Stable Isotopes of Macrofossils and Bulk Carbonates from the Late Miocene to Pleistocene Santa Rosalía Basin, Baja California Sur, Mexico

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A Senior Honors Thesis Presented to

the Faculty of the Department of Earth and Atmospheric Sciences

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science

Geology

By

Laura L. Taylor

December 2020

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Abstract

Modeling of the response to future climate change predict that northwest North America will become more arid. By studying sedimentary deposits from the late Miocene and Pliocene time periods, when mean global air temperatures were ~3 ºC warmer than today and sea-surface temperatures were 3-8 °C warmer than today, scientists can further address the potential future impact of climate change. The late Miocene to Pleistocene Santa Rosalía Basin, located along the western margin of the Gulf of California in Baja California Sur, Mexico has a complex history of sedimentation but the paleoenvironments of fluvial, marginal-marine, and marine deposits in this area are poorly understood and the late Miocene to early Pliocene climate is relatively unknown. In this study, bulk carbonates from the late Miocene Boleo Fm. and bivalve and barnacle macrofossils from the late Miocene Boleo Fm., early to middle Pliocene Tirabuzón Fm., late Pliocene Infierno Fm., and Pleistocene Santa Rosalía Fm. were collected and processed for petrography, species identification, X-ray diffraction, and stable oxygen and carbon isotope analyses. X-ray diffraction analysis and the covariation trends between $\delta^{18}O$ and $\delta^{13}C$ suggest that the values recorded in these deposits are original. Comparison between the $\delta^{18}O$ and $\delta^{13}C$ values in this study and common values for Quaternary carbonates reveals a strong freshwater signal on deposits that were previously regarded as marine. In this study, $\delta^{18}O$ and $\delta^{13}C$ values from the late Miocene Boleo Fm. and the Pliocene Tirabuzón and Infierno Fms. suggest a substantial freshwater source into the basin not present today. $\delta^{18}O$ and $\delta^{13}C$ values from the Pleistocene Santa Rosalía Fm. no longer record a freshwater influence, as the climate transitioned to the modern arid regime. This suggests that during the late Miocene and Pliocene warmer temperatures did not lead to increased aridity in this region

and instead this area was likely more humid than modern times. The Santa Rosalía Basin was likely influenced by a prolonged and intensified North American monsoon resulting from increased sea-surface temperatures and opening of the Gulf of California during the late Miocene and Pliocene.

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1. Introduction

As the global climate continues to warm, models predict that southwest North America will become more arid (Seager *et al*., 2007). This increased aridity will lead to worse droughts, drier soils, and reduced river flows that will greatly affect the vegetation, wildlife and humans that live in southwest North America. To better understand the potential landscape, flora, and fauna changes that will occur as the global climate warms, studies of paleoclimate and paleoenvironment during times of increased aridity and temperature in southwestern North America are on-going. The latest Miocene (7-5.33 Ma) is regarded as the driest part of the Tertiary (Chaplin, 2008), and global temperatures during the Pliocene (5.33-2.58 Ma) were 3-4 ºC warmer than today (Winnick *et al*., 2013), offering a parallel to future predictions of a warmer and drier climate. Studies of the paleoclimate in the western US during the late Miocene and Pliocene often suggest a resemblance to present day El Niño climates, with increased precipitation in the southwestern US and northern Mexico compared to non-El Niño years (Molnar and Cane, 2007; Winnick *et al*., 2013). Building on the work done by Molnar and Cane (2007) and Winnick *et al*. (2013), this study addresses the potential for a more-arid climate in southwest North America by analyzing sedimentary deposits formed during the latest Miocene and Pliocene. The Santa Rosalía Basin (SRB) in Baja California Sur, Mexico (Fig. 1) has the potential to address future climate predictions, as mining in the area offers excellent exposure of late Miocene and Pliocene marine and fluvial outcrops. Yet, after nearly a century of on-going research in this area, the paleoenvironments of marine and fluvial deposits are poorly understood and the paleoclimate of this area is relatively unknown.

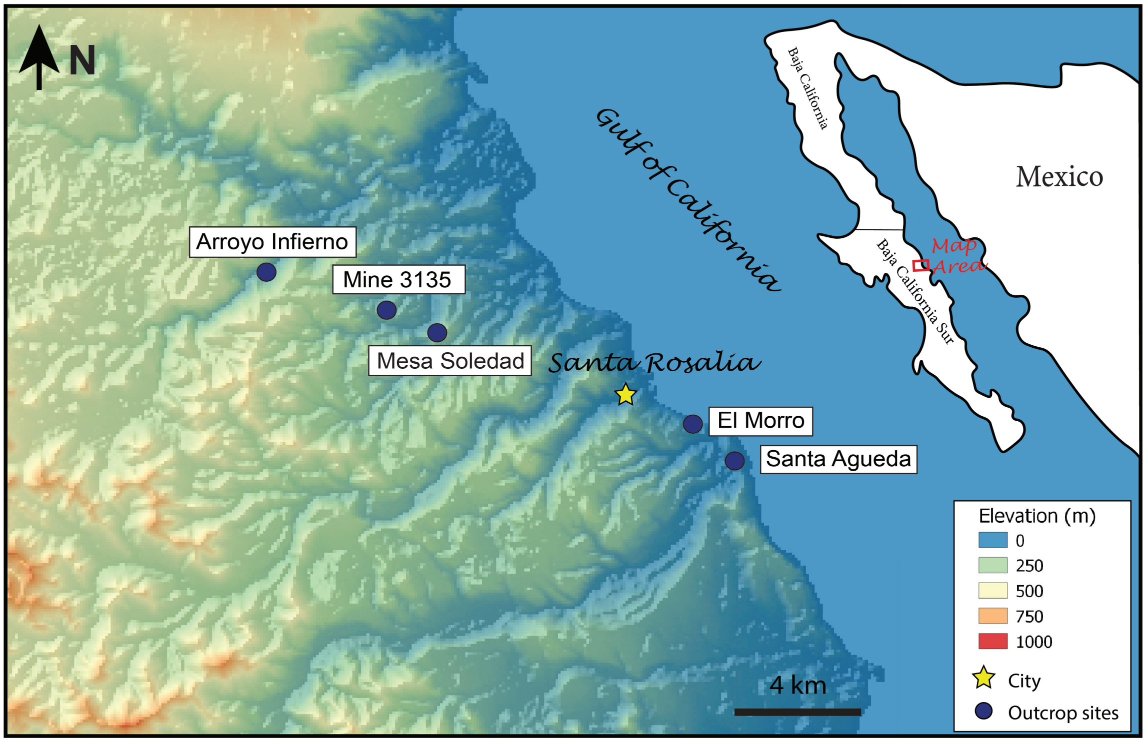

Figure 1. Elevation map of the Santa Rosalía area and outcrop sites. Blue dots refer to the outcrop sites where samples were collected. Yellow star marks the town of Santa Rosalía. Inset of the Baja California peninsula and mainland Mexico with red box showing the area of study.

Currently, there are very few stable isotope studies from the SRB and no published studies using oxygen and carbon stable isotopes as a proxy to determine paleoclimate of the late Miocene to Pleistocene SRB. The objectives of this study are to: (i) determine the depositional environments of sedimentary deposits within the SRB using field descriptions, petrography, and stable oxygen and carbon isotopes from macrofossils and bulk carbonates; (ii) better understand the paleoclimate of Baja California during late Miocene and Pliocene using stable carbon and oxygen isotopes from macrofossils and bulk carbonates; (iii) better understand the evolution and potential source of freshwater in the SRB from the late Miocene to Pleistocene. In this study, we identify late Miocene and

Pliocene fluvial, spring, and freshwater-influenced shallow-marine deposits. Oxygen and carbon isotopes suggest that the freshwater source diminished by the early Pleistocene, as the climate transitioned to the modern arid regime. We hypothesize that a potential source for freshwater into the basin is from a prolonged North American monsoon during the latest Miocene and Pliocene when sea-surface temperatures (SSTs) in the Gulf of California were several degrees warmer than today, in agreement with the permanent El Niño like state proposed by Molnar and Cane (2007). This finding is of particular importance for future climate predictions of the southwestern US and northern Mexico as it counteracts the prediction that as the global climate warms due to the anthropogenic input of greenhouse gases southwest North America will be more arid than modern times (Seager *et al*., 2007).

