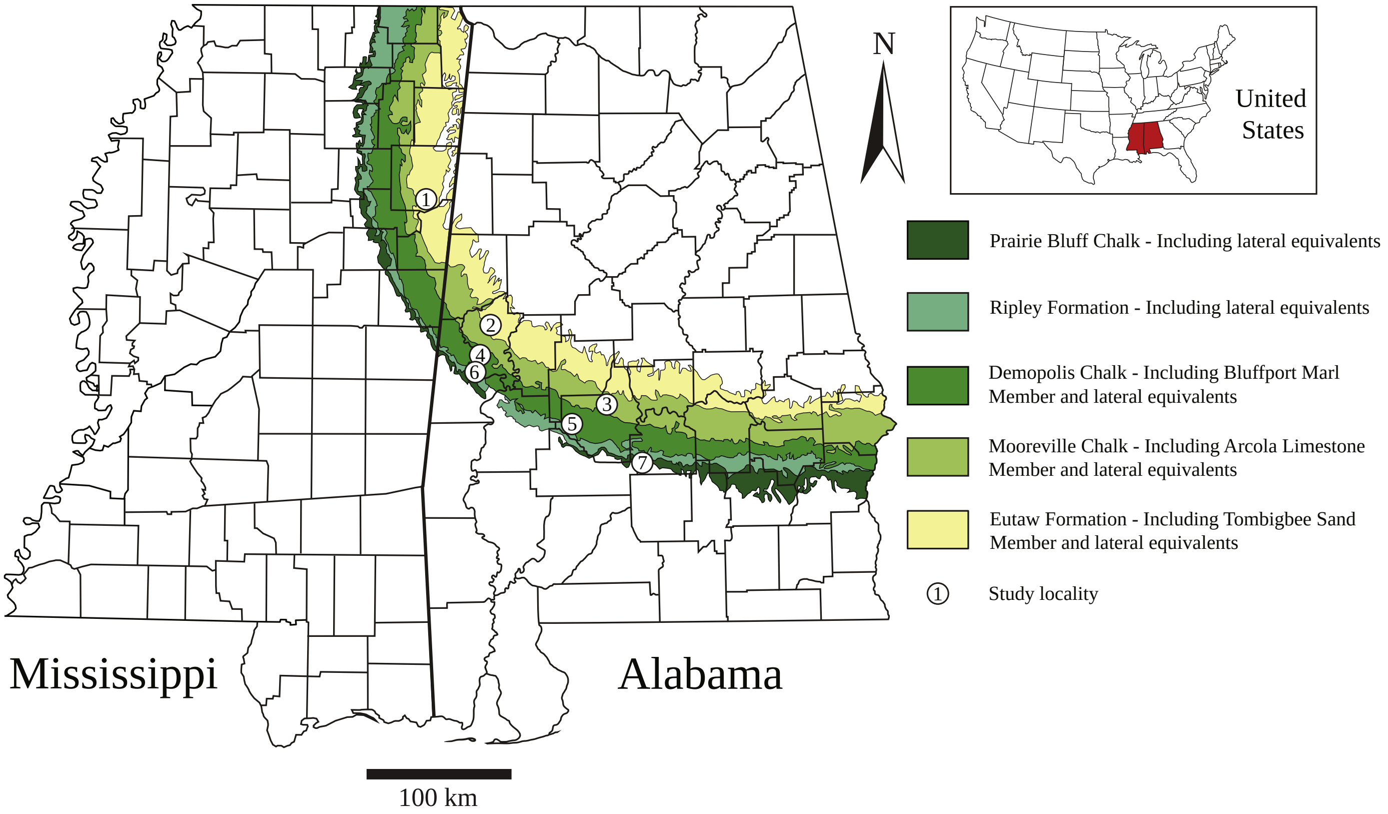

Fig. 4. Collection localities of specimens sampled in this study and outcropping Upper Cretaceous marine units in Alabama and Mississippi. Localities: **1** – BASF Fowlkes Mine (MGS-162, Tombigbee Sand), Monroe Co., MS; **2** – Trussell's Creek (AGr-43, Tombigbee Sand), Greene Co., AL; **3** – Harrell's Station (ADa-3UA and ADa-3DW, Mooreville Chalk; ADa-24, Demopolis Chalk), Dallas Co., AL; **4** – Boligee (Unnumbered site, Demopolis Chalk), Greene Co., AL; **5** – Safford (ADa-13, Demopolis Chalk), Dallas Co., AL; **6** – Belmont (Unnumbered Site, Bluffport Marl), Sumter Co., AL; **7** – Braggs (ALn-11, Ripley Fm; ALn-7, Prairie Bluff Chalk), Lowndes Co., AL.

a maximum thickness of approximately 34 m in central Alabama, however, it is completely absent in some areas of western Alabama (Raymond et al., 1988). In contrast to the highly siliciclastic lithology of the Ripley Formation, the overlying Prairie Bluff Chalk consists of fine, bluish-gray sand and chalk (Raymond et al., 1988). Fossil content of the Prairie Bluff Chalk includes well-preserved macroinvertebrates (Bryan, 1992), and a lesser number of vertebrate fossils than the underlying strata. A disconformity and temporal hiatus represents the upper contact of the Upper Cretaceous (Maastrichtian) Prairie Bluff Chalk with the overlying Paleocene (Danian) Clayton Formation, which has been interpreted as either a subaerial erosional surface resulting from a marine regression (Smith, 1997), or tsunami damage from the Chicxulub impact that occurred far to the south at the K/Pg boundary (Feldl et al., 2002).

