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On the reconciliation of biostratigraphy and strontium isotope stratigraphy of three southern Californian Plio-Pleistocene formations

Alexandra J. Buczek[1], Austin J.W. Hendy[2], Melanie J. Hopkins[1], and Jocelyn A. Sessa[3,†]

[1]*Division of Paleontology, American Museum of Natural History, Central Park West & 79th Street New York, New York 10024, USA*

[2]*Department of Invertebrate Paleontology, Natural History Museum of Los Angeles County, 900 Exposition Blvd., Los Angeles, California 90007, USA*

[3]*Department of Biodiversity, Earth and Environmental Science, Academy of Natural Sciences of Drexel University, 1900 Benjamin Franklin Parkway, Philadelphia, Pennsylvania 19103, USA*

ABSTRACT

The San Diego Formation, Pico Formation, Careaga Sandstone, and Foxen Mudstone of southern California are thought to be late Pliocene to early Pleistocene; however, numerical ages have not been determined. Following assessment of diagenetic alteration via multiple methods including scanning electron microscopy (SEM), X-ray diffraction (XRD), and minor elemental concentrations, we attempted to use strontium isotope stratigraphy to assign numerical ages. Using aragonitic fossils, we obtained ages of 2.0–1.85 Ma for the Careaga Sandstone and 2.0–1.75 Ma for the uppermost Foxen Mudstone, consistent with biostratigraphic work suggesting a Gelasian age for the Careaga Sandstone. Isotope ratios for aragonitic and calcitic fossils from the Pico Formation were poorly constrained, with the exception of one bed yielding ages of 5.1–4.3 Ma. Isotope ratios from the San Diego Formation were also inconsistent within beds, with the exception of two isolated outcrops that yielded ages of 5.0–4.5 Ma and 4.5–2.8 Ma, respectively. The age estimates for the Pico and San Diego Formations are older than most ages inferred from biostratigraphy. Noting that some aragonitic specimens from the San Diego Formation yielded isotope ratios indicative of ages as old as 19.4 Ma, we propose that some outcrops have been affected by diagenesis caused by groundwater flow through proximal granitic rocks and input from detrital sediment. Although we recommend that strontium isotope results for the Pico and San Diego Formations be interpreted with caution, the ages of the uppermost Foxen Mudstone and Careaga Sandstone can be confidently placed within the early Pleistocene.

†jsessa@drexel.edu.

INTRODUCTION

The mid-Pliocene warm period (ca 3 Ma; Jansen et al., 2007) was a time of high global temperatures (2 °C to 3 °C above pre-industrial temperatures) and high atmospheric CO_2 concentrations (360–400 ppm) (Jansen et al., 2007). These climatic conditions, combined with the fact that the continents and ocean basins were in their present geographic configuration, make the Pliocene a suitable analogue for modern climate change (Jansen et al., 2007; Haywood et al., 2011; Burke et al., 2018; Song et al., 2019) and offer a good opportunity to examine the response of biotic systems to warming similar to that predicted for the future. The subsequent cooling into the early Pleistocene (Fig. 1) also provides a chance to analyze the response of marine communities from a time of global warming through a sustained interval of cooling.

Investigation of past biotic responses to climate change requires rich, well-preserved, fossiliferous outcrops from well-dated lithostratigraphic units. The sedimentary basins of southern California (Fig. 2) provide a potential record of the response of nearshore marine communities to late Pliocene and early Pleistocene climatic shifts because they contain well-preserved, diverse, and extensive fossil records. The sedimentology and fossil content of the Foxen Mudstone and Careaga Sandstone of Santa Barbara County (Woodring and Bramlette, 1950), the Pico Formation of Los Angeles County (Winterer and Durham, 1962; Squires et al., 2006; Squires, 2012), and the San Diego Formation of San Diego County (Hertlein and Grant, 1944; Hertlein and Grant, 1972; Deméré, 1983; Vendrasco et al., 2012) in California have been thoroughly described (Fig. 2). Faunas preserved within these strata are diverse and closely related to the modern southern California biota (Woodring and Bramlette, 1950; Winterer and Durham, 1962; Deméré, 1983; Squires et al., 2006; Powell et al., 2009; Squires, 2012; Vendrasco et al., 2012). Based primarily on regional macrofossil and microfossil biostratigraphy, these units are hypothesized to be late Pliocene to early Pleistocene in age (Figs. 1 and 3), but no numerical ages exist to confirm this hypothesis. Previous age determinations must be revisited and reconciled with numerical ages because microfossil biostratigraphic schemes only broadly place these formations within region-specific biochronologies that are difficult to correlate with other strata globally (Figs. 1 and 3). Macrofossil biostratigraphy is somewhat limited because the exact age ranges for many index fossils are undetermined due to a lack of numerical dating (e.g., Vendrasco et al., 2012). The age designation "late Pliocene to early Pleistocene" lacks sufficient resolution to allow the various climatic fluctuations (discussed above, Fig. 1) to be differentiated, further hindering our ability to understand the climatic context of these communities.

Furthermore, the International Commission on Stratigraphy's (ICS) International Chronostratigraphic Chart was formally ratified in 2009, changing the base of the Pleistocene to coincide with the base of the Gelasian Stage (2.59–1.81 Ma), subsequently shifting the Gelasian from the uppermost stage of the Pliocene to the lowermost stage of the Pleistocene Series and extending the length of the Quaternary (Gibbard and Head, 2009; Gibbard et al., 2010, Cohen et al., 2019; Fig. 1). This change was adopted because the geological events that signaled the cooling phase used to define the base of the Quaternary Period actually occurred at the base of the Gelasian. Moving the base of the Quaternary brought concordance between the events and the definition of the boundary (see Gibbard and Head, 2009, and references therein). In this study, we attempt to refine the previous biostratigraphic age determinations for the Foxen Mudstone, Careaga Sandstone, Pico Formation, and

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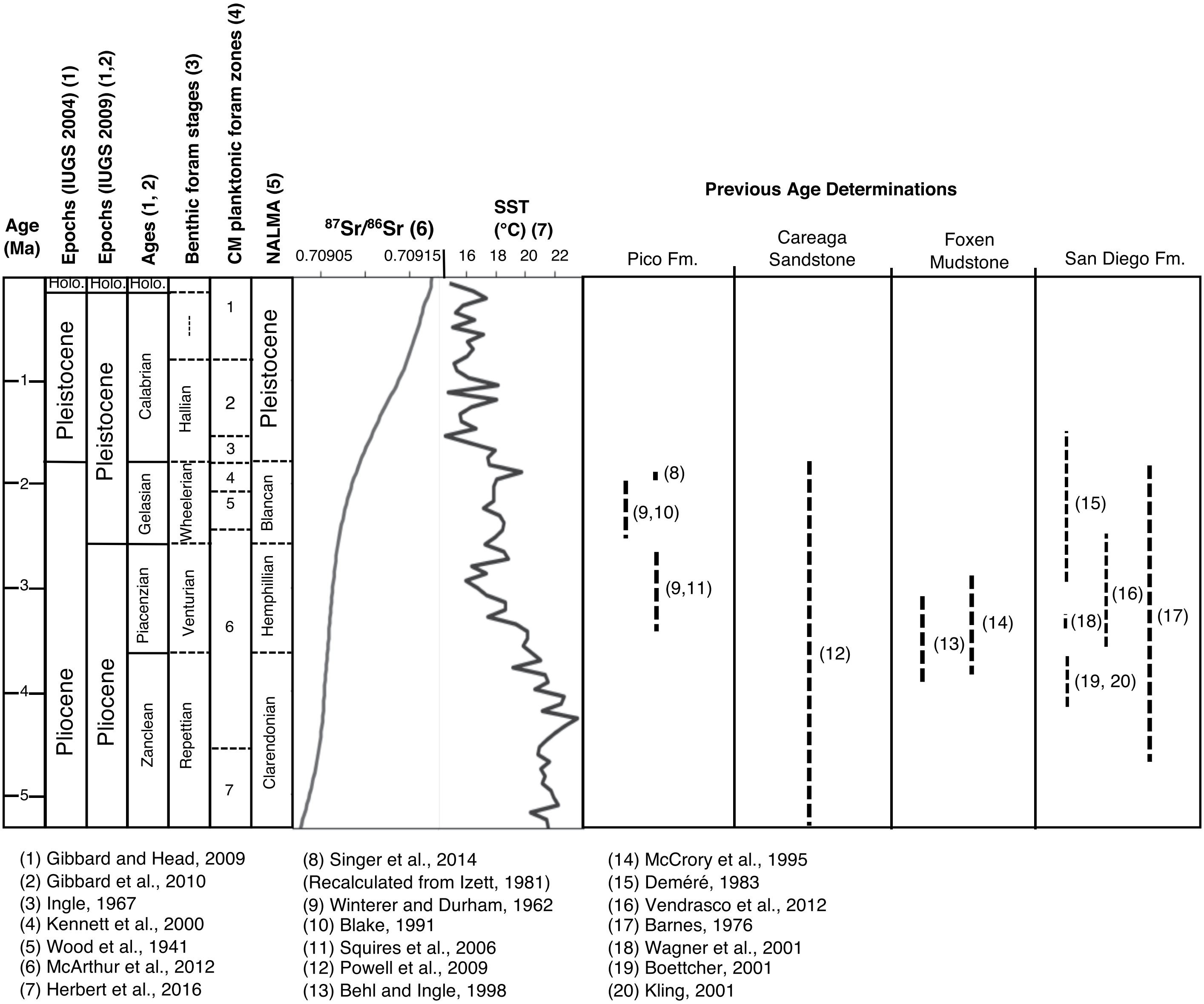

Figure 1. Previous age determinations are shown for the Pico Formation, Careaga Sandstone, Foxen Mudstone, and San Diego Formation within the chronostratigraphic and biostratigraphic framework for the Plio-Pleistocene of southern California and plotted against the strontium isotope curve (McArthur et al., 2012) and sea surface temperatures (SSTs) from sea surface alkenone data (Herbert et al., 2016). All biozones were published prior to the International Union for Geological Sciences 2009 ratification and are therefore based on the 2004 timescale. Neogene Californian margin foraminiferal zonations are based on evolutionary changes within the planktonic foraminifer *Neogloboquadrina* (Kennett et al., 2000). Zones are numerical and are based on foraminiferal ranges, co-occurrences of species, and gaps in occurrences. North American Land Mammal Ages (NALMA) are based on index fossils, first appearances, last appearances, and "characteristic fossils" (all defined within Wood et al., 1941). Dashed lines in biostratigraphic schemes represent approximate, hypothesized boundaries between biostratigraphic stages and are not equivalent to International Union for Geological Sciences (IUGS) epochs or ages. Dashed lines in previous age determinations represent possible potential age spans of the formations; they do not represent durations. CM—constitutive mixotroph; Fm.—formation.