2. Geologic Setting

2.1 Paleoclimate

Warming during the middle Miocene peaked around 17-15 Ma, a period commonly referred to as the mid-Miocene climate optimum (Zachos *et al*., 2001). Since the mid-Miocene climate optimum, the global climate has cooled resulting in a series of transitions and climatic events during the late Miocene and Pliocene that include the expansion of Antarctic and Arctic ice-sheets, increased aridity, diversification of C_4 vegetation, and an intensified North America monsoon (LaRiviere *et al*., 2012). Although the global climate has cooled since the mid-Miocene climatic optimum, the late Miocene and Pliocene were several degrees warmer than today. Knorr *et al*. (2011) found that from 11-7 Ma, most of the late Miocene (11.6-5.3 Ma), mean global air temperatures were ~3 ºC warmer than today. Although absolute values of mean global air temperatures for the latest

Miocene (7-5.33 Ma) have been difficult to constrain, this period is generally regarded as being warmer than today (Zachos *et al*., 2001; Knorr *et al*., 2011). Sea-surface temperatures in the North Pacific during the late Miocene are estimated to have been 5-8 ºC warmer than today (LaRiviere *et al*., 2012). During the Pliocene, east equatorial Pacific SSTs were 3-5 °C warmer than today (Winnick *et al*., 2013). As a result of this warming, the western US was wetter during the late Miocene-Pliocene, similar to modern El Niño summers (Molnar and Cane, 2007). The North American monsoon, a pattern of rainfall that occurs in summer months in southwest North America, was a source of increased precipitation during the late Miocene and Pliocene. Chaplin (2008) suggests that opening of the Gulf of California during the Miocene played a dynamic role in intensifying the North American monsoon, as it created a 1100-km-long conduit over very warm water, increasing advection of water vapor. Opening of the Gulf of California during the late Miocene and warm water temperatures during the late Miocene and Pliocene intensified the North American monsoon, resulting in a wetter than modern climate in the southwestern US and Mexico (Molnar and Cane, 2007; Chaplin, 2008; Winnick *et al*., 2013).

Terrestrial plants primarily use one of two photosynthetic pathways for carbon uptake, the C_3 pathway and the C_4 pathway (Anderson and Arthur, 1983). As the climate cooled and became drier in the late Miocene, there was a transition from C_3 vegetation to C_4 vegetation. Because they require less water, C_4 vegetation has an advantage over C_3 vegetation in arid climates. Although the exact time of this transition is still debated, many studies agree that the global expansion of C_4 vegetation occurred between 8-4 Ma, beginning earlier in the tropical regions before expanding into temperature regions at higher latitudes (Chaplin, 2008; Bowman *et al*., 2017; Fox *et al*., 2018). The evolution of terrestrial vegetation is recorded in terrestrial carbonates and fossils, with carbon isotope values becoming more positive. The opposite is seen in marine records where late Miocene marine records record a global decrease in the $\delta^{13}C$ value of dissolved inorganic carbon (DIC), which is thought to be due to the decrease in global biomass (Hodell *et al*., 1994) or from erosion of organic matter and shelf carbonate during a global sea-level drop (Vincent *et al*., 1980). Hodell *et al*. (1994) suggests that from 7.8 to 6.2 Ma, the global average $\delta^{13}C$ value of marine DIC decreased by 0.5‰.

2.2 Modern Climate

The modern climate of the Baja California peninsula is relatively arid, receiving on average 15.3 cm of precipitation a year (Hastings and Turner, 1965). An 18-year (1927-1945) study on precipitation in the Santa Rosalía area found that average precipitation was 12.6 cm/yr., slightly less than the average for the peninsula as a whole (Wilson and Rocha, 1955). Due to the aridity of the Santa Rosalía area, vegetation is predominantly cacti and other desert plants that require minimal water (Wilson and Rocha, 1955). During El Niño years, rainfall in the Baja California peninsula increases. During the 1977-1978 El Niño season, an additional 5 cm of precipitation was recorded on the peninsula compared to the 1955-56, 1973-74, and 1988-89 El Niña years (Minnich *et al*., 2000). Currently, northwestern Mexico (which includes Baja California) receives about 60% of its total annual rainfall between July-September, sourced from the North American monsoon (Mitchell *et al*., 2002). North American monsoon rainfall in northwestern Mexico occurs after SSTs in the Gulf of California reach 26 ºC. In the central gulf (where the SRB is located), SSTs fluctuate between 16-31 °C (Soto-Mardones *et al*., 1997), usually peaking in August and reaching a minimum in January or February (Mitchell *et al*., 2002; Marinone, 2003).

2.3 Stratigraphy

The Santa Rosalía Basin is a fault bounded continental rift basin (Conly *et al*., 2005) located along the eastern central coast of the Baja California peninsula. The SBR is adjacent to the Gulf of California, an oblique rift basin that formed from continental rifting between the Pacific and North America plates. During this rifting, which is estimated to have started as early as 12 Ma, the Baja California peninsula was transferred from the North American plate to the Pacific plate (Holt *et al*., 2000) with growth of strike-slip faults and pull-apart basins during the late Miocene (Umhoefer, 2011). The SRB has a complex history of sedimentation and faulting important for understanding the geologic evolution of the Gulf of California, but the paleoenvironments of marine and fluvial deposits in this area are poorly understood. The exposure and study of sedimentary deposits within the Baja California peninsula provides opportunities to understand the tectonic and climatic history of the peninsula.

Mining in the Santa Rosalía area began in 1885 and has continued intermittently till present day, where it is currently home to the Minera Boleo mine. Due to the economic importance of this area and the demand for copper in the United States, Wilson and Rocha (1955) mapped the Santa Rosalía area in great detail as part of a collaborative initiative between the US and Mexico. Many subsequent studies have followed, with current published literature focusing on the volcanic rocks and the Boleo Fm., due to its economic importance and because it provides the first evidence of marine incursion into the Santa Rosalía area.

The SRB consists of four main sedimentary formations: the late Miocene Boleo Fm., the early to middle Pliocene Tirabuzón Fm., the late Pliocene Infierno Fm., and the Pleistocene Santa Rosalía Fm. A generalized stratigraphic column for the SRB is shown in Figure 2. The sedimentary sequences in the SRB record a series of subsidence and seawater incursions from the late Miocene to Pleistocene (Ochoa-Landin *et al*., 2000). Although the precise sedimentology of each formations varies, each has deposits of marine and nonmarine origin and all are separated by an unconformity, recording several episodes of marine incursion. During the late Miocene, the formation of a marine embayment (*i.e*., the Gulf of California) and subsidence of the SRB led to the first evidence of marine incursion (Boleo Fm). As subsidence and seawater incursions continued during the Pliocene, the Tirabuzón and Infierno Fms. were deposited. This pattern continued into the Pleistocene with the deposition of the Santa Rosalía Fm.

The lower-most sedimentary sequence, the late Miocene Boleo Fm., records the first evidence of marine transgression into the area (Holt *et al*., 2000). Throughout the basin, the Boleo Fm. unconformably overlies the Comondu Fm. The Comondu Fm. consists of andesitic and basaltic flows, tuff, breccia, agglomerate, and tuffaceous sandstone (Ochoa-Landin *et al*., 2000; Conly *et al*., 2005). Ages for the volcanic rocks of the Comondu Fm. generally range from 24 Ma to 12 Ma (Sawlan and Smith, 1984), although there are volcanic rocks as young as 8 Ma beneath the Boleo Fm. (Conly *et al*., 2005).