2. Methods

Specimens of shark teeth were obtained with permission from the collections of the Alabama Museum of Natural History and the Mississippi Museum of Natural Science (Table 1). The specimens had been previously collected by museum staff over a period of many years. Specimens were selected by their recorded stratigraphic provenance and high-degree of tooth crown preservation. In some geologic units, two genera of sharks (*Squalicorax* Whitley 1939 and *Scapanorhynchus* Woodward 1889) were analyzed to determine if there are any differences in the $^{87}Sr/^{86}Sr$ signatures based on possible habitat preference of taxa. Biostratigraphic limitations of taxa required the use of four species of *Squalicorax* (*S.* cf. *yangaensis* (Dartevelle and Casier 1943), *S. lindstromi* (Davis 1890), *S. kaupi* (Agassiz 1843), and *S. pristodontus* (Agassiz 1843)) in the analysis (Fig. 3). When possible, three specimens from each geological unit in the study were selected for increased statistical significance of the results. Two *S. pristodontus* teeth (AL-13 and AL-14) from an associated dentition collected from the Bluffport Marl, and a *S. pristodontus* tooth (AL-16) associated with a *Mosasaurus hoffmanni* specimen from the Prairie Bluff Chalk, were analyzed to test the accuracy and precision of this analytical method.

One of the purposes of the study is to analyze $^{87}Sr/^{86}Sr$ ratios of shark teeth collected near a bentonite seam within the Tombigbee Sand in a Monroe County (Mississippi) mine and compare the results with the radiometric (K-Ar) age of the same bentonite layer reported by Obradovich (1993). Access to the high-wall at BASF Fowlkes Mine was restricted because of safety concerns and samples could not be directly acquired *in situ*. However, access was granted to the overburden spoil piles located near the active portion of the quarry and shark tooth samples from the Tombigbee Sand in Mississippi analyzed in the study were collected there.

Specimens were mechanically processed in the Department of Geological Sciences at the University of Alabama (USA). Specimens were first washed in an ultrasonic bath to remove any remaining traces of adhering matrix, rinsed with deionized water, and dried overnight. Each specimen was successively placed in a cleaned and dried agate mortar under a binocular dissecting microscope to collect the sample powders. A Dremel® rotary tool equipped with diamond drill bits was used to remove approximately 10 mg of sample powder from the outer tooth enameloid, which collected in the mortar. The sample powder was then transferred to weigh paper and measured on an electronic balance. The sample powders were placed in individually labeled microcentrifuge tubes for transport. Between specimens, the drill bits and mortar were cleaned with dilute trace metal grade nitric acid (HNO_3), rinsed with deionized water, and dried with Kimwipes® to prevent cross contamination.

The samples were transported to the Geochronology and Isotope Geochemistry Laboratory at the University of North Carolina-Chapel Hill (USA) for geochemical analysis. Between 2.5 and 5.0 mg of each sample powder was weighed on an electronic balance and transferred to new, individually labeled, microcentrifuge tubes. Approximately 550 μL of 3.5 M trace metal grade nitric acid (HNO_3) was added to each microcentrifuge tube to dissolve the samples. After dissolution, the samples were centrifuged to separate any undissolved particles. The sample solutions were then pipetted into individual separation columns filled with Eichrom® SR-B100-S (50 − 100 μm) strontium resin followed by four rinses with 3.5 M trace metal grade HNO_3. In acidic conditions, the strontium atoms in the solution are retained by the resin, while the remaining solution passes out of the column and collects in a waste beaker. The Sr-enriched columns were then transferred to clean, labeled collection cups and rinsed twice with Milli-Q® deionized water. The higher pH conditions resulting from the added water causes the resin to release the retained strontium and the solution collects in cups underneath the columns. One drop of 0.1 M phosphoric acid (H_3PO_4) was added to each of the collected solutions, which were then placed on a hotplate to dry. The end product of chemical processing is a grain-like pellet containing strontium derived from the sample.

Sample pellets were attached to rhenium filaments (99.98% Re) using tantalum pentachloride ($TaCl_5$) as an adherent and analyzed in a VG Micromass® Sector 54 thermal ionization mass spectrometer (TIMS). Each sample isotope ratio was collected 120 times at 8 s intervals and automated software analyzed the results. The ratios were calibrated against the long-term lab average for strontium standard NIST 987, resulting in an adjustment of -2.0×10^{-5} to each sample. No correction was made for rubidium content as this element behaves in a manner similar to potassium in vertebrate organisms and is primarily retained in soft tissues rather than hard tissues (Relman, 1956). Additionally, rubidium was not detected in previous strontium analyses of fossil shark teeth conducted in the study area (Becker et al., 2008).

Squalicorax pristodontus specimen AL-17 (ALMNH PV1991.0013.008) from the Prairie Bluff Chalk was initially cut in half prior to enameloid sampling, with one half of the tooth crown retained for scanning electron microscopy (SEM), conducted at the University of Alabama, to determine the quality of fossil preservation. The retained half of the tooth crown was first mounted in cold-setting epoxy resin, which was permitted to set for 24 h. The labial-lingual axial plane of the tooth was then manually flattened and polished against successively finer aluminum oxide grinding discs and polishing cloths. After polishing, the exposed tooth cross-section was etched with 2% trace metal grade hydrochloric acid (HCl) for 20 s, rinsed with deionized water, and allowed to dry overnight. The epoxy disc containing the sample was then placed in a vacuum chamber and a thin gold coating applied to help dissipate static charge in the SEM. An aluminum mounting post was applied to the bottom of the epoxy disc using carbon tape, and copper strips were used to cover unimportant areas on top of the epoxy disc to further dissipate charging. The specimen was then placed in a JEOL JSM-7000F® field emission scanning electron microscope operated under a 2.0×10^{-4} Pa vacuum, at 15 kV and 8.0 mA of current, using a working distance of between 27 and 29 mm. An unsampled tooth of *Scapanorhynchus texanus* from the Tombigbee Sand in Alabama was also subjected to the same SEM analysis for comparison of genera. Several digital micrographs of the tooth cross sections were recorded at a variety of magnifications and retained for further examination (Fig. 5).