San Diego Formation using strontium isotope stratigraphy (McArthur et al., 2001; McArthur et al., 2012) of mollusk shells, thus enabling these faunas to be used to understand the effects of climate changes on marine biota.

Strontium isotope stratigraphy relies on the $^{87}Sr/^{86}Sr$ ratio of marine carbonates (e.g., Elderfield, 1986; Veizer et al., 1997; McArthur, 1994; McArthur et al., 2001; McArthur et al., 2012) and is one of the few absolute dating methods available for recently deposited fossiliferous marine sediments. Although regional inputs of strontium to the ocean from continental weathering may vary, the world's oceans are homogeneous with respect to $^{87}Sr/^{86}Sr$ at any given time (Elderfield, 1986; McArthur et al., 2012), and the residence time of strontium (10^6 years) is far longer than the time it takes currents to mix the oceans (10^3 years; Elderfield 1986; McArthur et al., 2012). As a result, the oceans are thoroughly mixed

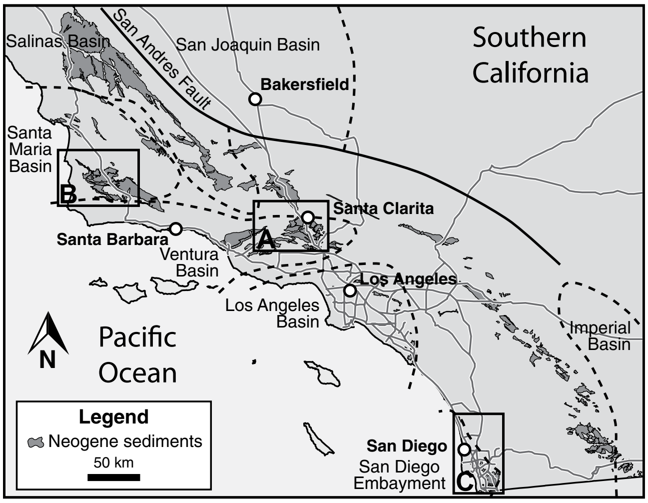

Figure 2. Geological map showing the positions of sampling localities relative to Neogene sediments and Plio-Pleistocene basins; the extent of each basin is denoted with a dashed line. Boxed areas are shown in more detail in Figure 4.

on time scales that are short relative to the rates of gain and loss of strontium (McArthur et al., 2012).

Mollusks are exemplar geochemical archives because they are known from a wide variety of climatic zones, are abundant throughout the Phanerozoic, are common taxa in marine environments, and can—under favorable conditions—withstand diagenetic alteration (Immenhauser et al., 2016). A multitude of studies from the 1950s to the present have demonstrated that the chemical composition of mollusk shells records the chemical and oceanographic parameters of their environment during shell formation (Vinogradov, 1953; Thompson and Chow, 1955; Odum, 1957; Wefer and Berger, 1991; Immenhauser et al., 2016). The biomineralization process and caveats of using mollusk shells as geochemical archives are well known and have been extensively studied (Vinogradov, 1953; Thompson and Chow, 1955; Odum, 1957; Wefer and Berger, 1991; Immenhauser et al., 2016). The isotopes recorded in mollusk shells have been utilized for paleoenvironmental reconstruction (e.g., paleothermometry, Goodwin et al., 2003; Ivany, 2012; Sessa et al., 2012) and strontium isotope stratigraphy. Although strontium

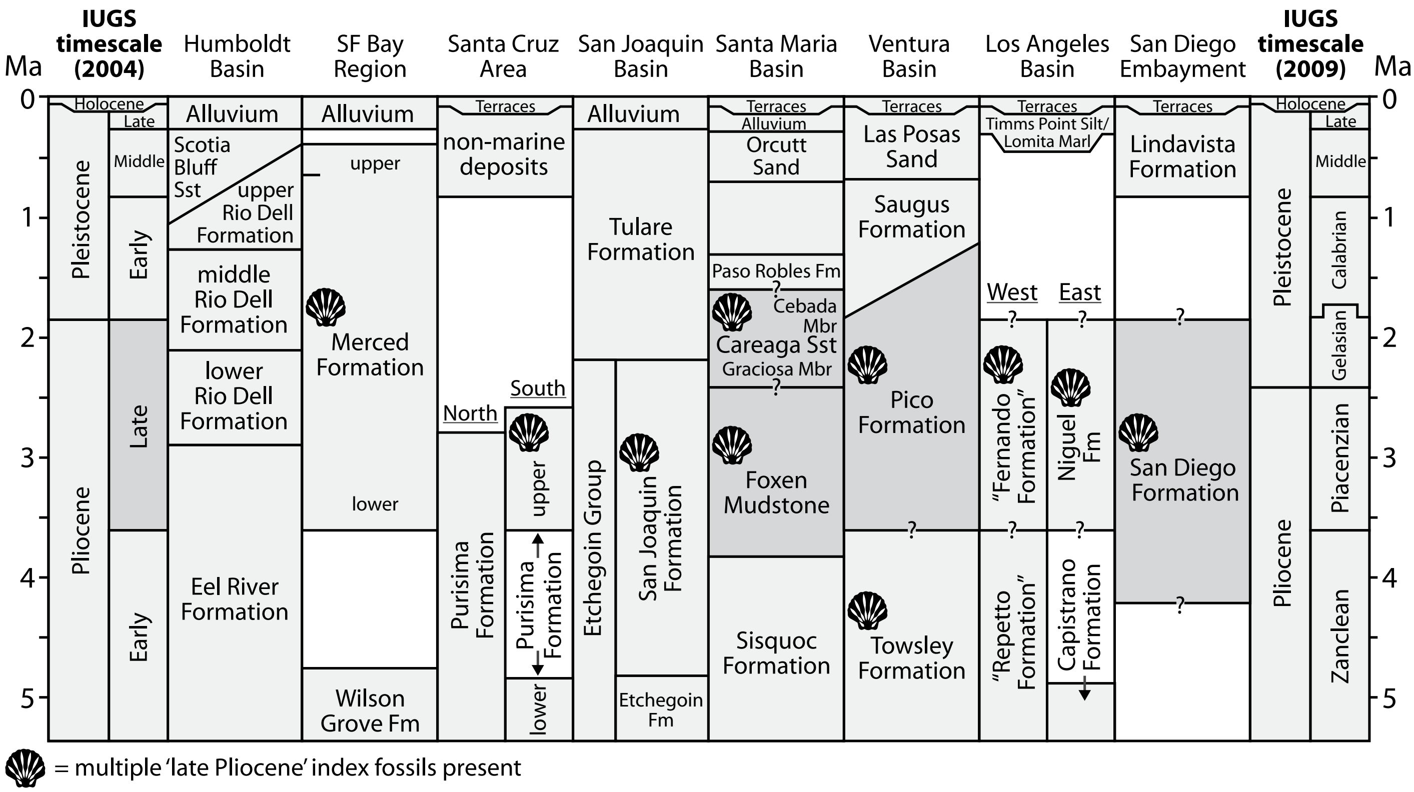

Figure 3. Lithostratigraphic correlation panel for the Plio-Pleistocene formations of California (modified from Bowersox, 2005). The presence of multiple "Pliocene index fossils" within each formation is noted. Critical ages are as follows: base of Foxen Mudstone at 3.8 Ma (Barron and Baldauf, 1986; Behl and Ingle, 1998); top of Foxen Mudstone uncertain; top of Careaga Formation at 1.6 Ma but poorly constrained (Namson and Davis, 1990); base of Careaga Formation uncertain; top of Pico Formation no younger than 1.2 Ma and with a diachronous contact with the Saugus Formation; base of Pico Formation uncertain; base of Merced Formation at 3.6 Ma (Ingram and Ingle, 1998); top of Eel River Formation at 3.0 Ma (Sarna-Wojcicki et al., 1982); lower Rio Dell Formation between 3.0 Ma and 2.0 Ma (Sarna-Wojcicki et al., 1982); middle Rio Dell Formation between 2.0 Ma and 1.2 Ma (Sarna-Wojcicki et al., 1982); top of Etchegoin Formation defined by the Lawlor Tuff at 4.83 Ma (Sarna-Wojcicki et al., 2011); San Joaquin Formation between Lawlor Tuff at 4.83 Ma and Ishi tuff (2.2 Ma) just below contact with Tulare Formation (Sarna-Wojcicki et al., 2011); base of San Diego Formation at 4.2 Ma (Boettcher, 2001; Kling, 2001); top of San Diego Formation uncertain. IUGS—International Union for Geological Sciences; Sst—Sandstone; Fm—Formation; Mbr—Member.

biomineralization pathways for biogenic carbonate have been insufficiently studied, biological, ontogenetic, crystallographic, and kinetic factors do not appear to have a significant effect on the $^{87}Sr/^{86}Sr$ ratio preserved within mollusk shells (Immenhauser et al., 2016).

Geological Setting and Previous Age Determinations

Due to the changes in boundaries and numerical ages discussed in the Introduction, throughout this section, we provide age determinations as published and also translate them to the modern usage of the ICS International Chronostratigraphic Chart v. 2019 (Cohen et al., 2019), which takes into account the formal 2009 ratification of the base of the Pleistocene.

The geology of California consists of narrow linear basins (Fig. 2) formed by the active transtensional tectonics of the California continental borderland (Howell, 1976; Vedder, 1987; Legg, 1991; Sedlock and Hamilton, 1991). Faulting and thrusting led to the formation of multiple sedimentary basins in California that were filled by Paleogene and Neogene sediments (Deméré, 1983; Namson and Davis, 1990; Yeats et al., 1994). Sedimentation within these basins was not continuous across the region due to local tectonic controls, sedimentary input, and their interaction with sea level fluctuations through the Plio-Pleistocene, making correlation between northern and southern basins difficult. Previous chronostratigraphic work has therefore relied heavily on local and regional biochronologies (Fig. 1).