The Boleo Fm. is the oldest and thickest sedimentary sequence in the basin, consisting of a basal limestone overlain by five coarsening-upward progradational fan-delta cycles (Conly *et al*., 2005), that formed as alluvial systems responded to basin subsidence (Ochoa-Landin *et al*., 2000). The Boleo Fm. reaches a maximum thickness of 350 m (Ochoa-Landin *et al*., 2000) but generally ranges from 50 to 250 m (Wilson and Rocha, 1955) with the basal limestone only accounting for 1 to 6 m (Miranda-Alviles *et al*., 2005). The facies within the Boleo Fm. are complex and interpretation of depositional environment can vary depending on location or section of study but with a general consensus that the Boleo Fm. contains both marine and nonmarine deposits that include, but are not limited to, gypsum, marine and nonmarine limestones, siltstones, tuffaceous sandstones, fossiliferous sandstones, and marine and non-marine conglomerates (Wilson and Rocha, 1955; Holt *et al*., 2000; Ochoa-Landin *et al*., 2000; Conly *et al*., 2005; Miranda-Alviles *et al*., 2005).

Whole-rock ^{40}K-^{40}Ar dating of an ignimbrite, which uncomformably underlies the basal limestone of the Boleo Fm. at the El Morro site (Fig. 1), had minimum ages of 8.0 and 7.9 Ma (Conly *et al*., 2005). Overlying the basal limestone is a series of siliciclastic fan-delta cycles. The fan-delta cycles of the Boleo Fm. are estimated to have been deposited between 7.1-6.2 Ma based on plagioclase ^{40}Ar/^{39}Ar dating of a tephra unit within the sequence and paleomagnetism data (Holt *et al*., 2000). Based on these ages, the basal limestone of the Boleo Fm. is estimated to have been deposited between 8.0 and 7.1 Ma. Within the clastic units of the Boleo Fm. are a series of stratiform ore beds, referred to as mantos, containing large reservoirs of Cu, Co, Zn and Mn oxides (Conly *et al*., 2011).

Mantos are numbered top-down, with manto 4 located near the base of the Boleo formation (Fig. 2).

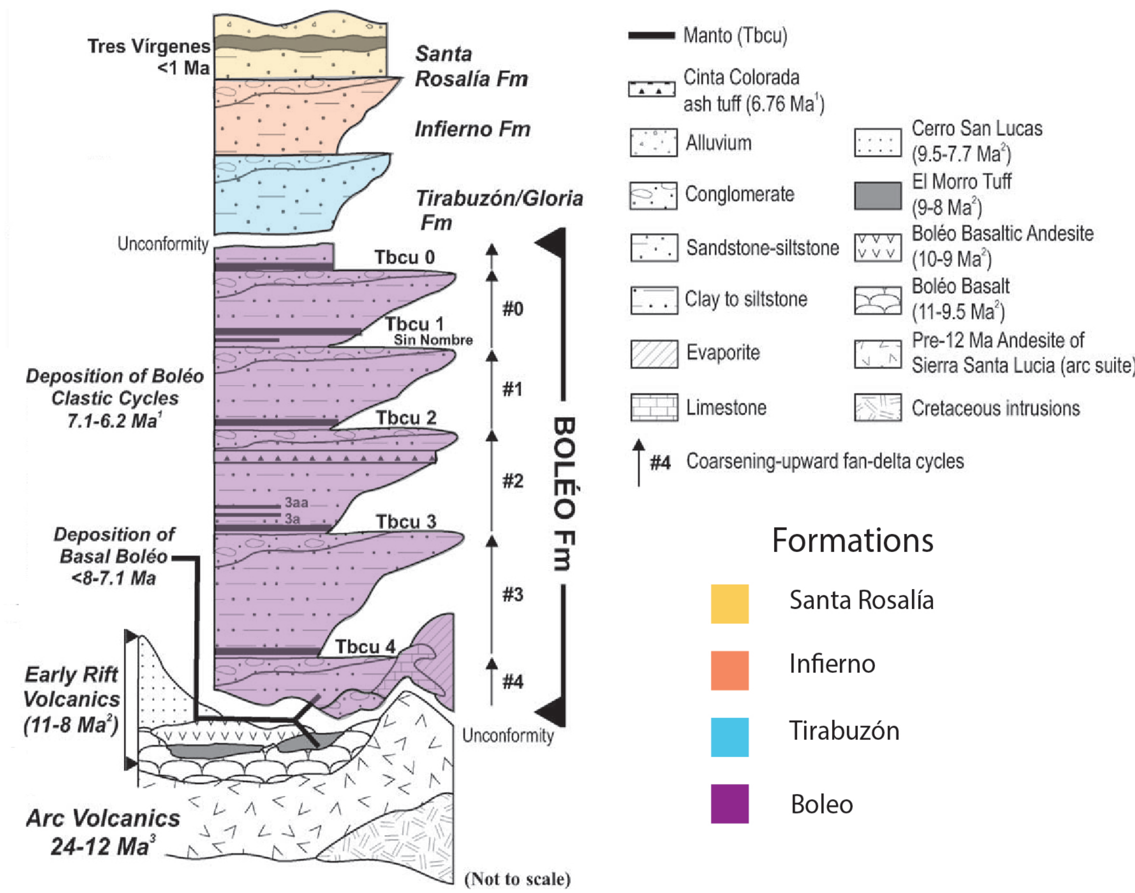

Figure 2. Idealized regional stratigraphy of the Santa Rosalía Basin. Colors indicate the different sedimentary formations. Purple indicates the Boleo Fm., which contains varying sedimentary deposits, although not all are seen throughout the basin, and volcanic tuff which has been dated. Arrows indicate the fan-delta cycles recorded in the Boleo Fm. Within the Boleo Fm. are a series of mantos (Tbcu #) which are numbered top down. Blue indicates the Tirabuzón Fm. Orange represents the Infierno sedimentary deposits and yellow for the Santa Rosalía Fm. Top line for the Santa Rosalía Fm. is uneven, representing the erosion of the Santa Rosalía Fm. Ages from Sawlan and Smith (1984), Holt et al. (2000) and Conly *et al*. (2005). For more information on the volcanics underlying the Boleo Fm. reader is referred to Conly *et al*. (2005) and Sawlan and Smith (1984). Figure is not to scale. Modified from Conly *et al*. (2005).

The Tirabuzón Fm., previously referred to as the Gloria Fm. (Wilson and Rocha, 1955), uncomformably overlies the Boleo Fm. The Tirabuzón Fm. predominately consists of marine sandstones and carbonates atop a basal conglomerate and an overlying conglomerate, which grades into nonmarine facies inland (Wilson and Rocha, 1955; Conly *et al*., 2005). Based on biostratigraphy, deposition of the Tirabuzón Fm. is thought to have occurred during the early to middle Pliocene (Wilson and Rocha, 1955; Ortlieb and Colletta, 1984). The Tirabuzón Fm. reaches a maximum thickness of 185 m, average closer to 60 m, and is widely exposed throughout the basin (Wilson and Rocha, 1955). Based on foraminifera assemblages and ichnology, paleo-water depth estimates for the marine units of the Tirabuzón Fm. range from 55-90 m (Wilson, 1985) to 200-500 m (Carreno, 1982; Shroat-Lewis, 2007) although it is has been suggested that most of the Tirabuzón Fm. was deposited in less than 200 m of water (Shroat-Lewis, 2007). The overlying nonmarine conglomerate was deposited as sea level fell and there was a seaward migration of the shoreline (Wilson and Rocha, 1955).

The Infierno Fm., which unconformably overlies the Tirabuzón Fm., consists of fossiliferous marine sandstones with an overlying conglomerate unit, which depending on the location is of marine or nonmarine origin. Towards the gulf, the conglomerate is of marine origin and further inland the marine sandstone wedges out into nonmarine conglomerate. Thickness of the Infierno Fm. ranges from 5-90 m with an average of about 55 m (Wilson and Rocha, 1955). Fossils within the marine sandstones establish an age of late Pliocene (Wilson and Rocha, 1955) but deposition of the Infierno Fm. could have also occurred during the early Pleistocene (Ortlieb and Colletta, 1984). The Infierno Fm. was probably deposited over much of the region but has since been eroded (Wilson and Rocha, 1955). Similar to the nonmarine conglomerate of the Tirabuzón Fm., the overlying conglomerate of the Infierno Fm. suggests a seaward migration of the shoreline at the time of deposition (Wilson and Rocha, 1955).