3. Results

The results of the analysis are presented in Table 2 and Figs. 6 and 7. Numerical ages of the samples were obtained from McArthur et al. (2012) using look-up table Version 5. All samples in the analysis collected from the Upper Cretaceous strata yielded $^{87}Sr/^{86}Sr$ ratios that correlate with Late Cretaceous numeric ages (Table 2). Although teeth from some of the lower geologic units vary considerably in age, the general trend in the plotted $^{87}Sr/^{86}Sr$ results shows that overlying strata are progressively younger (Fig. 6).

Specimens from the Tombigbee Sand in Mississippi produced mixed results (Mean = 80.61 Ma). Four of the six samples analyzed from the BASF Fowlkes Mine produced numeric ages (Mean = 79.48 Ma) that are too young for the Tombigbee Sand or Mooreville Chalk present in the quarry (Fig. 7). Two of the samples yielded dates (Mean = 82.88 Ma) that are younger than the underlying bentonite layer (84.09 ± 0.4 Ma) at the bottom of the quarry and are comparable to the age of strata exposed in the high wall. Specimens from the Tombigbee Sand in Alabama produced older results (Mean = 82.06 Ma) although there was less consistency between the samples. The mean age produced by samples from the Mooreville Chalk in Alabama is 78.88 Ma and, similar to the Tombigbee Sand in Alabama, there is considerable variation in the individual results. The lower unnamed member of the Demopolis Chalk (Mean = 74.10 Ma) is more uniform between individual samples than the underlying Mooreville Chalk whereas the Bluffport Marl Member of the Demopolis Chalk (Mean = 71.73 Ma) is even more so. Only one specimen from the Ripley Formation was suitable for sampling, which produced an age of 67.85 Ma. The Prairie Bluff Chalk was uppermost Cretaceous unit analyzed in the study, and yielded a mean age of 68.12 Ma.

4. Discussion and conclusions

4.1. Numeric ages of stratigraphic units

Overall, the numeric ages derived from $^{87}Sr/^{86}Sr$ ratios in the samples correlate reasonably well with the currently accepted ages of the Upper Cretaceous strata of the Mississippi Embayment (Fig. 6). A random sampling of previously published stratigraphic columns from the region is provided in Fig. 6 for simple comparison with the strontium isotope derived ages. Although the numeric ages do not correlate precisely with any single previously published stratigraphic column of Alabama, the column produced by Raymond et al. (1988) compares best with the strontium isotope derived ages for the younger Cretaceous geologic units. The column published by Dockery (1996) correlates better with the results than Raymond et al. (1988); however, that column is only representative of Upper Cretaceous strata in Mississippi as biostratigraphic research and sequence stratigraphy has shown that geologic ages differ between some of the same Cretaceous units in Mississippi and Alabama (Mancini and Puckett, 2005; Liu, 2007).

The strontium isotope numeric ages of shark teeth analyzed from Alabama show a steady trend from older to younger moving upsection in the stratigraphic column (Fig. 6), and the ages of samples become more precise in the younger strata, ranging from the Demopolis Chalk through the Prairie Bluff Chalk. The increased precision may be related to the species of shark sampled from these upper geologic units. *Squalicorax pristodontus* is a large Cretaceous shark (see Shimada and Cicimurri (2005) on size differences in species of *Squalicorax*) whose first occurrence in Alabama, based on material present in the ALMNH collections, is in the lower unnamed member of the Demopolis Chalk (or possibly upper Mooreville Chalk), which then persists to the uppermost portion of the Prairie Bluff Chalk. Adult *S. pristodontus* teeth are comparatively large and