A number of marine units preserving sediments broadly constrained as "late Pliocene to early Pleistocene" are exposed along the coast of southern California: the Fernando, Niguel, San Joaquin, Merced, Purisima, Pico, and San Diego Formations, and the Careaga Sandstone and Foxen Mudstone (Fig. 3, Woodring and Bramlette, 1950; Hertlein and Grant, 1972; Schoellhamer et al., 1981; Ingram and Ingle, 1998; Bowersox, 2006; Squires et al., 2006; Powell et al., 2007, 2009). The ages and correlation of many of these formations have been established using so-called "Pliocene index fossils" such as the bivalves *Anadara trilineata, Euvola bella, Patinopecten healeyi, Swiftopecten parmeleei, Pycnodonte erici,* and the gastropods *Crepidula princeps, Opalia varicostata, Calicantharus fortis angulata,* and "*Cancellaria*" *arnoldi* (Powell et al., 2009; Fig. 3). Most of these species are absent from younger units (Grant and Gale, 1931; Hertlein and Grant, 1972; Moore, 1987; Fig. 3). This large faunal turnover was taken to be indicative of a shift from the warm late Pliocene to cooler early Pleistocene climate (Powell et al., 2009).

The ages of some of these units have been further constrained via microfossil biostratigraphy and radiometric dating methods (Woodring and Bramlette, 1950; Hertlein and Grant, 1972; Schoellhamer et al., 1981; Ingram and Ingle, 1998; Bowersox, 2006; Squires et al., 2006; Powell et al., 2007, 2009). A late Pliocene age was assigned to the Fernando and Niguel Formations based on foraminiferal biostratigraphy (Schoellhamer et al., 1981). Strontium isotope analysis of foraminifera in the Merced Formation yielded ages of 3.6–0.62 Ma (Ingram and Ingle, 1998; Boessenecker, 2018). Radiometric dates from tephra layers have constrained the Purisima Formation to between 6.9 Ma and 3.3 Ma (Powell et al., 2007), while a combination of lithostratigraphic, biostratigraphic, and chronostratigraphic data constrained the age of the San Joaquin Formation to between 5.3 Ma and 2.2 Ma (Bowersox, 2006). This study aside, no attempts have been made to use Sr-isotope stratigraphy or radiometric methods to determine the ages of the Fernando, Niguel, Pico, San Diego, Careaga, or Foxen units. Only the latter four units were selected for this study. The Fernando Formation was not considered as its status as a formal lithostratigraphic unit remains inadequate; many of the sediments previously assigned to the "Fernando Formation" have been reassigned to the Niguel and Pico Formations (Davis, 1998; Campbell et al. 2014). Furthermore, most of the outcrops of the Fernando and Niguel Formations were destroyed during city expansion in Los Angeles and Orange Counties, rendering systematic bulk sampling from measured stratigraphic sections difficult.

Pico Formation

The Pico Formation of the Ventura Basin (Fig. 2) comprises an ~5000-m-thick succession, representing deep marine through fluvial depositional environments (Campbell et al., 2014). The upper 450 m of the Pico Formation is exposed near Valencia, California, directly north of the Ed Davis Park at Towsley Canyon off the Old Road (Fig. 4A). The depositional environment of the exposure is described in detail by Squires et al. (2006). Briefly, the lower 350 m of the Pico Formation at this location are primarily muddy siltstone with pebble or cobble conglomerate channels. The lower siltstone is devoid of macrofossils. The lowest macrofossil bed occurs in the overlying very fine sandstone and is dominated by brachiopods, along with oysters and pectinids (Squires et al., 2006). The lower to middle half of the upper part of the unit contains very fine- to fine-grained sandstone with multiple shell beds. As the formation grades into the Saugus Formation, no further macrofossil beds are present.

The Pico Formation was constrained to the late "Pliocene," equivalent in the modern context to the Piacenzian through the Gelasian stages, based on benthic foraminiferal biostratigraphy, macrofossil biostratigraphy, and numerical age estimates of the overlying and underlying formations (Fig. 1). The recovery of *Bulimina subacuminata* in the lower part of the formation constrains this portion of the unit to the regional Californian Venturian benthic foraminiferal stage, which was correlated to the late Pliocene by Winterer and Durham (1962; Ingle, 1967; Fig. 1). The top of the formation also contains *Uvigerina peregrina* and *Epistominella pacifica,* which are characteristic of the regional Californian Wheelerian benthic foraminiferal stage, which is correlated to the Gelasian in the revised timescale (Ingle, 1967; Winterer and Durham, 1962; Blake, 1991; Fig. 1). Squires et al. (2006) cited the presence of eight mollusk species as evidence of a Pliocene age for the outcrop at Ed Davis Park at Towsley Canyon. These species include the bivalves *Patinopecten healeyi, Argopecten invalidus,* and *Securella kanakoffi* among others (Fig. 3). The base of the Pico Formation is constrained by the Huckleberry Ridge tephra layer (Sarna-Wojcicki et al., 1984, 1987), which has been dated to between 2.084 Ma and 2.07 Ma using $^{40}Ar/^{39}Ar$ sanidine and U-Pb zircon ages (Singer et al., 2014 recalculated from Izett, 1981; Fig. 1). However, K-Ar dating often gives a younger age than the true age of the material (McDougall and Harrison, 1999). Magnetostratigraphy of the overlying Saugus Formation constrains its deposition between 2.3 Ma and 0.5 Ma (Levi and Yeats, 1993). Thus, all previously published evidence indicates a Piacenzian to Gelasian age for the Pico Formation (Fig. 1).

Foxen Mudstone and Careaga Sandstone

The geology and stratigraphy of the Foxen Mudstone and Careaga Sandstone and their adjacent units in Santa Maria, Santa Barbara County, California, (Fig. 2) were extensively studied by Woodring and Bramlette (1950). The Foxen Mudstone consists primarily of gray mudstone and clayey siltstone with diatomaceous shale interbedded in its lower part. Limestone concretions and phosphatic pellets are widespread throughout. Lenticular conglomerates are present at the base of the section. The Careaga Sandstone consists of two members: the lower fine-grained Cebada Member and the upper coarse-grained Graciosa Member. The Cebada Member consists of fine- to very fine-grained massive gray to yellow sand. The Graciosa Member is distinguished by a lower coarse- to medium-grained brownish sandstone and conglomerate, and an upper coarse-grained gray sand grading into conglomerate.

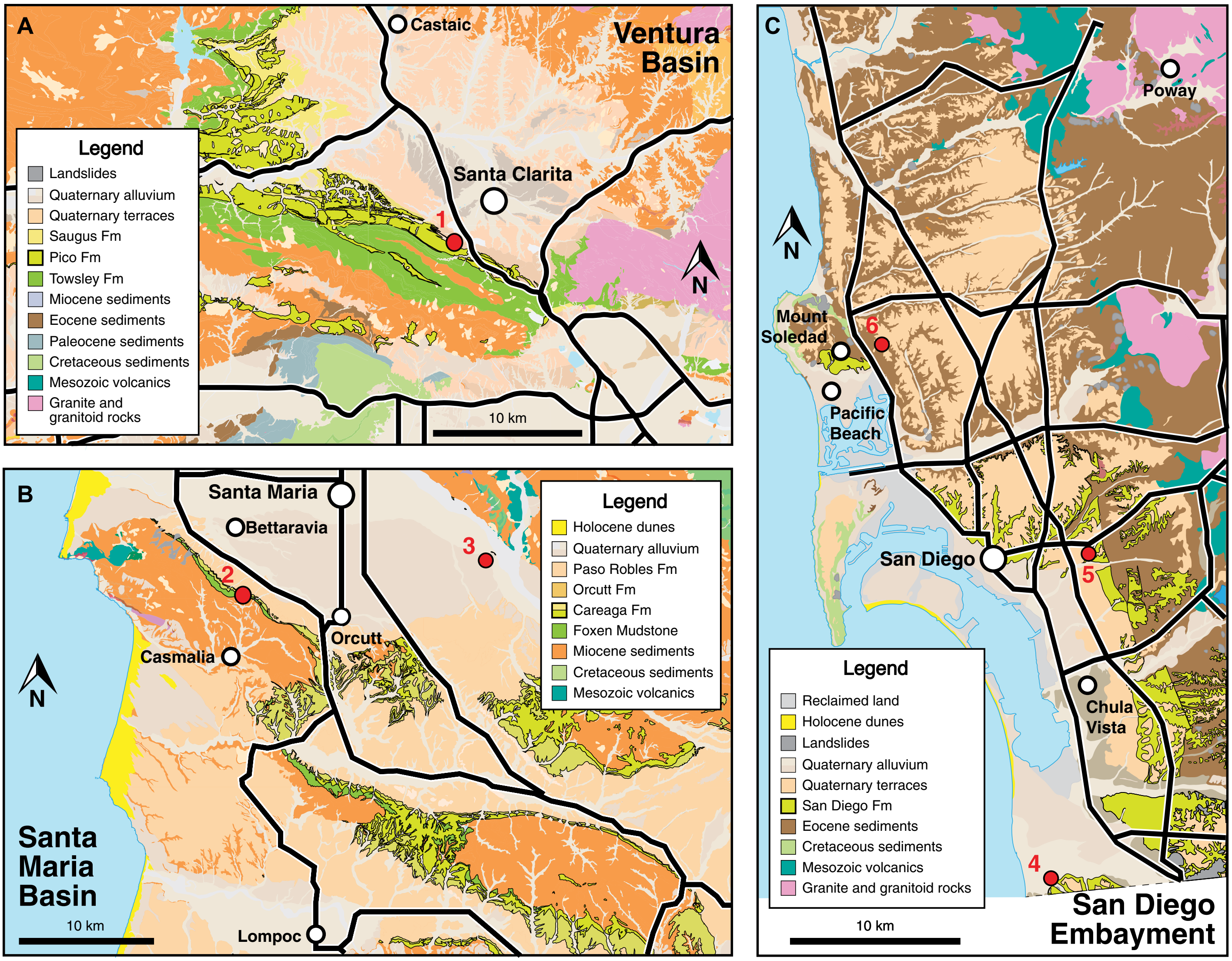

Figure 4. Geological maps (of "boxed areas" in Fig. 2) showing the sampling localities in each Plio-Pleistocene basin. (A) Ventura County (adapted from Dibblee and Ehrenspeck, 1991, 1992a, 1992b, 1992c, 1993a, 1996), showing sampling localities of the Pico Formation. The proximity of granitic rocks and especially plutonic bedrock to the sampling localities may be associated with the diagenetic alteration of $^{87}Sr/^{86}Sr$ values preserved within sampled specimens through contact with pore water. (B) Santa Maria County (adapted from Dibblee et al., 1994a, 1994b, 1994c; Dibblee and Ehrenspeck, 1988; Dibblee and Ehrenspeck, 1989a, 1989b, 1993b, 1993c, 1994), showing sampling localities of the Careaga Sandstone and Foxen Mudstone. (C) San Diego County (adapted from Kennedy et al., 2008), showing sampling localities of the San Diego Formation. Groundwater flow from the Peninsular Range to the east of the sampling localities is a possible source of diagenetic alteration of $^{87}Sr/^{86}Sr$ values in sampled specimens. Red circles indicate sampling localities: (1) Ed Davis Park at Towsley Canyon and Chiquella Lane; (2) Shuman Cut; (3) Fugler Point; (4) Border Field State Park; (5) Malcolm X Library; (6) Jutland Drive. Field codes and locality numbers described in the text, and tables may be matched to geo-coordinates using Appendix 3 (see footnote 1). Fm.—formation.