Overlying the Infierno Fm, separated by an unconformity, is the Pleistocene Santa Rosalía Fm. Ortlieb and Colletta (1984) regard the Santa Rosalía Fm. as being approximately 1 Ma in age. The Santa Rosalía Fm. consists of thin, marine, and fossiliferous sandstones and conglomerates (Wilson and Rocha, 1955) that grades into loosely consolidated nonmarine clastic sediments (Carreno and Smith, 2007). The Santa Rosalía Fm. is not widely exposed in the SRB due to recent erosion (Wilson and Rocha, 1955) or is covered by Quaternary colluvium (Ortlieb and Colletta, 1984) and is the thinnest of all the sedimentary formations, having a thickness of 5-15 m (Wilson and Rocha, 1955). Less detail is known about the origin of the marine and nonmarine deposits of the Santa Rosalía Fm., likely due to how thin it is, and lack of exposure compared to the other formations.

The field sites in this study are all within the SRB. Two of the five sites of study, Mesa Soledad and Mine 3135, were located within the Minera Boleo mine with a third, Arroyo Infierno, located outside the mine but was still actively being mined for limestone. The remaining two were located along the gulf coast. The location of all field sites is shown in Figure 1.

3. Biomineralization and Stable Isotopes of Marine Invertebrates

Organisms take naturally occurring elements from the environment and turn them into the complex minerals that make up their shells or exoskeletons, a process called biomineralization (Swift, 2010). The process of biomineralization is often complicated (Gillikin, 2005), but a basic understanding for the organisms used in this study are presented that guided sampling and interpretation of mineralogy and stable isotopic data.

3.1 Bivalves

Aquatic bivalves, a class belonging to the phylum Mollusca, are found in a variety of fresh, brackish, and marine environments, shallow to deep seas, and between the poles to the equator (Immenhauser *et al*., 2016). Aquatic bivalves are composed of a mantle and shell, subdivided into an inner and outer shell. Biomineralization takes place as ions from surrounding water enter the extrapallial fluid (EPF), a liquid between the shell and mantle, via the gills or gut of the bivalve. Calcification occurs as shell layers precipitate from the EPF (Gillikin, 2005). Shell layers of a bivalve can differ with respect to their $CaCO_3$ polymorphs. Shell layers can consist of calcite, aragonite, and less commonly, vaterite (Immenhauser *et al*., 2016). Oysters and pectens, the bivalves used in this study, are usually composed of calcite for the both the inner and outer shell (Immenhauser *et al*., 2016) or aragonite for the inner shell and calcite for the outer shell (Gillikin, 2005). Knowing the suspected polymorph of $CaCO_3$ in the shell is important when collecting stable isotope data, as aragonite and calcite fractionate oxygen isotopes differently (Anderson and Arthur, 1983) and differ in respect to diagenetic potential (Sharp, 2017). For this study, the calcite outer shell of bivalves was processed for stable isotopes.

3.2 Barnacles

Barnacles are sessile crustaceans belonging to the phylum Arthropoda and are found attached to hard substrates in marine environments. Barnacles biomineralize their exoskeleton by precipitating calcite with mantle epithelial cells which are in close contact with the inner shell surface (Burgess *et al*., 2010). The mantle epithelial cells supply HCO_3^- and Ca^{2+} ions necessary for the precipitation of calcite (Rodriguez-Navarro *et al*., 2006). As barnacles grow, they molt their exoskeleton but unlike other crustaceans they do not shed their entire shell and instead build a series of thick plates that surround the animal (Rodriguez-Navarro *et al*., 2006). Unlike bivalves, which may be composed of many $CaCO_3$ polymorphs, barnacles generally secrete low-Mg calcite (Ullman *et al*., 2018). For this study, the low-Mg calcite exoskeleton was used for stable isotope analysis.

4. Methods

4.1 Field Work

The Boleo Fm. was identified at three sites: El Morro, Arroyo Infierno and Mine 3135. At Santa Agueda, the Tirabuzón Fm. was identified and at Mesa Soledad the Tirabuzón, Infierno and Santa Rosalía Fms. were identified. Location of outcrops were recorded using GPS and sections were measured from four sites: Mesa Soledad, Santa Agueda, El Morro, and Arroyo Infierno (Fig 2). At Mesa Soledad two sections were measured, the remainder have only one measured section. No section was measured at Mine 3135 but detailed notes, along with photos aided in making a representative stratigraphic column post-field work. Field descriptions focused on logging lithology, ichnology, fossils, and sedimentary structures. Macrofossil and bulk carbonate samples were collected in situ from outcrops for petrographic, mineralogical, and stable isotope analysis.

4.2 Petrography

Thin sections of bulk carbonate samples were prepared from the El Morro site as original fossil material preserved at this site was sparse. Thin sections were prepared by National Petrographic Service Inc. Petrographic analysis was completed using a Nikon Eclipse LV100POL petrographic microscope to screen for diagenesis and to determine which samples had the highest calcite content. After screening, samples were processed for stable isotopes and X-ray diffraction (XRD). Scholle and Ulmer-Scholle (2003) was used to identify the types of microfossils present in thin sections.

4.3 Fossil Identification

Wilson and Rocha (1955) published common invertebrate fossils observed in the formations of the SRB. Using Wilson and Rocha (1955) as a guide, mollusk samples were compared to Moore (1984) and Moore (1987) for identification. Identification of mollusk samples was based on physical descriptions, geographic distribution, and comparisons of photographs in published literature. Barnacle samples were compared to descriptions published by Pérez-Losada (2014) and Newman and Ross (1976) for identification.

4.4 X-ray Diffraction

Samples were powdered to be processed for XRD. Macrofossils were powdered using a Dremel drill with a diamond point drill bit attached. Bulk samples were powdered using a mortar and pestle. Powdered samples were placed onto a glass slide containing a

25.4 x 25.4 x 1 mm cavity then placed into the Rigaku Smartlab X-Ray Diffractometer equipped with SmartLab Guidance software at the University of Houston. Once analyzed, the identified peaks were compared with the Minerology Database (http://www.webmineral.com) to determine mineralogy.

4.5 Stable Isotopes

Macrofossils were micro-drilled for powder using a drill attached to a binocscope and bulk samples were powdered using a mortar and pestle. Contamination procedures included removing any sedimentary material attached to the sample, removing a thin layer of carbonate material from shells, spraying with methanol and using compressed air to dry the samples before processing for powder. Powder sample amounts ranged from 60-100 µg. Powdered samples were placed into individual vials before being vacuum roasted at 200 °C to remove volatiles. After roasting and cooling, samples were placed into glass vials and into a carousel. The carousel with samples were loaded into a Thermo Scientific Kiel IV Carbonate Device interfaced to the inlet of a Thermo Finnigan MAT 253 dual inlet mass spectrometer. Briefly, atmospheric gases were removed, samples reacted with three drops of 100% H_3PO_4 at 70 °C, resulting CO_2 was cryogenically separated and transferred to MAT 253 for analysis. $\delta^{13}C$ and $\delta^{18}O$ isotope data are reported relative to Vienna PeeDee Belemnite (VPDB) and expressed as standard per mille (‰). Precision was monitored through daily analysis and is reported as better than 0.10‰ for $\delta^{13}C$ and $\delta^{18}O$. Stable isotope analysis was completed at the University of Kansas.

5. Results

5.1 Field Descriptions

The Mesa Soledad site included 66 m of measured section from two adjacent sites, referred to the north and south site (Fig. 3). The south site included 31 m of measured section from the Tirabuzón and Santa Rosalía Fms. The Tirabuzón Fm. at the south site consisted of a sandstone containing pectens, oysters, other unidentified bivalve fragments and molds, Echinoidea body fossils and thin pebble beds. Above the sandstone sits a conglomerate, which was not sampled for this project. Oyster and pecten samples (17-10-01) were collected from the sandstone for stable isotope analysis. Above the Tirabuzón Fm., separated by a disconformity, sits the Santa Rosalía Fm. which contains a lower pebble-rich calcareous sandstone containing bivalves and gastropod molds and an upper calcareous sandstone.