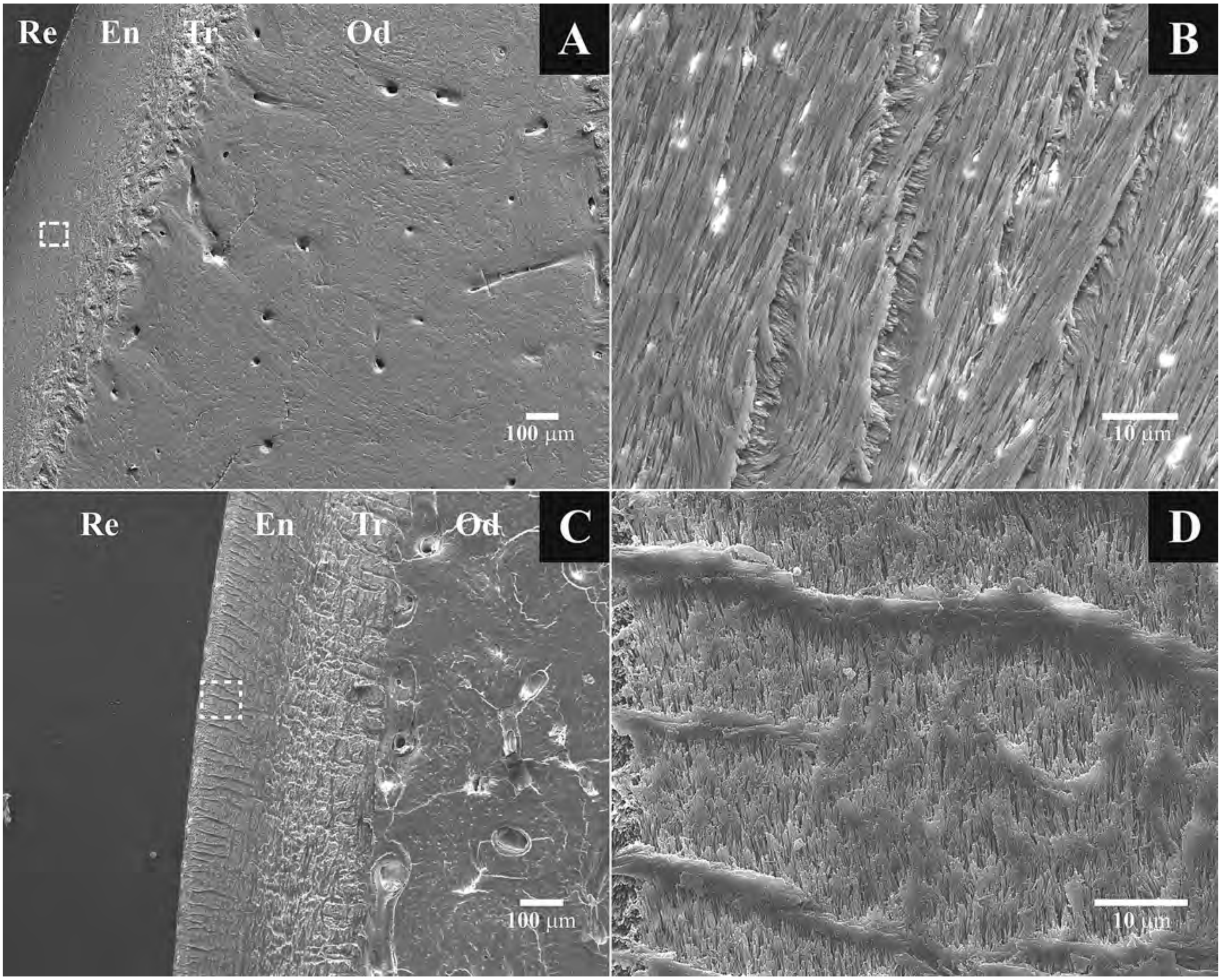

Fig. 5. Scanning electron micrographs (SEM) of *Squalicorax pristodontus* (A and B, Sample AL-17, Tables 1 and 2) and *Scapanorhynchus texanus* (C and D, unsampled specimen from the Tombigbee Sand in Alabama) in labial–lingual axial cross section showing high quality enameloid preservation. **A** – Low magnification SEM of *Squalicorax pristodontus* showing different regions of internal tooth structure. **B** – Magnified view of enameloid layer. Note relative lack of porosity in enameloid. Cross hatched pattern of bundles containing bioapatite crystals are apparent. **C** – Low magnification SEM of *Scapanorhynchus texanus* showing different regions of internal tooth structure. Dashed line indicates region present in image D. **D** – Magnified view of enameloid layer showing well preserved bioapatite crystals. Note significant structural difference between the two shark genera. Re – Mounting resin; En – Enameloid; Tr – Transition zone; Od – Osteodentine. Dashed line in left image indicates region magnified in right image.

are often more than 2 cm across the base of the crown. During specimen sampling, it was noted that the outer enameloid layer appeared relatively thicker than that observed in the older, smaller species *S. kaupi*, *S. lindstromi*, and *S.* cf. *yangaensis*. This thicker enameloid layer in *S. pristodontus* facilitated obtaining the necessary 10 mg of sample powder, with little risk of contamination from the underlying diagenetically-altered osteodentine. The thicker enameloid from the larger *S. pristodontus* teeth is therefore the likely cause of the increased precision upsection. SEM analysis of the enameloid layers in *S. pristodontus* and *Scapanorhynchus texanus* specimens analyzed in this study shows that it is very well preserved in both genera (Fig. 5), with bioapatite crystallite bundles that are structurally similar to those present in the enameloid of extant shark species (Enax et al., 2012; Enax et al., 2014). The impermeable nature of the chalks, marlstones and clayey sands of the upper strata also likely helped to preserve the original strontium isotope signature in the shark teeth by preventing diagenetic alteration by groundwater flowing through the region (Davis, 1987).

The analysis of shark teeth from the Tombigbee Sand show mixed results in both Mississippi and Alabama (Figs. 6 and 7). Only two shark teeth sampled from the Tombigbee Sand in each state produced strontium isotope ages that are comparable to the generally accepted age of the geologic unit (Table 2). It is interesting to note that the better correlating samples from Alabama (AL-1 and AL-2) are considerably older than the better correlating samples (relative to the radiometric age of the bentonite) from Mississippi (MS-2 and MS-6), where the mean age of the Alabama samples is 84.9 Ma and the Mississippi average is 82.88 Ma. This finding is in agreement with the age difference of the Tombigbee Sand in Mississippi and Alabama based on biostratigraphic methods, in which the upper Tombigbee Sand in Mississippi is younger than the upper Tombigbee in Alabama and the Tombigbee Sand–Mooreville Chalk contact is diachronous (Mancini et al., 1996).

Two separate teeth from the same fossil shark were analyzed during the course of this study to test the precision of fossil shark tooth enameloid strontium analysis. Samples AL-13 and AL-14

Table 2
Measured strontium isotope ratios ($^{87}Sr/^{86}Sr$) in analyzed samples adjusted for laboratory bias (-2.0×10^{-5}). Numerical ages determined from McArthur et al. (2012) using look-up table Version 5.

Sample #	$^{87}Sr/^{86}Sr$ Adjusted	2σ abs	Error −	Age Ma	Error +
MS-1	0.707531	0.000010	78.65	**79.20**	79.90
MS-2	0.707475	0.000010	81.90	**82.80**	83.80
MS-3	0.707521	0.000008	79.15	**79.65**	80.45
MS-4	0.707532	0.000008	78.65	**79.15**	79.75
MS-5	0.707517	0.000010	79.20	**79.90**	80.80
MS-6	0.707473	0.000010	82.05	**82.95**	83.90
AL-1	0.707438	0.000010	84.45	**85.45**	86.25
AL-2	0.707453	0.000010	83.40	**84.35**	85.35
AL-3	0.707509	0.000008	79.70	**80.45**	81.20
AL-4	0.707562	0.000009	77.55	**78.00**	78.50
AL-5	0.707567	0.000008	77.40	**77.85**	78.10
AL-6	0.707451	0.000008	83.70	**84.50**	85.35
AL-7	0.707642	0.000009	74.65	**75.10**	75.60
AL-8	0.707561	0.000009	77.60	**78.05**	78.50
AL-9	0.707663	0.000011	73.95	**74.40**	74.90
AL-10	0.707614	0.000010	75.65	**76.25**	76.70
AL-11	0.707744	0.000010	71.10	**71.65**	72.35
AL-12	0.707716	0.000008	72.55	**72.95**	73.20
AL-13	0.707756	0.000011	70.50	**71.15**	71.80
AL-14	0.707757	0.000011	70.45	**71.10**	71.75
AL-15	0.707817	0.000010	66.25	**67.85**	68.70
AL-16	0.707819	0.000008	66.25	**67.70**	68.50
AL-17	0.707819	0.000011	66.25	**67.70**	68.70
AL-18	0.707798	0.000010	68.10	**68.95**	69.80

The bold type signifies the interpreted age of the samples.