The base of the Foxen Mudstone was assigned an early Pliocene age based on the occurrence of the diatoms *Nitzschia reinholdii* and *Thalassiosira oestrupii* (Barron and Baldauf, 1986). The entire unit is considered to be age-equivalent to Californian Repettian benthic foraminiferal stage deep-water sediments in the offshore Santa Maria basin, which correlates to the Zanclean in the revised timescale (Dunham et al., 1991; McCrory et al., 1995; Fig. 1), but its foraminiferal fauna cannot be strictly assigned to the stage due to the absence of defining marker species (Behl and Ingle, 1998; Fig. 1). The Pliocene index fossil *Patinopecten healeyi* was also found in the Foxen Mudstone (Woodring and Bramlette, 1950). The Careaga Sandstone was assigned a Pliocene age due to the occurrence of the multiple index fossils including the bivalves *Anadara trilineata* and *Patinopecten healeyi* and the gastropods *Strioterebrum martini* and *"Cancellaria" arnoldi* (Woodring and Bramlette, 1950). The units were also regarded as Pliocene in age by Powell et al. (2009). No detailed microfossil biostratigraphic scheme has yet been developed for the Careaga Sandstone, and no numerical ages have been assigned to either unit.

San Diego Formation

Outcrops of the San Diego Formation are exposed from the south slope of the San Diego

River in California into Mexico as well as on the bluffs of Pacific Beach, and on the slopes of Mount Soledad (Hertlein and Grant, 1944; Hertlein and Grant, 1972; Figs. 2 and 4C). The formation consists of blue-gray to yellow-brown, fine-grained sandstone, with some areas grading into conglomerate or gravel. It has been proposed that the formation consists of two members: a lower fine-grained sandstone and an upper coarse-grained sandstone (Deméré, 1983). Due to the urban environment of downtown San Diego, continuous fossiliferous sections are almost non-existent in the modern era except for the outcrop at Pacific Beach. Most localities are isolated shell beds on road cuts or behind buildings.

The age of the San Diego Formation is still debated, with estimates ranging from "early Pliocene" to the "early Pleistocene" (Fig. 1). Microfossil biostratigraphic analyses have resulted in conflicting interpretations. Based on planktonic foraminifera within the formation, Deméré (1983) argued that the formation could be no older than 3.0 Ma and no younger than 1.5 Ma. However, a subsequent study of planktonic foraminifera and nannoplankton from an outcrop at Mount Soledad indicate an older age of 4.2–3.8 Ma (See Vendrasco et al., 2012, and references therein). The presence of the planktonic foraminifer *Neogloboquadrina asanoi* at Border Field State Park indicates deposition during the Californian margin planktonic foraminiferal zone 6 (following Kennett et al., 2000), which ranges from 3.25 Ma to 2.5 Ma (Vendrasco et al., 2012; Fig. 1). Mammal fossils from non-marine facies of the lower member of the San Diego Formation suggest a Blancan III Land Mammal Age of 4.8–1.8 Ma (Barnes, 1976; Fig. 1). Using magnetostratigraphy, researchers correlated these beds to the upper reversal interval in the Gilbert chron and the lower normal interval of the Gauss chron, resulting in an age of 3.6 Ma for them (Wagner et al., 2001; Fig. 1). Powell et al. (2009) used the presence of warm-water macrofossils such as *Architectonica* to correlate the formation with the mid-Pliocene warm event and also cited the presence of Pliocene index fossils such as the bivalves *Anadara trilineata* and *Patinopecten healeyi* and the gastropod *Calliostoma coalingensis* (Fig. 1). Thus, most previously published data suggest a late Pliocene age for the San Diego Formation.

Preservation and Diagenesis

Because the $^{87}Sr/^{86}Sr$ ratio preserved within carbonates can be altered with diagenesis, the preservation of material should be assessed prior to analysis. Many studies have found that mollusk specimens with good macroscopic preservation can display microscopic alteration and have stressed that microscopy methods such as Scanning Electron Microscopy (SEM) must be used to ensure good microscopic preservation (McArthur et al., 2001; Cochran et al., 2010; Knoll et al., 2016). Furthermore, McArthur (1994) emphasized that no method of detecting alteration is infallible and multiple methods should be used. McArthur et al. (1994) tested multiple methods of identifying diagenetic alteration and found that binocular microscopy and X-Ray diffractometry (XRD) were both effective methods, however, the authors concluded that SEM was the best at identifying alteration. Cochran et al. (2010) also tested the effect of variable microstructure preservation of gastropod, bivalve, and ammonite shells on Sr, C, and O isotope composition using SEM. The authors found that as microstructure preservation decreased, the mean $^{87}Sr/^{86}Sr$ ratio decreased and standard error between samples increased (Cochran et al., 2010).

It is also possible to evaluate diagenesis of carbonates through the measurement of minor elemental concentrations, although they are not diagnostic of alteration. As carbonate comes in contact with diagenetic waters, concentrations of Fe and Mn can increase, while Sr and Mg concentrations can decrease, as the elemental composition of the carbonate shifts to equilibrium with the interstitial, meteoric water (Veizer, 1977; Brand and Veizer, 1980; Veizer, 1983; Hodell et al., 1990; Veizer et al., 1999). Although high Fe and Mn values (when compared to the range of living mollusks) can indicate diagenesis, low values do not guarantee a lack of alteration (Veizer, 1977; Brand and Veizer, 1980; Veizer, 1983; Hodell et al., 1990; Veizer et al., 1999). Nonetheless, when combined with other methods, such as SEM of microstructure, minor elemental concentrations can lend evidence to assessments of diagenetic alteration.

MATERIALS AND METHODS

Sampling Localities

Pico Formation

The samples for this study were collected from a fossiliferous roadcut on Chiquella Lane (now called Old Road) in Santa Clarita, California, (Ventura Basin; Fig. 4A; Appendix 1A[1]). This roadcut is LACMIP locality 15719 of Squires et al. (2006), and LACMIP localities 41823–41829 of the present study, and is located in the shallow water interval near the top of the formation (Squires et al., 2006). Approximately 26 m of the Pico Formation are exposed in this section. The outcrop is mainly massive sand and contains nine fossiliferous lenses interspersed with lenses of concretionary sandstone (Appendix 1A). A number of these shell beds contain late Pliocene "index fossils," including the bivalves *Anadara trilineata* and *Patinopecten healeyi* and the gastropods *Crepidula princeps* and *"Cancellaria" arnoldi*.

Foxen Mudstone and Careaga Sandstone

The majority of samples (LACMIP localities 41795–41803) for the present study were collected from the Foxen Mudstone and Careaga Sandstone of the Shuman railroad cut (Shuman Cut, herein) originally described by Woodring and Bramlette (1950; Fig. 4B). The section contains 16 fossiliferous beds that were identified and sampled (Appendix 1B; see footnote 1), with several containing late Pliocene "index fossils," including the bivalves *Anadara trilineata* and *Patinopecten healeyi* and the gastropods *Crepidula princeps* and *"Cancellaria" arnoldi*.

Samples were also collected from a small and isolated outcrop of the Careaga Sandstone at the Fugler Point locality (LACMIP localities 41807–41811, Fig. 4B) that was also first described by Woodring and Bramlette (1950). The outcrop is at least 14 m thick, with 12 m of the Cebada Member and 1.8 m of the Graciosa Member exposed. Interspersed throughout the outcrop are masses of naturally occurring asphalt. There are three fossiliferous beds at this locality: two beds of tightly packed brachiopods and one bed dominated by the *Anadara trilineata.*

San Diego Formation

Samples for the present study were collected from three localities in San Diego, California: Border Field State Park (LACMIP localities 41849–41855), Malcolm X Library (LACMIP locality 41860), and Jutland Drive (LACMIP 41863) (Fig. 4C). The outcrops at Border Field State Park are considered part of the lower member (Scott Rugh, 2019, personal commun.) and contain multiple stratigraphically isolated, fossiliferous shell beds in a bluish-gray fine-grained sand containing abundant *Anadara trilineata*, *Patinopecten healeyi*, and *Crepidula princeps*. The dense overgrowth of shrubs and complex topography of this area makes the stratigraphic relationships of sampled beds difficult to discern. Many fossils were chalky and easily broken by even light touch. An isolated fossiliferous bed is exposed near Malcom X Library on Market Street in San Diego, and it is composed of very fine-grained, blue-gray sandstone with abundant aragonitic shells weathering out, including the

[1]GSA Data Repository item 2020187, Appendices 1–4, full Sr analysis report, is available at http://www.geosociety.org/datarepository/2020 or by request to editing@geosociety.org.

bivalve *Anadara trilineata*. The outcrops at Jutland Drive are considered to be part of the upper member (Scott Rugh, 2019, personal commun.), and samples (LACMIP localities 41861–41863) are derived from one of several shell beds consisting of conglomeratic light brown, fine-grained sand that fines upward. These contain *Anadara trilineata* and *Crepidula princeps.*