The Mesa Soledad north site included 35 m of measured section from the Tirabuzón, Infierno, and Santa Rosalía Fms. The Tirabuzón Fm. consisted of a thick conglomerate, an overlying fine- to medium-grained sandstone topped by a conglomerate cut into by a calcareous sandstone of the Infierno Fm. Above the Infierno Fm. calcareous sandstone sits a predominately medium-grained sandstone containing pectens, gastropods, and shell fragments with inner beds of pebbly conglomerate. The upper-most deposit of the Infierno Fm. is a massive conglomerate. A pecten and barnacle sample (17-10-07) was collected from the Infierno Fm. medium-grained sandstone. The Santa Rosalía Fm. which sits disconformably above the Infierno Fm. consisted of, in ascending stratigraphic order, a lower calcareous sandstone, a breccia, and a coarse-grained sandstone. Samples collected from the Santa Rosalía Fm. included a pecten, oyster and barnacle (17-11-10) from the coarse-grained sandstone and a pecten (17-11-15) from the calcareous sandstone.

The Santa Agueda site included 34 m of measured section from the Tirabuzón Fm., divided into 16 units (Fig. 3). The lowest unit was a calcareous conglomerate with no fossils present. The next 14 units were calcareous sandstones containing bivalves with changes in grain size marking new units. A pecten (BA17-2) and oyster (BA16-1) sample was collected from a lower calcareous sandstone (unit 3). Above the calcareous sandstone units sits a calcareous conglomerate containing bivalves and barnacles. A pecten, oyster and barnacle (16-18-14) was collected from the upper calcareous conglomerate.

No section was measured at Mine 3135 but detailed notes along with field photos were taken to document the sedimentology and stratigraphic height of sample collection. A stratigraphic column, made post-field work from notes and photos, documents the three units at Mine 3135 and is shown in Figure 3. All units are from Boleo Fm. above manto 4 (refer to Fig. 2 for generalized stratigraphy of SRB). The lowest unit was a fossiliferous sandstone containing many broken and whole mollusks. Stratigraphically above the fossiliferous sandstone was a conglomerate topped by another fossiliferous sandstone containing many broken and whole mollusks, similar to the lower fossiliferous sandstone. Two mollusk samples, a pecten and oyster fragments (BA17-1B), were collected from the lower fossiliferous sandstone.

The El Morro site included 15 m of measured section divided into 7 units all within the Boleo Fm (Fig. 3). The lower two units consisted of conglomerate followed by five units of limestone and siliciclastic deposits. The unit above the conglomerate base consisted of limestone with thin interbeds of fossil hash. Above this limestone was a sandy limestone filled with broken fossil fragments. Six bulk carbonate samples were collected from the limestone units: three from the lower limestone (BA12-1, BA12-3B & BA14-1) and three from the sandy limestone directly above (BA12-4, BA12-5, & BA14-2). Atop the sandy limestone was a sandstone containing a few interbeds of fossil hash and bivalve molds, followed by two sandstones no longer containing fossil fragments or molds with a change in grain size separating the two. No samples were collected for further analysis from the siliciclastic units.

At Arroyo Infierno 7 m of section was measured all within the Boleo Fm (Fig. 3). and subdivided into 6 units. The units, listed in stratigraphic order, consisted of a breccia, a pebbly sandstone, a pebbly siltstone containing pumice fragments, a packed grainstone, a coarse-grained packstone with many bivalve fragments and molds, and laminated calcite and siltstone rhythmites. A barnacle sample (BA18-4) was collected from the pebbly sandstone and bivalve shells (BA18-2) were collected from the coarse-grained packstone. Complete, intact fossils at this site were sparse, the two samples collected were the only intact specimens seen in the field.

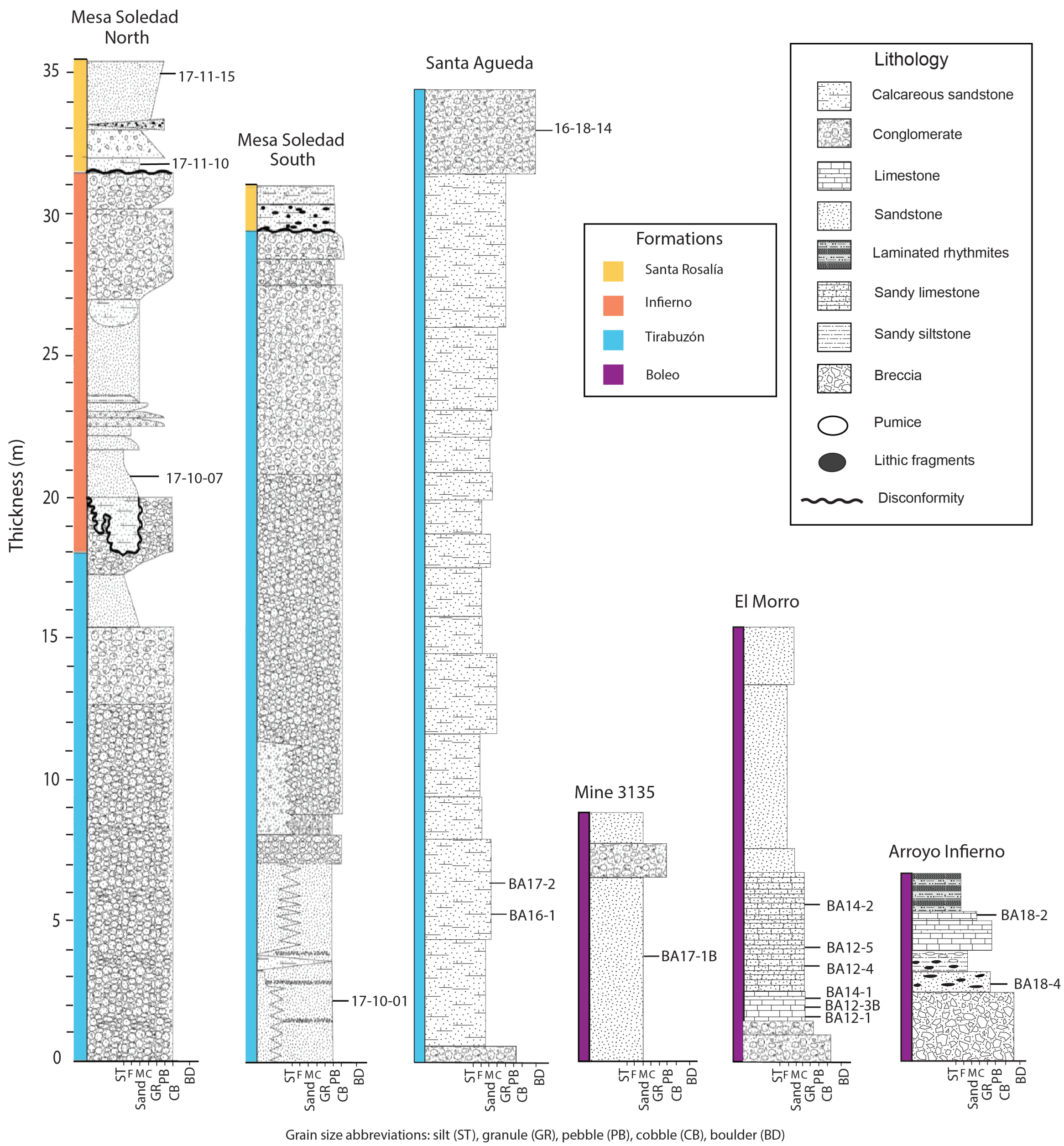

Figure 3. Stratigraphic columns from all sites. Labels indicate sample names and location of collection. Colors to the left of the columns denote the formation.

5.2 Petrography

Thin sections revealed both micritic and sparry calcite textures. Although species of foraminifera were not identified, trochoid and milioloid test morphologies of foraminifera are visible in thin section (Fig. 4B, C and E). Complete ostracods and disarticulated ostracods valves were seen in one sample (Fig. 4C), as well as coated grains in another (Fig. 4B).