(Table 1) were obtained from a partial skeleton of *Squalicorax pristodontus* that included more than 20 teeth and numerous cartilage fragments from the Bluffport Marl in Sumter County, Alabama. Results of the analysis show that these two samples produced nearly identical $^{87}Sr/^{86}Sr$ ratios, with a separation of only 1.0×10^{-6} (Table 2). The $^{87}Sr/^{86}Sr$ ratios for AL-13 and AL-14 equate to numeric ages of 71.15 Ma and 71.1 Ma respectively, which compare well with the age of the Bluffport Marl reported by Dockery (1996) and Raymond et al. (1988). This finding demonstrates that fossil shark tooth enameloid, if carefully sampled, can be utilized for numeric age dating with a high degree of precision and accuracy.

Squalicorax pristodontus specimen AL-16 was recovered from a skeleton of *Mosasaurus hoffmanni* skeleton (ALMNH PV 1988.0018), a large marine reptile of the Late Cretaceous, during its preparation. Shark teeth are commonly recovered during the preparation of marine vertebrate fossils at the Alabama Museum of Natural History. Sharks in the Late Cretaceous, as they are now, were often scavengers of carcasses (Schwimmer et al., 1997) and during the course of feeding would shed loose teeth into the tissues of food items. These coeval shark teeth are ideal for age dating fossils where sampling damage to the teeth of the primary specimen is undesirable, or where teeth are non-existent, as in marine turtles. The strontium isotope age of *Squalicorax pristodontus* specimen AL-16 is 67.70 ± 0.8 Ma (the younger error limit is difficult to ascertain in this specimen due to a peak that occurs in the LOWESS curve at the K/Pg boundary, See Fig. 1), meaning that the *M. hoffmanni* specimen from which the shark tooth was recovered is very likely the same age. This strontium isotope age fits well with the known stratigraphic range for *M. hoffmanni* of late Campanian to latest Maastrichtian (Harrell and Martin, 2015), and provides additional evidence as to the accuracy of this dating method.

4.2. Strontium isotope age vs. radiometric age

The Tombigbee Sand in Monroe County, Mississippi, contains two closely deposited beds of bentonite clay (Stephenson and Monroe, 1940) that are of commercially exploitable thicknesses and have subsequently been exposed by several open pit mining operations in the area. Sanidine crystals obtained from this bentonite couplet were radiometrically dated by Obradovich (1993), who reported an age of 84.09 ± 0.40 Ma for the layer. Fossil shark tooth specimens analyzed in this study were collected from the Fowlkes Bentonite Mine (MMNS locality number: MGS 162), where the Obradovich bentonite samples were obtained. Six specimens (Table 1: MS-1 through MS-6) were collected by the third author (GP) from overburden spoil piles located away from the active high wall. The bentonite couplet in this region of Mississippi is positioned near the base of the Tombigbee Sand, and the approximately 30 m thickness of this geologic unit in eastern Mississippi (Stephenson and Monroe, 1940) is exposed in its entirety in the high wall of the mine. As the contact with the overlying Mooreville Chalk is gradational, and approximately 39 m of strata are present in the mine, it is hypothesized that the lowermost portions of the Mooreville Chalk may also be exposed in the upper reaches of the high wall. The Tombigbee Sand–Mooreville Chalk contact in eastern Mississippi has been reported to be early Campanian in age based on the highest occurrence surface (HOS) of the foraminifera *Dicarinella asymetrica* which is located immediately above the contact (Smith and Mancini, 1983; Dowsett, 1989; Puckett, 1995; Mancini et al., 1996). This means that the Santonian–Campanian boundary in east-central Mississippi is positioned within the upper part of the Tombigbee Sand. The currently accepted age of the Santonian–Campanian boundary is 83.6 ± 0.2 Ma according to the most recent chronostratigraphic chart (ver. 2015/01) published by the International Commission on Stratigraphy (Cohen et al., 2013). Four of the specimens in the present study (Table 2: MS-1, MS-3 through MS-5) produced strontium isotope numeric ages that are too young for the strata exposed in the mine but are comparable with the ages reported by Becker et al. (2008) from the Tombigbee Sand in Alabama (Figs. 2 and 7). However, two specimens (Table 2: MS-2 and MS-6) produced strontium isotope ages of 82.80 Ma and 82.95 Ma respectively that, when their error ranges are included, are comparable with the radiometric age of the bentonite layer in the mine and the age of the Santonian–Campanian boundary (Fig. 7). The reason for the discrepancy between the accurate and inaccurate age dates is not known. As the Tombigbee Sand was deposited in a relatively nearshore environment (Mancini and Soens, 1994), freshwater influx from nearby rivers may have influenced the original strontium isotope signature in individuals with the less accurate age dates, whereas the more accurate samples may have belonged to individuals who migrated in from more offshore areas with normal strontium isotope ratios. Another explanation is that the differences may be due to sampling error as a result of the inclusion of diagenetically altered osteodentine in the enameloid obtained from smaller *Squalicorax* cf. *yangaensis*, *Squalicorax lindstromi*, and *Scapanorhynchus texanus* teeth (Fig. 3). The observed discrepancies could also be attributed to diagenetic leaching of the strontium content in the shark teeth by groundwater present in the Tombigbee Sand (Davis, 1987), whereas the shark teeth with more accurate age dates may have been deposited in the more calcareous, less-porous layers of the Tombigbee Sand (Stephenson and Monroe, 1940), which protected them from alteration. As the teeth from the mine could only be obtained from overburden spoil piles located away from the high wall, it is uncertain as to the precise lithologic layer from which each was derived.