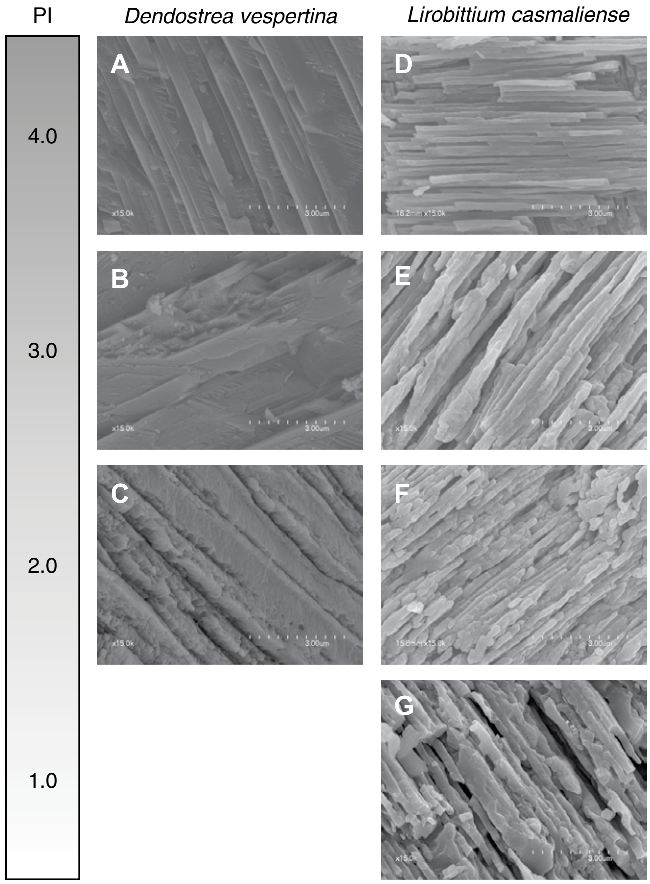

Figure 5. Scanning electron microscopy images representing preservation indices (PI) for foliated and crossed lamellar microstructures of specimens from this study. A–C, Calcitic foliated microstructure of the bivalve *Dendostrea vespertina*. D–G, Aragonitic crossed lamellar microstructure of the gastropod *Lirobittium casmaliense*. A, D "Very good" preservation (PI 4); B, E "Good" preservation (PI 3); C, F "Fair" preservation (PI 2); G "Poor" preservation (PI 1). Calcitic foliated microstructure (A–C) appears to be better preserved than aragonitic crossed lamellar microstructure (D–G), as no specimens representing a PI 1 were found. Scale bar is 3 µm. All photos are shown at 15k magnification.

Preservation Assessment

We used binocular microscopy, SEM, XRD, and minor elemental concentration analysis to test for diagenetic alteration. Shell beds were first judged on whether they contained shells resilient enough to endure wet sieving. Only those beds with shells that could withstand being handled without disintegrating were sampled. Specimens with worn away ornamentation and/or iron oxide deposits evident to the naked eye were not further considered. Specimens were then examined with a binocular microscope for signs of alteration. Microstructure of remaining specimens was assessed via SEM.

Scanning Electron Microscopy (SEM)

In total, 261 specimens (241 aragonitic and 20 calcitic) from seven localities were analyzed for microstructure preservation via SEM (Appendix 2; see footnote 1). Specimens chosen for SEM were cleaned by dry brushing and with water to remove any sediment and were broken into rectangular fragments. Multiple fragments of dorsoventral and mediolateral cross sections were mounted on SEM stubs, coated in gold-palladium using a Denton IV Desk Vacuum sputter coater, and examined with a Hitachi S-4700 FE-SEM at the Microscopy and Imaging Facility (MIF) at the American Museum of Natural History (AMNH). Following the methodology of Cochran et al. (2010) and Knoll et al. (2016), images were taken of each fragment using 10 kV voltage and 15 µA current at 5 K, 10 K, and 15 K magnification.

Images of aragonitic cross-lamellar microstructure were compared with those of Knoll et al. (2016), and the preservation index (PI) scale of Knoll et al. (2016) was used to gauge the degree of alteration. The PI, from 1.0 (poor) to 5.0 (excellent), uses the level of discernible directionality, degree of overgrowth, and sharpness of crystal boundaries to determine the level of microstructure preservation (Fig. 5). Cochran et al. (2010) found that $^{87}Sr/^{86}Sr$ remains relatively constant above a preservation index of 3.0 (good), and thus only those aragonitic specimens with a preservation index of greater than or equal to 3.0 on the scale established by Knoll et al. (2016) were chosen for analysis. Calcitic specimens were compared to photographs of foliated microstructure in freshly killed *Crassostrea gigantea* specimens in Carriker et al. (1980), and the PI scale of Knoll et al. (2016) for crossed lamellar microstructure is adapted here for foliated microstructure (Fig. 5). Calcitic specimens with a microstructure preservation index of 3.0 and greater were sent for XRD and minor elemental concentration analyses.

X-Ray Diffractometry (XRD)

We carried out XRD on presumed calcitic specimens to determine their mineralogy. A fragment of each specimen was powdered using a mortar and pestle. XRD was conducted in the Earth and Planetary Sciences Department in the AMNH using an EQUINOX 100 X-ray Diffractometer. Data was gathered for 5 min per sample, and results were compared against a pure calcite standard to determine the mineralogical composition. All samples were found to be calcite and thus sent for minor elemental analysis.

Inductively Coupled Plasma–Mass Spectrometry (ICP–MS)

Dendostrea vespertina specimens that were deemed well-preserved via microstructure assessment were sent to the Facility for Isotope Research and Student Training (FIRST) at Stony Brook University for elemental concentration analyses. Analyses were carried out using an Agilent 7500cx quadrupole inductively coupled plasma–mass spectrometer (ICP–MS). Samples between 0.06 g and 0.07 g were diluted to signal match mixed calibration standards, and unknown concentrations were calculated based on standard calibration curves, with standards run frequently between unknowns to monitor for drift in signal intensity. International standards JCp-1 and JCT-1 were also run with the samples as unknowns to test accuracy.

Fe cutoffs have been proposed between 100 ppm and 1000 ppm (see Schneider et al., 2009, and references therein); we only selected specimens with Fe concentrations equal to or less than 100 ppm. Mn cutoffs have been proposed between 100 ppm and 300 ppm (see Schneider et al., 2009, and references therein); we only selected specimens with Mn concentrations equal to or less than 250 ppm (Table 1).

Strontium Isotope Mass Spectrometry

Strontium isotope mass spectrometry was conducted at the FIRST at Stony Brook University. Fragments from each specimen were weighed out to between 0.02–0.025 g. Samples

TABLE 1. CALCITE GEOCHEMISTRY RESULTS

Specimen ID	LACMIP locality	Ca (wt%)	Mg (ppm)	Mn (ppm)	Fe (ppm)	Sr (ppm)	$^{87}Sr/^{86}Sr$*	Uncertainty (2sd)	Age† (Ma)	
									Maximum	Minimum
San Diego Formation										
Border Field State Park										
180104_O2	41852	39.10	731	59	30	840	0.709062	0.000011	3.45	2.85
180104_O3	41852	38.90	2659	343	33	784	N.D.§	N.D.	N.D.	N.D.
180104_O4	41852	38.90	1367	214	30	686	0.709053	0.000011	4.45	3.60
180104_O5	41852	38.90	1923	252	30	791	N.D.	N.D.	N.D.	N.D.
180104_O6	41852	39.00	809	136	30	837	0.709059	0.000011	3.80	3.05
180106_O1	41854	37.80	7094	148	29	650	N.D.	N.D.	N.D.	N.D.
180106_O2	41854	38.60	1152	83	31	811	0.709063	0.000011	3.30	2.75
180106_O4	41854	38.40	1823	67	31	841	0.709049	0.000011	4.65	3.95
180106_O5	41854	38.10	2728	96	30	772	N.D.	N.D.	N.D.	N.D.
180106_O6	41854	38.40	1157	93	32	810	0.709053	0.000011	4.45	3.60
Pico Formation										
Chiquella Lane#										
180607_O1	41835	38	928	51	32	1019	0.709039	0.000011	5.05	4.75
180607_O2	41835	37.9	1361	136	36	974	0.709043	0.000011	4.90	4.50
180607_O3	41835	37.9	1104	82	32	1007	0.709045	0.000011	4.85	4.40
180607_O4	41835	36.7	4025	625	196	1150	N.D.	N.D.	N.D.	N.D.
180607_O5	41835	38.6	1160	75	32	930	0.709047	0.000011	4.75	4.25
170512_O1	41829	39	1336	207	41	741	0.709065	0.000011	3.05	2.65
170512_O2	41829	39.5	1086	126	31	896	N.D.	N.D.	N.D.	N.D.
170512_O3	41829	39.4	2439	127	34	865	0.709046	0.000011	4.80	4.30
170512_O5	41829	39.6	1615	123	35	834	0.709046	0.000011	4.80	4.30
170512_O6	41829	39.2	1849	248	40	804	0.709049	0.000011	4.65	3.95

*All data have been normalized to an SRM-987 value of 0.710248.
†Estimate ages determined from Sr data and the LOWESS 5 table from McArthur et al. (2012).
§Not determined.
#The name "Chiquella Lane" is from Squires et al. (2006). On modern maps, this road is called "Old Road."

were then dissolved in 800 µl of 2 M nitric acid and loaded into gravity columns with 300 µl of strontium-specific ion exchange resin to separate Sr from interfering elements. Samples were dissolved in 8 M nitric acid and ~200 ng Sr aliquots were loaded onto Re-filaments along with TaCl5 "loader" solution. Filaments were dried down and loaded into an Isotopx Phoenix X62 Thermal Ionization Mass Spectrometer (TIMS). Samples were run alongside standards including NIST SRM-987. The long-term average was used to correct the unknown samples to the certified NIST value ($^{87}Sr/^{86}Sr = 0.710248$). An in-run mass bias correction was applied to all sample and standard analyses using the in-run measured $^{87}Sr/^{86}Sr$, which was corrected to the natural abundance of 0.1194 using an exponential relationship. Analytical uncertainty was determined from the 2-σ uncertainty of repeated analyses of SRM-987 (Appendix 4; see footnote 1) before and during the time of analysis. The average 2-standard deviation reproducibility of the lab is currently 11 ppm. Age estimates were determined using the LOWESS Look-Up Table Version 5 (McArthur et al., 2012).