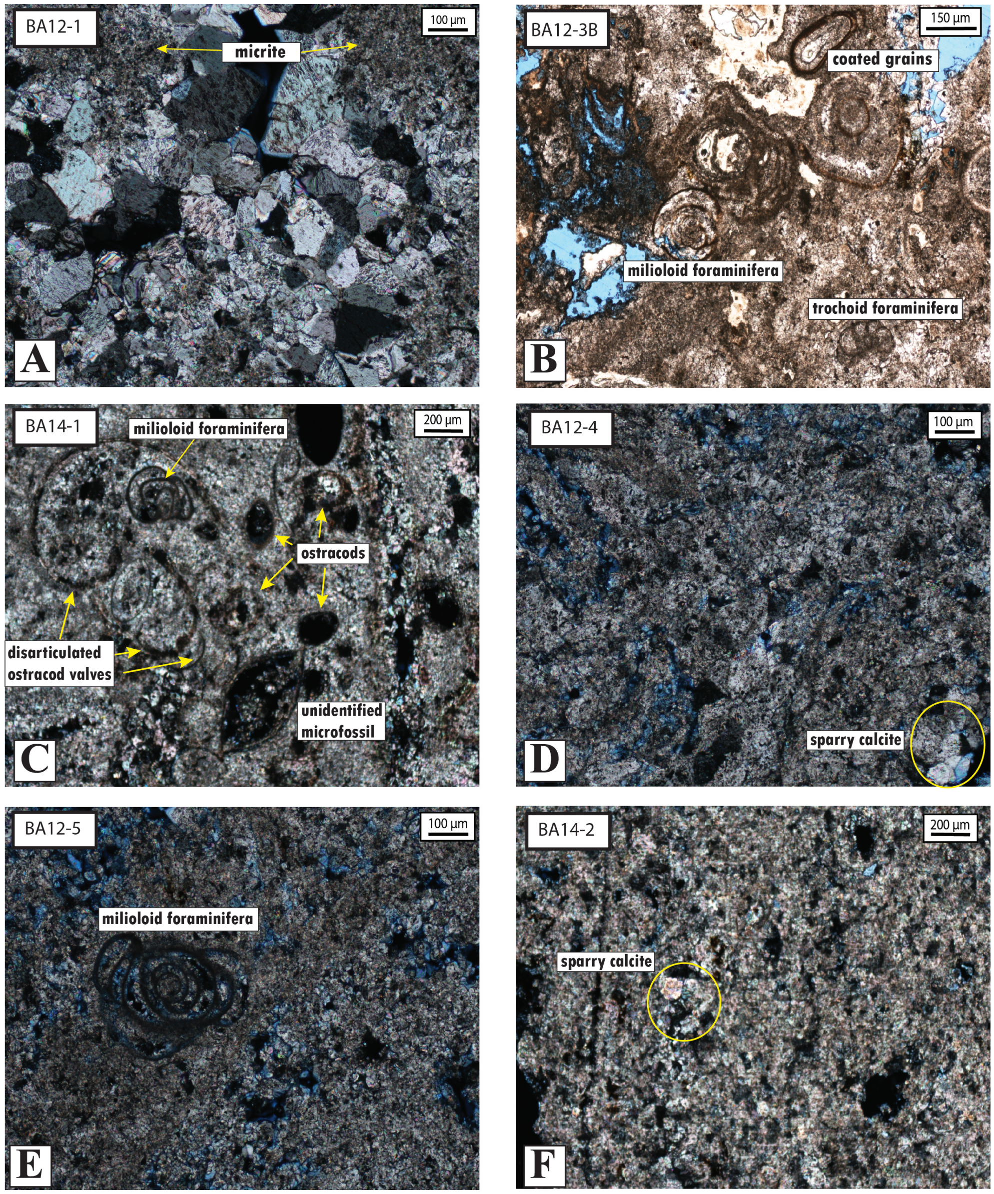

Figure 4. Thin section images from El Morro bulk samples. A) subequal spar and micrite (XPL) B) biomicrite with coated grains (PPL) C) ostracod-rich biomicrite with ~20% sparry calcite grains (XPL) D) Predominately micrite with <10% sparry calcite grains (XPL) E) biomicrite F) predominately micrite with <10% sparry calcite grains.

5.3 Fossil Identification

Due to poor preservation, only the most complete samples were determined down to the species level and most were identified to a suborder or family. For simplicity in referring to fossil specimens, fossils are subdivided into three categories based on common names: oysters (n=5), pectens (n=7) and barnacles (n=4). All barnacle samples were sessile barnacles and three were identified as belonging to the suborder Balanomorpha (Fig. 5A and B). Only one oyster sample was identified down to the species level and the remainder to a common name of oyster. Many oyster samples were missing key body parts needed for identification or were just fragments of oyster shells. The single oyster identified is shown in Figure 5D and was identified as *Ostreola megodon*. Pecten samples were all identified as belonging to the Family *Pectinidea* with three identified to the species level (Fig. 5C, E and F).

Figure 5. Representative macrofossil samples collected from outcrop. A) Balanomorpha encrusted on *Pectinidea* from the Tirabuzón Fm. at Santa Agueda. B) Balanomorpha encrusted on *Pectinidea* from the Infierno Fm. at Mesa Soledad. C) *Argopecten invalidus* collected at Mine 3135 D) *Ostreola megodon* collected from the Tirabuzón Fm. at Mesa Soledad E) *Argopecten abietis abietis* collected from the Santa Rosalía Fm. at Mesa Soledad F) *Leopecten bakeri* collected from the Tirabuzón Fm. at Santa Agueda.

5.4 X-ray Diffraction

Of the 17 fossil samples collected, 15 were processed for mineral identification using XRD. The two samples not analyzed were too small to obtain enough material for XRD without risking contamination. XRD analyses of powdered fossil samples indicated all fossils are low-Mg calcite (Fig. 6A, B and D). Powdered bulk samples are strictly low-Mg calcite, except for two samples. One of the two bulk samples, BA12-3B, included minor amounts of quartz (Fig. 6C) and the other, BA14-1, had a mix of dolomite and low-Mg calcite (Fig. 6C).