4.3. $^{87}Sr/^{86}Sr$ Ratios in different shark taxa

Samples analyzed in the study were acquired from two genera, *Scapanorhynchus* and *Squalicorax*, to determine if possible habitat preference of either taxon could affect the $^{87}Sr/^{86}Sr$ ratios present

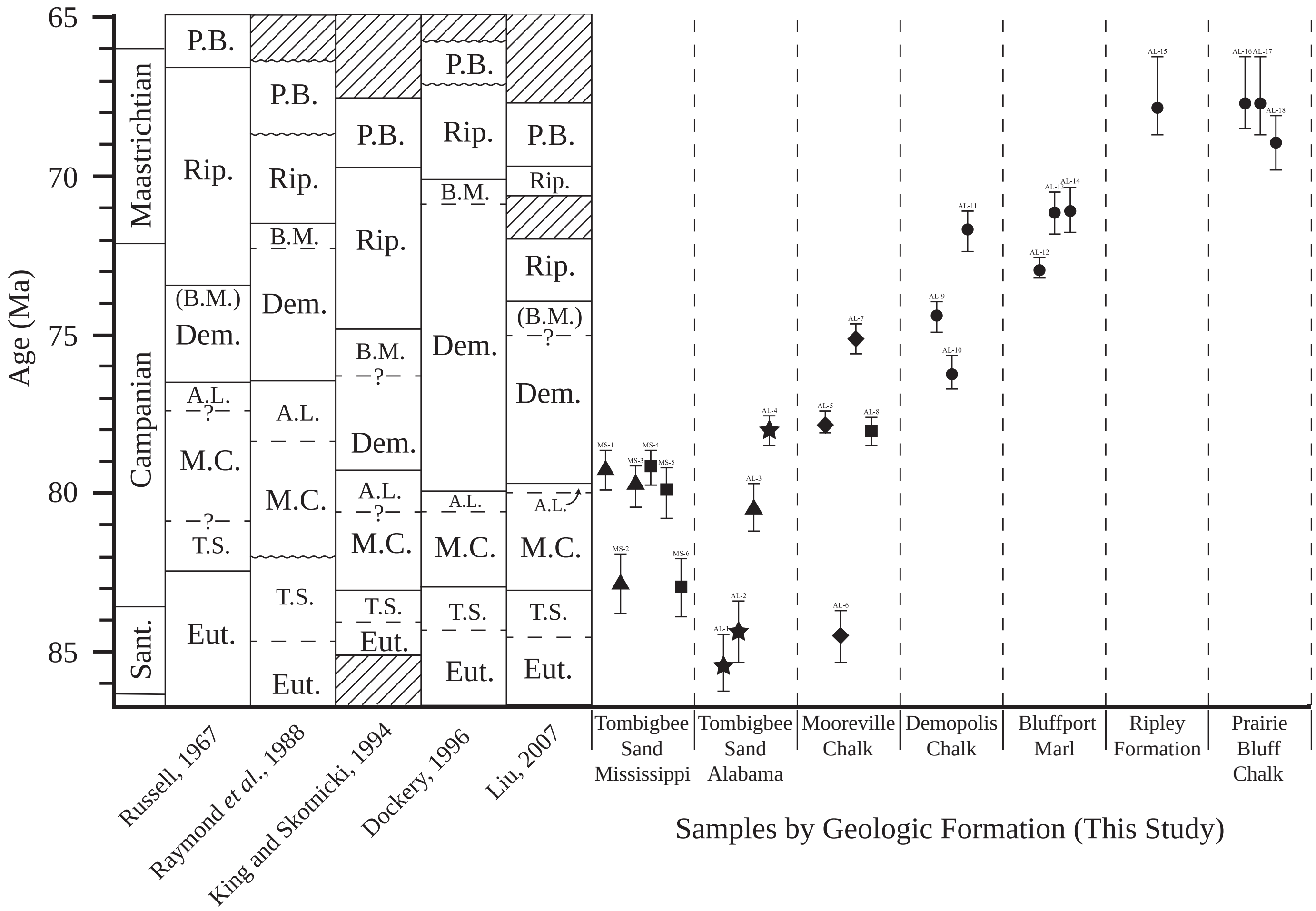

Fig. 6. Results of the present study plotted against numeric age and published stratigraphic columns of Upper Cretaceous formations of Alabama and Mississippi. Dockery (1996) pertains to Mississippi outcrops only. **Triangles** – *Squalicorax lindstromi*; **Stars** – *Squalicorax* cf. *yangaensis*; **Diamonds** – *Squalicorax kaupi*; **Circles** – *Squalicorax pristodontus*; **Squares** – *Scapanorhynchus texanus*. Specimens are plotted in order from Table 2. Error bars represent the 2 standard error (95%) confidence range. Geologic time scale is based on Cohen et al. (2013; updated to Version 2015/01), however previously published stratigraphic columns are based on time scales available at their time of publication. See Fig. 2 for explanation of geologic abbreviations.