The $^{87}Sr/^{86}Sr$ curve has a very low slope throughout during the early and middle Pliocene (5–3 Ma), but the slope increases from the latest Pliocene into early Pleistocene (3–1.5 Ma) (McArthur et al., 2012; Fig. 6). Therefore, any ratios generated from truly Pliocene beds should be considered rough estimates, and ratios from those beds that are proximal to the Pliocene-Pleistocene boundary should be more precise. We chose 54 out of 70 well-preserved specimens for analysis: six aragonitic specimens from the Careaga Sandstone, three aragonitic specimens from the Foxen Mudstone, 18 specimens (10 aragonitic, 8 calcitic) from the Pico Formation, and 27 specimens (21 aragonitic, 6 calcitic) from the San Diego Formation (Table 2). Specifically, three aragonitic specimens each were chosen from the lowermost bed of the Foxen Mudstone (LACMIP locality 417601) and uppermost fossiliferous bed (LACMIP locality 41814) of the Careaga Sandstone exposed at the Shuman Cut (Table 2, Appendix 1B). Three aragonitic specimens were chosen from a single bed of the Careaga Sandstone at the Fugler Point locality (Table 2). Originally, three aragonitic specimens each were chosen from the bottom (LACMIP locality 41826) and top (LACMIP locality 41828) beds of Pico Formation at Chiquella Lane (Table 2, Appendix 1A); however, inconsistent Sr isotope results in the first run of analyses (Table 3) led us to analyze an additional two aragonitic and four calcitic specimens from the lowermost (LACMIP locality 41829, Appendix 1A) and uppermost (LACMIP locality 41835, Appendix 1A) fossiliferous beds of the Ed Davis Towsley Canyon State Park section of the Pico Formation. Originally, three aragonitic specimens each were chosen from seven isolated fossiliferous beds from the San Diego Formation (LACMIP locality 41849, SDNHM 6242, SDNHM 6243, LACMIP locality 41863, LACMIP locality 41852, LACMIP locality 41860, LACMIP locality 41854; Table 2). Following inconsistent Sr isotope results, an additional three calcitic specimens each were chosen from LACMIP localities 41852 and 41854 for additional analyses and to test consistency between aragonitic and calcitic specimens from the same locality (Table 2).

RESULTS

Preservation

Preservation of aragonitic, cross-lamellar specimens ranged from poor (1.0) to very good (4.0). Preservation of calcitic specimens of *Dendostrea vespertina* ranged from fair (2.0) to very good (4.0). Out of all specimens imaged and analyzed for microstructure preservation, 70 specimens (27% of all assessed) had a preservation index of 3.0 or greater (Appendix 2). Of these specimens, 20 were calcitic and were further analyzed for minor elemental concentrations. Out of these specimens, 17 had Fe concentrations below 100 ppm and Mn concentrations below 250 ppm (Table 1) and were considered for Sr analysis.

Strontium Isotope Stratigraphy

Foxen Mudstone and Careaga Sandstone

Aragonitic specimens from the Foxen Mudstone at the Shuman Cut locality had $^{87}Sr/^{86}Sr$ values ranging between 0.709086 and 0.709095 ± 0.000008 (Table 3). Ages derived from these isotopic ratios range between 2.00 and 1.75 Ma (Gelasian, early Pleistocene; Fig. 6). Specimens from the Careaga Sandstone at the Shuman Cut locality yielded $^{87}Sr/^{86}Sr$ values between 0.709078 and 0.709089 ± 0.000008 (Table 3), yielding derived ages ranging

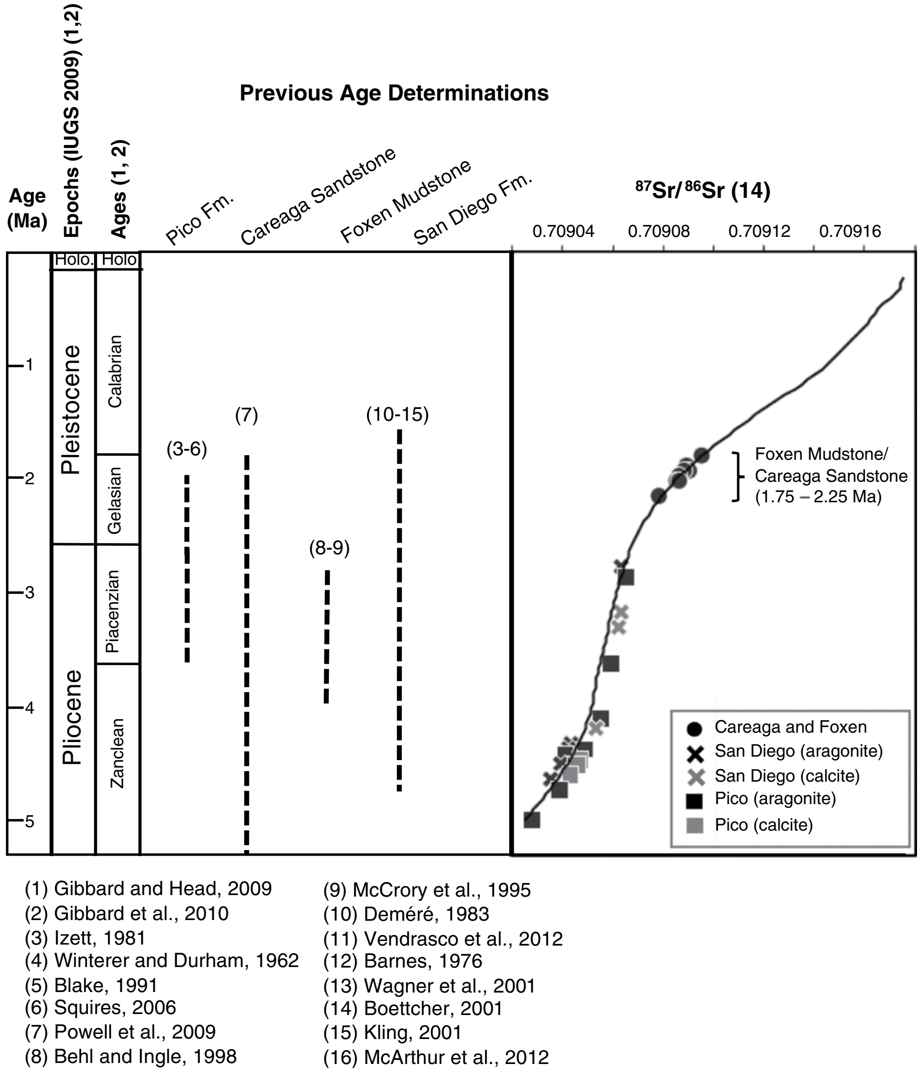

Figure 6. Results of the Sr-isotope stratigraphy of the Careaga Sandstone, Foxen Mudstone, Pico Formation, and San Diego Formation are plotted versus previous age determinations and the International Union for Geological Sciences (IUGS) 2009 timescale. The age results of the Careaga Sandstone and Foxen Mudstone are bracketed to highlight consistency. San Diego Formation results span past the represented time interval. Only results up to the early Pliocene are figured as all other results are inconsistent with all previous age determinations. Fm.—formation.

between 2.25 Ma and 1.85 Ma (Gelasian, early Pleistocene; Fig. 6). Specimens from the Careaga Sandstone at the Fugler Point locality yielded $^{87}Sr/^{86}Sr$ values between 0.709085 and 0.709090 ± 0.000007, yielding derived ages ranging between 2.0 Ma and 1.85 Ma (Gelasian, early Pleistocene; Fig. 6).

Pico Formation

$^{87}Sr/^{86}Sr$ values of aragonitic specimens from the Chiquella Lane section ranged between 0.709011 and 0.709065 ± 0.000008 (Table 3), yielding derived ages ranging from 5.65 Ma (late Messinian, uppermost Miocene) to 2.65 Ma (Piacenzian, late Pliocene) (Fig. 6). The smallest difference between specimens within a single bed was 0.000006, with derived ages ranging from 5.05 Ma to 4.4 Ma (LACMIP locality 41835; Tables 2 and 3). The largest difference between specimens within a single bed was 0.000048 (LACMIP localities 41826 and 41828; Tables 2 and 3).

The $^{87}Sr/^{86}Sr$ values of the calcitic specimens from the Chiquella Lane section span 0.709039–0.709065 ± 0.000011 (Table 1), corresponding to derived ages ranging from 5.05 Ma to 2.65 Ma (Zanclean, early Pliocene; Fig. 6). The calcitic specimens from LACMIP locality 41835 also had the smallest difference between specimens (0.000008), with derived ages for isotopic ratios ranging between 5.05 Ma and 4.25 Ma (Tables 1 and 2). The largest difference between calcitic specimens within a single bed was 0.000016 (LACMIP locality 41829; Tables 1 and 2).

San Diego Formation

Aragonitic specimens from the Border Field locality of the San Diego Formation had a wide range of $^{87}Sr/^{86}Sr$ values and are much more poorly constrained within beds than the other units studied. Isotopic ratios ranged from 0.708466 to 0.709043 ± 0.000007 (Table 3), corresponding to derived ages ranging from 19.4 Ma (early Burdigalian, early Miocene) to 6.2 Ma (mid-Messinian, late Miocene). The largest difference between specimens from a single bed was 0.000332 (LACMIP locality 6243; Tables 2 and 3). The smallest difference between specimens from within a single bed was 0.000059 (LACMIP locality 6242; Tables 2 and 3).

In contrast, $^{87}Sr/^{86}Sr$ values of calcitic specimens from the same locality span from 0.709049 to 0.709063 ± 0.000011 (Table 1) with derived ages ranging between 4.65 Ma (Zanclean, early Pliocene, Fig. 6) and 2.75 Ma (Piacenzian, late Pliocene, Fig. 6). Specimens from LACMIP locality 41852 had a range of 0.000009, with derived ages ranging from 4.45 Ma to 2.85 Ma, while specimens from LACMIP locality 41854 had a range of 0.000014 (Tables 1 and 2), with derived ages ranging from 4.65 Ma to 2.75 Ma.