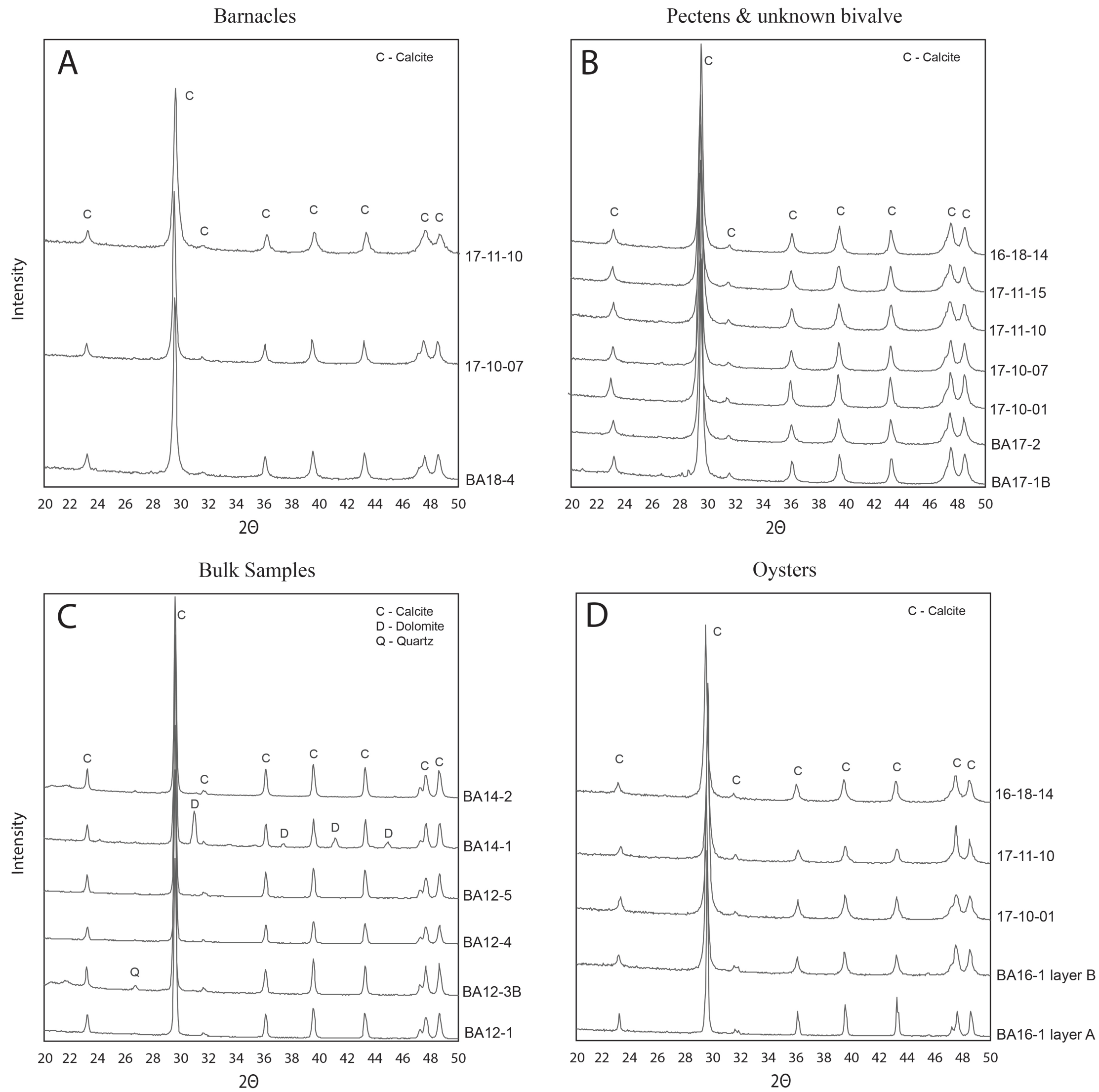

Figure 6. XRD data from samples organized by sample type. A) XRD patterns from calcite barnacle shells. B) XRD patterns from pectens and an unidentified bivalve, all displaying calcite patterns. C) XRD patterns from bulk carbonate samples collected at El Morro, with all samples showing calcite patterns. Sample BA12-3B pattern showing the presence of quartz and sample BA14-1 showing dolomite. D) XRD patterns from calcite oyster shells. Sample BA16-1 was sampled from two locations on the specimen, the location of layer A & B is shown in Figure 7.

5.5 Stable Isotopes

Macrofossil $\delta^{18}O$ and $\delta^{13}C$ analysis consisted of barnacles (n=4), oysters (n=5), pectens (n=7), and an unknown bivalve (n=1). $\delta^{18}O$ and $\delta^{13}C$ data for all samples are available in Appendix 1. A single oyster sample was processed across multiple layers (Fig. 7) with average $\delta^{18}O$ and $\delta^{13}C$ values of -4.9‰ and -0.8‰, respectively. Henceforth, this sample will only be interpreted based on the averaged $\delta^{18}O$ and $\delta^{13}C$ values. All other macrofossil samples were only analyzed from one location on the specimen. Comparisons were made to observe the relationship between the $\delta^{18}O$ and $\delta^{13}C$ values of fossils identified to the species level versus those identified to a common name, family, or suborder. No clear trends were observed between the $\delta^{18}O$ and $\delta^{13}C$ values based on fossil identification.

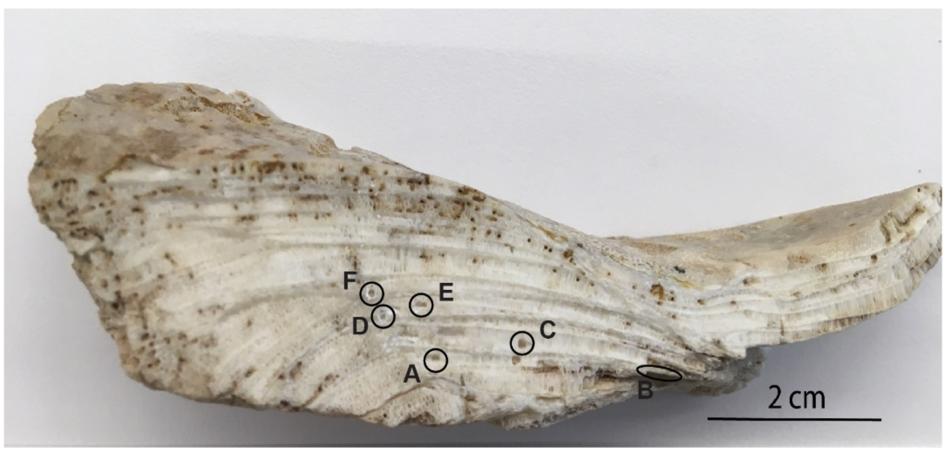

Figure 7. Oyster sample (BA16-1) collected from the Tirabuzón Fm. at Santa Agueda. Labels mark the different areas of the sample that was micro-drilled for stable isotope and XRD analysis.

Table 1. Average $\delta^{18}O$ and $\delta^{13}C$ data by formation

Site	Formation	$\delta^{18}O$ (‰VPDB) average	$\delta^{13}C$ (‰ VPDB) average	*n*
Mesa Soledad	Santa Rosalía	-1.4	-0.7	4
	Infierno	-6.2	-6.9	2
	Tirabuzón	-7.6	-7.8	2
Santa Agueda	Tirabuzón upper	-4.1	-1.7	3
	Tirabuzón lower	-2.2	0.0	2
Arroyo Infierno	Basal Boleo	-9.9	-7.5	2
Mine 3135	Boleo (above manto 4)	-4.4	-1.4	2
El Morro	Basal Boleo	-9.1	-2.7	6

Averages for $\delta^{18}O$ and $\delta^{13}C$ stable isotope data by site and formation are shown in Table 1. Due to spatial variability, as many sites are several km apart, overall trends for all samples from the same formation are difficult to interpret. Instead interpretation is focused based on site of study and the formation(s) at a given site. Cross-plots of $\delta^{18}O$ and $\delta^{13}C$ data are shown by site of sample collection in Figure 8. Nearly all samples have negative ^{18}O and ^{13}C values (Figs. 8A-E) and averages of $\delta^{18}O$ and $\delta^{13}C$ for all formations are negative (Table 1). When $\delta^{18}O$ and $\delta^{13}C$ values are averaged by formation, the values are not similar at other sites. This is best shown by comparing Boleo Fm. samples collected at different sites (Figs. 8A, C and E). $\delta^{18}O$ values from El Morro and Arroyo Infierno are ~5‰ lower than Mine 3135 and average $\delta^{13}C$ values from Arroyo Infierno are 6.1‰ to 4.8‰ lower than Boleo Fm. samples at El Morro and Mine 3135. $\delta^{18}O$ and $\delta^{13}C$ values at Mesa Soledad are 0.5‰ to 9.3‰ higher up section (Fig 8B), with averages from the Tirabuzón Fm. (lowest unit) and Santa Rosalía Fm. (highest unit) having differences of 6.2‰ and 7.1‰ for $\delta^{18}O$ and $\delta^{13}C$ values.