in their enameloid. Although the $^{87}Sr/^{86}Sr$ ratio in present day oceans is relatively uniform on a global scale, nearshore regions close to large rivers may have a diluted or ^{87}Sr-enriched signature (McArthur et al., 2012). If a particular taxon of shark preferred to live in this type of nearshore or brackish water environment, its $^{87}Sr/^{86}Sr$ ratio would likely differ from that of the known coeval marine values of the LOWESS curve (Fig. 1). An equal number of specimens ($n = 3$) of each genus were sampled from the Tombigbee Sand exposed in the Fowlkes Mine in Mississippi. Although the sample number is small, results show no discernable difference between taxonomic groups. The mean age of the *Squalicorax lindstromi* specimens from the site is 80.55 Ma whereas the average for *Scapanorhynchus texanus* is 80.67 Ma. Although the average ages of both taxa are significantly younger that the currently accepted age of the Tombigbee Sand, two of the six samples produced ages that are within the range of this geologic unit (Table 2, Fig. 7). Among the Upper Cretaceous strata in the Gulf Coastal Plain, the Eutaw Formation including the Tombigbee Sand Member has the highest level of porosity and permeability (Mancini et al., 2008). Another possible explanation for the unusually young numerical age is that the Tombigbee Sand was deposited in a relatively nearshore environment (King and Skotnicki, 1994), in which the strontium isotope ratio was altered by the influx of freshwater drainage from the nearby Appalachian subcontinent. In any case, this finding suggests that both shark taxa likely inhabited similar marine environments due to their nearly identical analytical results. Three teeth of *Squalicorax kaupi* and one tooth of *Scapanorhynchus texanus* from the Mooreville Chalk near Harrell Station in Dallas County, Alabama were also analyzed in the present study (Table 1). Two of the *Squalicorax* samples (Table 2: AL-6 and AL-7) produced strontium age dates that are not comparable with any recently reported age of the Mooreville Chalk (Fig. 6). The reason for this discrepancy is not known but may be the result of sampling error in the comparatively small *S. kaupi* teeth (Fig. 4). However, *S. kaupi* sample AL-5 and the lone *Scapanorhynchus texanus* sample (AL-8) resulted in very similar ages that are compatible with the age of the Mooreville Chalk reported in older stratigraphic columns published by Russell (1967) and Raymond et al. (1988). This again suggests that the two shark taxa likely inhabited similar marine environments.

In addition to the analysis of two genera of shark, four different species of *Squalicorax* were sampled during the study due to the biostratigraphic limitations of each species. *Squalicorax* cf. *yangaensis* and *S. lindstromi* are species that are relatively abundant in the upper Santonian Tombigbee Sand of the Mississippi Embayment region. However, the comparatively small adult tooth size of these taxa makes it difficult to obtain the necessary 10 mg

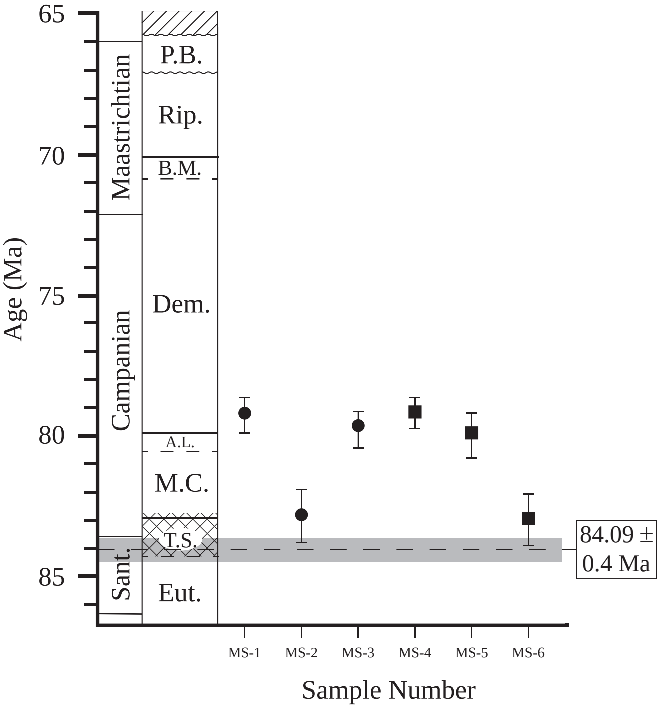

Fig. 7. Strontium isotope age of specimens collected from BASF Fowlkes Bentonite Mine, Monroe County, Mississippi (MGS-162) compared with radiometric age of bentonite layer (84.09 ± 0.4 Ma, dashed horizontal line and gray zone) reported by Obradovich (1993). Strata present in the quarry are indicated by the cross-hatched zone in the geologic column. **Circles** – *Squalicorax lindstromi*; **Squares** – *Scapanorhynchus texanus*. See Fig. 2 for geologic abbreviations.

enameloid sample without contamination from the underlying dentine tissues. *Squalicorax kaupi* is more common in the lower Campanian Mooreville Chalk and has slightly larger teeth than *S. yangaensis* or *S. lindstromi* that are still somewhat difficult to sample. *Squalicorax pristodontus* is common in strata that are mid-Campanian to Maastrichtian in age, ranging from the Demopolis Chalk through the Prairie Bluff Chalk in Alabama. Teeth of adult *S. pristodontus* are comparatively large and the 10 mg sample of enameloid is easily obtained with little risk of penetrating into the underlying dentine material. The results of the present analysis (Table 2; Fig. 6) show better precision and accuracy in specimens acquired from younger Cretaceous strata, which may simply be the result of less-contaminated enameloid sampling of the larger *S. pristodontus* teeth, or perhaps because they were deposited in a more favorable depositional environment. A more precise method of sampling such as micro-milling or laser ablation may be necessary to properly analyze enameloid from smaller shark taxa to ensure more reliable results, as it is difficult to obtain the 10 mg of enameloid sample powder required by the current analytical method from smaller teeth. Limited funding and time constraints on the first author (LH) prevented the exploration of these possible alternate sampling techniques although they may be addressed in future analyses.