$^{87}Sr/^{86}Sr$ values of aragonitic specimens from locality AB180115 (Jutland Drive) span from 0.709039 to 0.709063 ± 0.000007 (Table 3) with derived ages ranging from 4.8 Ma (Zanclean, early Pliocene, Fig. 6) to 2.75 Ma (Piacenzian, late Pliocene, Fig. 6). The $^{87}Sr/^{86}Sr$ values of aragonitic specimens from Malcolm X Library (LACMIP locality 41860) span 0.709035–0.709043 ± 0.000007 (Table 3) with derived ages ranging from 4.95 Ma to 4.5 Ma (Zanclean, early Pliocene; Fig. 6).

DISCUSSION

Stratigraphic Interpretation

Foxen Mudstone and Careaga Sandstone

Both shell beds tested from the Shuman Cut contain well-preserved specimens (preservation indices [PIs] between 3.0–4.0; Appendix 1B), and the $^{87}Sr/^{86}Sr$ values are consistent with a Gelasian age (2.25–1.75 Ma; Table 3). The error estimates for two of the three values from a single horizon within the Careaga Sandstone cause an overlap in their derived ages (1.95–1.85 Ma), while a third value (2.25–2.15 Ma) is considerably older (Table 3; Fig. 6). The isotope

TABLE 2. STATISTICAL SUMMARY OF SR RESULTS

Field no.	LACMIP locality no.	Bed	Mineralogy	Number of specimens	$^{87}Sr/^{86}Sr$ ratio maximum	$^{87}Sr/^{86}Sr$ ratio minimum	$^{87}Sr/^{86}Sr$ ratio range	Age max*	Age min*
San Diego Formation									
Border Field State Park									
SDNHMC	6242	N.A.[##]	aragonite	3	0.708944	0.708885	0.000059	9.95	7.10
SDNHMB	6243	N.A.	aragonite	3	0.708702	0.708466	0.000236	19.40	16.25
180101	41849	N.A.	aragonite	3	0.708918	0.708735	0.000183	15.85	8.55
180104	41852	N.A.	aragonite	3	0.708978	0.708646	0.000332	17.10	6.20
180104	41852	N.A.	calcite	3	0.709062	0.709053	*0.000009*[§§]	4.45	2.85
180106	41854	N.A.	aragonite	3	0.708953	0.70884	0.000113	11.65	6.80
180106	41854	N.A.	calcite	3	0.709063	0.709049	0.000014	4.65	2.75
Malcolm X[†]									
180112	41860	N.A.	aragonite	3	0.709043	0.709035	*0.000008*	4.95	4.50
Jutland Drive[§]									
180115	41863	N.A.	aragonite	3	0.709063	0.709039	0.000024	4.80	2.75
Pico Formation									
Chiquella Lane[#]									
170631	41826	Middle	aragonite	3	0.709041	0.709011	0.00003	5.65	4.65
170511	41828	Middle	aragonite	3	0.709059	0.709028	0.000031	5.35	3.05
170512	41829	Low	aragonite	2	0.709065	0.709049	0.000016	4.65	2.65
170512	41829	Low	calcite	4	0.709065	0.709046	0.000019	4.80	2.65
180607	41835	High	aragonite	2	0.709045	0.709039	*0.000006*	5.05	4.40
180607	41835	High	calcite	4	0.709047	0.709039	*0.000008*	5.05	4.25
Careaga Sandstone									
Fugler Point**									
170615	41809	N.A.	aragonite	3	0.709090	0.709085	*0.000005*	2.00	1.85
Shuman Cut[††]									
170620	41814	High	aragonite	3	0.709089	0.709078	*0.000011*	2.25	1.85
Foxen Mudstone									
Shuman Cut[††]									
170601	41795	Low	aragonite	3	0.709095	0.709086	*0.000009*	2.00	1.75

*Estimate ages were determined from Sr data and the LOWESS 5 table from McArthur et al. (2012).
[†]The name "Malcolm X" is an informal designation.
[§]The name "Jutland Drive" is an informal designation.
[#]The name "Chiquella Lane" is from Squires et al. (2006). On modern maps, this road is called "Old Road."
**The name "Fugler Point" is taken from Woodring and Bramlette (1950).
[††]The name "Shuman Cut" is taken from Woodring and Bramlette (1950).
[§§]Italics indicate low ranges in isotope values.
[##]Not applicable.

ratios for the Careaga at Fugler Point also support a Gelasian age (Table 3). These results are consistent with the previous relative age assignments for the unit (e.g., Woodring and Bramlette, 1950; Powell et al., 2009; Fig. 6) and allow us to further constrain key sections of the unit to the Gelasian Age (Fig. 6). The three samples from the uppermost Foxen Mudstone are roughly concordant (2.0–1.75 Ma), and so too support a Gelasian age (Table 3). This is unsurprising as the Foxen Mudstone and Careaga Sandstone appear to have a conformable contact. We discount the validity of the oldest date from the Careaga Sandstone at Shuman Cut as it is outside the error estimates of other samples within the same stratigraphic horizon, is considerably older than those from the Fugler Point section of the same unit, and is older than ages from the uppermost Foxen Mudstone that underlies it.

Pico Formation

Strontium isotope analyses yielded 15 $^{87}Sr/^{86}Sr$ values (7 out of 8 calcitic specimens and 8 out of 10 aragonitic specimens) indicative of a Zanclean age (5.3–3.6 Ma; early Pliocene; Tables 1 and 3), with the most tightly constrained bed indicating a Zanclean age (5.1–4.3 Ma; early Pliocene; Table 2) for both calcitic and aragonitic specimens. This latter bed (LACMIP 41835) is from the upper part of the Chiquella Lane section (Appendix 1A). Two aragonitic specimens (from LACMIP 41828 and 41829) and one calcitic specimen (from LACMIP 41829) yielded ratios that suggest Piacenzian (late Pliocene) and Gelasian (early Pleistocene) ages, respectively (Tables 1 and 3). A Zanclean age for the Pico Formation is older than that inferred from microfossil and macrofossil biostratigraphic work (Winterer and Durham, 1962; Blake, 1991; Squires et al., 2006; Fig. 6).

San Diego Formation

Most results from the Malcolm X and Jutland Drive localities (three out of three from Malcolm X and two out of three from Jutland Drive) are consistent with a Zanclean age (4.95–4.5 Ma, early Pliocene; Table 3). One specimen from Jutland Drive reflected a late Piacenzian age (2.85–2.75 Ma, late Pliocene; Table 3). Results from aragonitic specimens from the Border Field locality were internally inconsistent; within a single shell bed, results ranged from an age of 17.10–6.2 Ma (Tables 2 and 3). The majority of aragonitic specimens from the Malcolm X and Jutland Drive localities suggest ages that are older than those from microfossil biostratigraphy (Barnes, 1976; Deméré, 1982, 1983; Boettcher, 2001; Kling, 2001; Powell et al., 2009; Vendrasco et al., 2012).

Results from the six calcitic specimens are more constrained than aragonitic specimens, particularly those from LACMIP locality 41852 (range in isotope values of 0.000009, Table 2), which are consistent with a late Zanclean to Piacenzian age (early–late Pliocene) of 4.45–2.85 Ma. Similarly, all three calcitic specimens from LACMIP locality 41854 are consistent with a late Zanclean to Piacenzian age (early–late Pliocene) of 4.65–2.75 Ma for the Border Field State Park locality (Tables 1 and 2, Fig. 6), though the range in isotopic values is somewhat higher (0.000014, Table 2). These results suggest the possibility that the formation may be older than previously inferred from biostratigraphy, with the exception of the Zanclean age proposed for a single outcrop of the lower member based on planktonic foraminifera and nannoplankton biostratigraphy (Boettcher, 2001; Kling, 2001; Fig. 1).

Diagenetic Overprinting

Diagenesis is apparent in all units as less than 27% of all specimens analyzed had "good" preservation (PI > 3.0; Appendix 2), and inconsistencies among aragonitic specimens from the same shell beds of the Pico and San Diego Formations resulted in large age range estimates. Cochran

TABLE 3. ARAGONITE GEOCHEMISTRY RESULTS

Specimen ID	LACMIP locality	Species	Mineralogy	^{87}Sr/^{86}Sr*	Uncertainty (2sd)	Age[†] (Ma)	
						Maximum	Minimum
San Diego Formation							
Border Field State Park							
180101_A1	41849	*Anadara trilineata*	Aragonite	0.708735	0.000007	15.85	15.80
180101_A4	41849	*A. trilineata*	Aragonite	0.708918	0.000007	9.00	8.55
180101_A5	41849	*A. trilineata*	Aragonite	0.708859	0.000007	10.85	10.80
180104_A2	41852	*A. trilineata*	Aragonite	0.708978	0.000007	6.25	6.20
180104_N1	41852	*Cryptonatica affinis*	Aragonite	0.708646	0.000007	17.10	17.05
180104_T1	41852	*Turritella cooperi*	Aragonite	0.708974	0.000007	6.30	6.25
180106_A2	41854	*A. trilineata*	Aragonite	0.708935	0.000007	7.55	7.50
180106_A4	41854	*A. trilineata*	Aragonite	0.708840	0.000007	11.65	11.60
180106_A6	41854	*A. trilineata*	Aragonite	0.708953	0.000007	6.85	6.80
SDNHMB_N3	6243[§§]	*C. affinis*	Aragonite	0.708472	0.000007	19.20	19.15
SDNHMB_N4	6243	*C. affinis*	Aragonite	0.708702	0.000007	16.30	16.25
SDNHMB_N5	6243	*C. affinis*	Aragonite	0.708466	0.000007	19.40	19.35
SDNHMC_A2	6242	*A. trilineata*	Aragonite	0.708885	0.000007	9.95	9.90
SDNHMC_A3	6242	*A. trilineata*	Aragonite	0.708944	0.000007	7.15	7.10
SDNHMC_A4	6242[§§]	*A. trilineata*	Aragonite	0.708915	0.000007	8.75	8.70
Malcolm[§]							
180112_M1	41860	*Macoma nasuta*	Aragonite	0.709043	0.000007	4.60	4.50
180112_M2	41860	*M. nasuta*	Aragonite	0.709041	0.000007	4.70	4.65
180112_M3	41860	*M. nasuta*	Aragonite	0.709035	0.000007	4.95	4.90
Jutland Drive[#]							
180115_C1	41863	*Callianax biplicata*	Aragonite	0.709063	0.000007	2.85	2.75
180115_C2	41863	*C. biplicata*	Aragonite	0.709039	0.000007	4.80	4.75
180115_C3	41863	*C. biplicata*	Aragonite	0.709042	0.000007	4.65	4.60
Pico Formation							
Chiquella Lane							
180607_T1	41835	*T. cooperi*	Aragonite	0.709039	0.000011	5.05	4.75
180607_T3	41835	*T. cooperi*	Aragonite	0.709045	0.000011	4.80	4.40
170511_S1	41828	*Lirobittium casmaliense*	Aragonite	0.709055	0.000007	4.35	3.35
170511_S7	41828	*L. casmaliense*	Aragonite	0.709059	0.000007	*3.80*	*3.05*
170511_S9	41828	*L. casmaliense*	Aragonite	0.709028	0.000007	5.35	5.15
170631_T1	41826	*T. cooperi*	Aragonite	0.709011	0.000007	5.65	5.60
170631_T2	41826	*T. cooperi*	Aragonite	0.709014	0.000007	5.55	5.50
170631_T3	41826	*T. cooperi*	Aragonite	0.709041	0.000007	4.70	4.65
170512_T1	41829	*T. cooperi*	Aragonite	0.709065	0.000011	*2.95*	*2.65*
170512_T5	41829	*T. cooperi*	Aragonite	0.709049	0.000011	4.65	3.95
Careaga Sandstone							
Fugler Point**							
170615_N5	41809	*C. affinis*	Aragonite	0.709085	0.000007	2.00	1.95
170615_N2	41809	*C. affinis*	Aragonite	0.709090	0.000007	1.90	1.85
170615_N3	41809	*C. affinis*	Aragonite	0.709086	0.000007	2.00	1.95
Shuman Cut[††]							
170620_Liro_S9	41814	*L. casmaliense*	Aragonite	0.709088	0.000008	1.95	1.90
170620_Liro_S11	41814	*L. casmaliense*	Aragonite	0.709089	0.000008	1.90	1.85
170620_Liro_S12	41814	*L. casmaliense*	Aragonite	0.709078	0.000008	2.25	2.15
Foxen Mudstone							
Shuman Cut							
170601_Liro_S8	41795	*L. casmaliense*	Aragonite	0.709086	0.000008	2.00	1.95
170601_S4	41795	*L. casmaliense*	Aragonite	0.709095	0.000008	1.80	1.75
170601_Liro_S10	41795	*L. casmaliense*	Aragonite	0.709089	0.000008	1.90	1.85

*All data have been normalized to an SRM-987 value of 0.710248.
[†]Estimate ages were determined from Sr data and the LOWESS 5 table from McArthur et al. (2012).
[§]The name "Malcolm X" is an informal designation.
[#]The name "Jutland Drive" is an informal designation.
**The name "Fugler Point" is taken from Woodring and Bramlette (1950).
[††]The name "Shuman Cut" is taken from Woodring and Bramlette (1950).
[§§]San Diego Natural History Museum collections number.

et al. (2010) found that good preservation (PI > 3.0) narrowed the range of ^{87}Sr/^{86}Sr ratios while Knoll et al. (2016) found that specimens with good microstructural preservation (PI > 3.5) could yield still large ranges in carbon and oxygen isotope values. These studies find variable results because diagenesis is place and time specific, emphasizing the need to assess diagenesis via multiple methods and in the context of other chrono- or bio-stratigraphic estimates of age.

Natural waters are known to have a wide range of Sr isotopic compositions due to their interaction with different minerals (e.g., Banner, 1995). For example, interactions with mantle-derived volcanic rocks can generate fluids with ^{87}Sr/^{86}Sr values that are lower than expected for Phanerozoic marine carbonates (Goldstein and Jacobsen, 1987; Franklyn et al., 1991; Banner, 1995). The altered ^{87}Sr/^{86}Sr values are then preserved in recrystallized carbonates and carbonate cements, causing analysis to reflect altered rather than original values (Banner, 1995).

Detrital constituents of the Pico Formation are derived from a plutonic source dated between 80–70 Ma (Bateman and Wahrhaftig, 1966; Compton, 1966; Yeats and McLaughlin, 1970). We hypothesize that contact with these plutonic-derived detrital constituents altered pore water in the formation, subsequently changing the ^{87}Sr/^{86}Sr values recorded in some specimens. The modern San Diego Basin is bounded to the east by the Peninsular Ranges batholith, which has a high concentration of plagioclase feldspar (Kimbrough et al., 2015). Groundwater flowing through the batholith has an ^{87}Sr/^{86}Sr ratio of 0.703–0.708, which is much lower than that expected for Plio-Pleistocene marine sediments (DePaolo, 1981). Groundwater flow within the San Diego region is generally from east to west (i.e., from the batholith to the study area), with at least a small amount of recharge occurring within the Peninsular Ranges batholith (R. Gannon and W. Danskin, 2019, personal commun.), possibly leading to the alteration of Sr signal in aragonite preserved within the San Diego Formation. Furthermore, much of the inorganic matrix of the formation is composed of sediments derived from the weathering of the Peninsular Ranges batholith (Kennedy, 1975), providing another mechanism for the alteration of aragonite via the interaction of pore water with host sediments.

Within the Border Field State Park locality, $^{87}Sr/^{86}Sr$ values from aragonitic specimens are particularly incongruent with respect to values from calcitic specimens from the same beds. Although multiple precautions (i.e., checking superficial preservation, microstructure preservation, and minor elemental concentration) were taken when choosing specimens for strontium analysis, many were chalky to the touch and had preservation indices no greater than the minimum cutoff. McArthur et al. (1994) reported aberrant $^{87}Sr/^{86}Sr$ ratios when attempting to use mollusks with seemingly well-preserved aragonite (assessed using multiple methods) to construct the seawater strontium curve for the U.S. Western Interior Seaway. Marcano et al. (2015) cited multiple studies in which aragonitic specimens with no indication of diagenetic alteration by cathodoluminescence or Fe/Mn concentration yielded ambiguous $^{87}Sr/^{86}Sr$ ratios and proposed that the recrystallization of the original aragonite into inorganically precipitated aragonite was the cause of the anomalous values. We propose a similar explanation for the San Diego Formation, since coastal San Diego has been hydrologically dynamic over the last 800 k.y. (Spratt and Lisiecki, 2016), causing sediments to have been saturated frequently by both seawater and freshwater and possibly leading to the dissolution and recrystallization of aragonite within fossils.

Implications for Biostratigraphic Determination

Prior to this study, the presence of overlapping regional "index fossils" such as the bivalves *Anadara trilineata, Patinopecten healeyi, Euvola bella, Pycondonte erici,* and *Swiftopecten parmeleei* and the gastropods *Calicantharus fortis angulata,* "*Cancellaria*" *arnoldi, Crepidula princeps,* and *Opalia varicostata* (Arnold, 1903; Woodring and Bramlette, 1950; Squires et al., 2006; Powell et al., 2009; Squires, 2012) was used as evidence of a "Pliocene" age (e.g., Fig. 3). For example, several of these species are present within the Purisima Formation (6.5–2.5 Ma, Powell et al., 2007) and the San Joaquin Formation (4.8–2.2 Ma, Scheirer and Magoon, 2008), giving rise to the "San Joaquin" California Provincial Molluscan Stage of Addicott (1972). With the newly constrained ages of the Careaga Sandstone (2.0–1.85 Ma) and the uppermost Foxen Mudstone presented within this study (2.0–1.75 Ma), a number of these fossil species now extend into the early Pleistocene (as recently redefined), and their designation as Pliocene index fossils is problematic for future work. Nevertheless, records of the mollusks *Anadara trilineata, Swiftopecten parmeleei, Opalia varicostata,* and *Pycnodonte erici* in the Careaga Sandstone, Pico Formation, Fernando Formation, Niguel Formation, and San Diego Formation are among the last occurrences of these species prior to their extinction, as they are not found in any younger, overlying sediments (Grant and Gale, 1931; Hertlein and Grant, 1972; Moore, 1987). The presence of these four species can therefore be interpreted as being indicative of the Pliocene through the early Pleistocene ages.

CONCLUSIONS

Herein we have presented the first ages, derived from strontium isotope stratigraphy, for the Foxen Mudstone, Careaga Sandstone, Pico Formation, and San Diego Formation. We have confirmed that the upper part of the Foxen Mudstone ranges into the Gelasian (early Pleistocene). All sampled localities from Careaga Sandstone yielded ages equivalent to the Gelasian (early Pleistocene), consistent with macrofossil biostratigraphy. Calcitic specimens have indicated a Zanclean to Piacenzian age (Pliocene) for both the Pico and San Diego Formations. These ages are older than most previous age determinations based on biostratigraphy. Although microscopic alteration was assessed by typical methods (e.g., SEM and elemental concentrations), only ~30% of all specimens were considered sufficiently preserved to be analyzed, and many were chalky to the touch, indicating that preservation is variable throughout the units. Furthermore, strontium isotope ratios from aragonitic specimens of the Pico and San Diego Formations were almost always internally inconsistent within beds and often considerably older than previous biostratigraphic age determinations. Many specimens, therefore, appear to have been altered during diagenesis. Diagenetic alteration of aragonitic specimens within the San Diego Formation could have resulted from groundwater flow from surrounding igneous rocks, pore water in contact with granitic constituents of the inorganic matrix of the formation, and the frequent saturation of sediments due to sea level changes during the Pleistocene. Similarly, diagenetic alteration of aragonitic specimens within the Pico Formation could have been caused by pore water in contact with granitic detrital constituents derived from a granitic pluton. We stress that a thorough consideration of the influence of surrounding rock types, meteoric water flow paths, proximity to freshwater bodies, and surrounding salinity levels is of the utmost importance when interpreting the validity and accuracy of strontium isotope analyses. Results from this study demonstrate that species previously used as "Pliocene index fossils" range into the Gelasian (early Pleistocene epoch) and should no longer be used to constrain formations as Pliocene in age, in part due to the recent assignment of the Gelasian to the Pleistocene epoch. The occurrence of the "Pliocene" index fauna within multiple stratigraphically correlated units in conjunction with the new dates of the Careaga Sandstone and uppermost Foxen Mudstone presented in this study provide evidence that the "Pliocene" formations of southern California also contain Pleistocene sediments.

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