4.4. Possible diagenetic effects

The analytical results from the Tombigbee Sand and Mooreville Chalk were less consistent than those from overlying carbonate strata. The reason for this inconsistency is not certain but may be related to either the depositional environment or diagenesis. The Tombigbee Sand, lowermost Mooreville Chalk, and portions of the Ripley Formation were deposited in relatively nearshore environments (King, 1990; King and Skotnicki, 1990) that may have had different strontium isotope ratios in comparison with the open ocean (McArthur et al., 2012). The carbonate-rich formations analyzed in this study were deposited in more offshore marine environments (King, 1990; King and Skotnicki, 1990; Puckett, 1994; Liu, 2007), likely with normal strontium isotope ratios.

According to Hoppe et al. (2003), there are four primary ways in which strontium can be diagenetically incorporated into fossil bioapatites: 1) secondary mineral crystallization in pore spaces, 2) recrystallization of bioapatites, 3) direct exchange of diagenetic strontium with strontium or calcium in the original bioapatite crystals, and 4) absorption in microfractures or on surfaces of the original bioapatites crystals. Incorporation of secondary strontium-bearing minerals in pore spaces and microfractures is a more likely candidate for diagenetic alteration in the sandier, water-bearing geologic units of the eastern Gulf Coastal Plain, as the large bioapatite crystals in shark tooth enameloid do not experience much recrystallization as they fossilize (Schmitz et al., 1997; Becker et al., 2008). The passive tectonic margin and shallow burial depth of the Cretaceous strata on the eastern Gulf Coastal Plain (Liu, 2009) would suggest that no diagenetic alteration of the fossil teeth occurred from recrystallization of the bioapatite crystals due to geothermal activity and pressure.

Long term exposure to groundwater may alter the strontium isotope ratios in fossil shark teeth in two ways: 1) by leaching strontium from the original bioapatites, and 2) deposition of secondary strontium-bearing minerals in pores and microfractures. The Tombigbee Sand and Ripley Formation both contain significant quantities of groundwater, whereas the carbonate-rich Cretaceous strata in the region are impermeable (Davis, 1987). The Tombigbee Sand and Ripley Formation also contain impermeable, clay-rich layers (Stephenson and Monroe, 1940) that would likely protect fossil shark teeth in those beds from diagenetic alteration by groundwater. Although the specimens sampled in the analysis were recovered from their reported geologic units, they had been weathered from their specific stratigraphic horizons and therefore it is uncertain as to whether they were deposited in sandy or clayey beds. This difference in intraformational lithology might explain why some of the results from the Tombigbee Sand are relatively accurate whereas others do not correlate well with the previously established age of the unit (Figs. 6 and 7). The lowermost portion of the Mooreville Chalk near the gradational contact with the underlying Tombigbee Sand of the Eutaw Formation also contains a significant quantity of sand (Liu, 2007).

4.5. Stratigraphic correlation and petroleum production

The Upper Cretaceous marine strata of the eastern Gulf Coastal Plain are significant reservoirs of hydrocarbons in the United States, with approximately 2 billion barrels of oil and 7.4 trillion cubic feet of natural gas recovered as of 2002 (Mancini and Puckett, 2002; Mancini and Puckett, 2003), and possess considerable potential for future production (Mancini et al., 2008). Much of the hydrocarbon potential of these geologic units depends on their stratigraphic position in relation to marine transgressive-regressive cycles, with the majority of hydrocarbons produced by strata deposited during transgressive or back-stepping phases (Mancini and Puckett, 2002). The correlation of these strata with hydrocarbon-rich Cretaceous marine strata in the western Gulf Coastal Plain (Condon and Dyman, 2006) and Western Interior Basin (Higley and Cox, 2007) of the United States largely depends on sequence stratigraphy used in conjunction with biostratigraphy of microfossils. Correlation of stratigraphic units is useful for prospecting geological formations that may have high potential as hydrocarbon sources or reservoirs. Many foraminifera and other microorganisms are dependent on environmental conditions (Tappan, 1951), which unfortunately may not exist on a global scale and therefore may not be widely distributed at a synchronous stratigraphic level, resulting in suboptimal correlation of marine strata. The use of strontium isotope ratios present in fossil shark tooth enameloid, which appear to be relatively stable in certain geologic conditions, may therefore be of use in constraining the timing of eustatic sea-level changes and age relations of marine strata in areas of conflicting or indeterminate biostratigraphic data. The uniform distribution of strontium isotopes in oceanic water (McArthur et al., 2012), aside from very nearshore environments, suggests that fossil shark tooth enameloid may be used to help correlate marine strata on a global scale regardless of depositional environment, based on the findings of the current study.

4.6. Conclusions

1. Stable strontium age dating of fossil shark tooth enameloid correlates to numerical ages that are relatively precise and accurate in younger Late Cretaceous strata of the Mississippi Embayment region and compare well with some previously published stratigraphic columns. The strontium isotope dates obtained in this study compare best with the stratigraphic column published by Raymond et al. (1988).
2. One-third of the stable strontium isotope ages obtained from specimens from the Fowlkes Bentonite Mine in Monroe County, Mississippi, compare well with the radiometrically derived age of the bentonite layer and the age of the Santonian–Campanian boundary exposed in the strata whereas the remaining specimens produced numeric ages that are younger than the currently accepted age of the strata.
3. Of the specimens that were analyzed in this study, no differences in strontium isotope ratios were observed between the fossil shark genera or species. Larger *Squalicorax pristodontus* teeth, with their thicker enameloid layer, produced more accurate and precise strontium isotope numeric ages relative to their respective geologic units than the smaller *S.* cf. *yangaensis*, *S. lindstromi* and *S. kaupi*, and *Scapanorhynchus texanus* teeth. Better enameloid sampling methods are needed for analyzing smaller shark teeth to reduce potential contamination from underlying osteodentine material.
4. Non-porous geologic strata that contain high percentages of chalk, marlstone, or clay appear to preserve original strontium isotope ratios in fossil shark teeth better than sandy strata that contain large quantities of groundwater. Geologic units deposited in relatively nearshore environments, such as the Tombigbee Sand, produced poorer results than geologic units deposited in deeper, offshore environments.

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