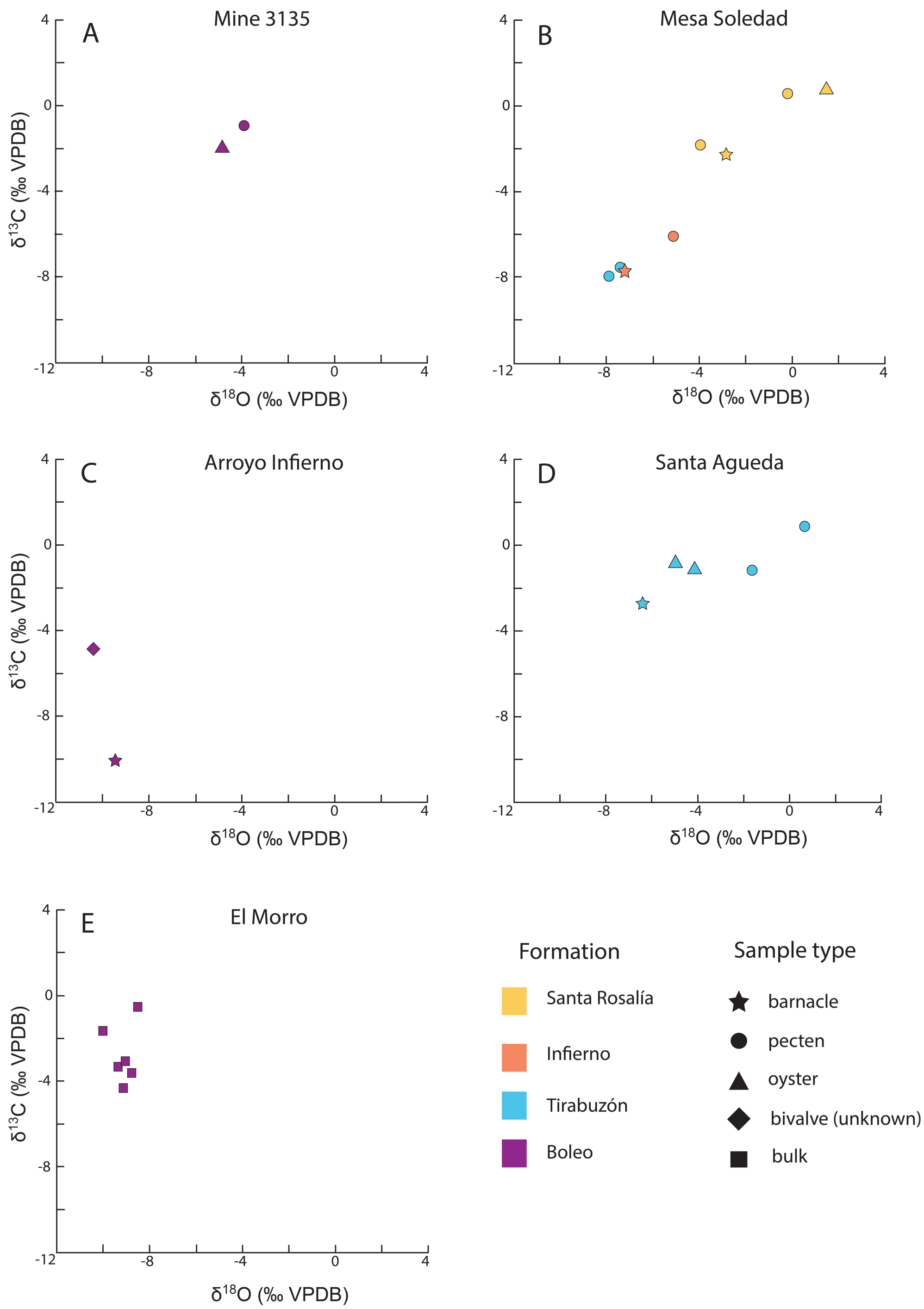

Figure 8. Cross-plots of $\delta^{18}O$ and $\delta^{13}C$ data for all samples displayed by site of sample collection. A) $\delta^{18}O$ and $\delta^{13}C$ data from mollusk samples collected at Mine 3135. B) $\delta^{18}O$ and $\delta^{13}C$ data from pecten, oyster and barnacle samples collected at Mesa Soledad. C) $\delta^{18}O$ and $\delta^{13}C$ data from a bivalve and barnacle sample collected at Arroyo Infierno. D) $\delta^{18}O$ and $\delta^{13}C$ data from pecten, oyster and barnacle samples collected at Santa Agueda. E) El Morro bulk carbonate $\delta^{18}O$ and $\delta^{13}C$ data.

Boleo Fm. samples at El Morro have a consistent range of $\delta^{18}O$ values between -10.0‰ to -8.5‰ and a larger range of $\delta^{13}C$ values from -4.3‰ to -0.5‰ (Fig. 8E). Boleo Fm. samples at Arroyo Infierno have lower values in both $\delta^{18}O$ and $\delta^{13}C$ with averages of -9.9‰ and -7.5‰, respectively. Boleo Fm. samples collected from Mine 3135, stratigraphically above Boleo Fm. samples collected at El Morro and Arroyo Infierno, also have negative $\delta^{18}O$ and $\delta^{13}C$ values with averages of -4.4‰ and -1.4‰, respectively. Although all Boleo Fm. samples have negative $\delta^{18}O$ values, $\delta^{18}O$ values from samples collected at Mine 3135 are not nearly as low as El Morro and Arroyo Infierno samples.

The Tirabuzón Fm. at Santa Agueda is subdivided into a lower and upper section for isotopic interpretation. This division is not documented in previous literature but is done because of the drastic lithologic changes and stratigraphic height from where samples were collected. Lower section samples were collected from a calcareous sandstone between 5-6.5 m, whereas upper section samples were collected from a calcareous conglomerate at 33 m (Fig. 3). Lower section $\delta^{18}O$ and $\delta^{13}C$ values have averages of -2.2‰ and 0.0‰ and upper section values average -4.1‰ and -1.7‰, respectively.

Mesa Soledad is the only site to have $\delta^{18}O$ and $\delta^{13}C$ signatures from multiple formations: the Tirabuzón, Inferno and Santa Rosalía. The lower two formations, the Tirabuzón and Infierno, have isotopically lower signals compared to the upper most formation, the Santa Rosalía. The Tirabuzón Fm. has average $\delta^{18}O$ and $\delta^{13}C$ values of -7.6‰ and -7.8‰, respectively. The Inferno Fm. has average $\delta^{18}O$ and $\delta^{13}C$ values of -6.2‰ and -6.9‰, respectively. The Santa Rosalía Fm. has average $\delta^{18}O$ and $\delta^{13}C$ values of -1.4‰ and -0.7‰, respectively.

6. Discussion

6.1 Effects of Vital Effects and Diageneses on Stable Isotopes

Fossil sample isotopic signatures are interpreted without the influence of diagenesis greatly altering the original $\delta^{18}O$ and $\delta^{13}C$ values. All fossil samples displayed low-Mg calcite (Fig 6, A, B, & D) which was the expected mineral for the location of micro-drilling on fossil samples. Low-Mg calcite has a lower diagenetic potential compared to aragonite and high-Mg calcite, and therefore, organisms that secrete low-Mg tend to reflect original $\delta^{18}O$ and $\delta^{13}C$ values (Sharp, 2017). Organisms may secrete their carbonate shells out of oxygen or carbon isotope equilibrium with surrounding waters, a process called the vital effect. Vital effects and resulting disequilibrium values for biogenic carbonate can be due to metabolic processes of the organism (Sharp, 2017). Metabolic processes can affect the $^{13}C/^{12}C$ ratio in biogenic carbonates as the process of calcification can involve carbon from both sounding water DIC and metabolic DIC. Metabolic DIC is composed of respiratory CO_2 which is depleted in respect to ^{13}C and can become a component of the internal carbon pool of body fluids used for calcification for some organisms (Gillikin, 2005).

Three out the 4 barnacle samples collected in this study were attached to mollusks. Of those 3, all showed $\delta^{18}O$ values 2.1‰ to 4.8‰ lower and $\delta^{13}C$ values 1.6‰ to 3.0‰ lower compared to the mollusks they were encrusted onto (Fig. 9). Killingley and Newman (1982) found that sessile barnacles tend to be enriched in $\delta^{18}O$ by ~1.3‰ compared to mollusks. Some studies counteract the work done by Killingley and Newman (1982) and found that barnacles form in close isotopic equilibrium with ambient water (Brand *et al*., 1987; Schone *et al*., 2006; Burgess *et al*., 2010) whereas others do not account for this apparent enrichment for interpretation (Crossey *et al*., 2015; Bright *et al*., 2018). Applying the 1.3‰ $\delta^{18}O$ enrichment to the barnacles in this study caused a greater offset compared with the $\delta^{18}O$ values from the mollusks they were encrusted onto. Because of this greater offset and the disagreement from previous studies on $\delta^{18}O$ enrichment, all barnacle data is interpreted without the 1.3‰ correction.

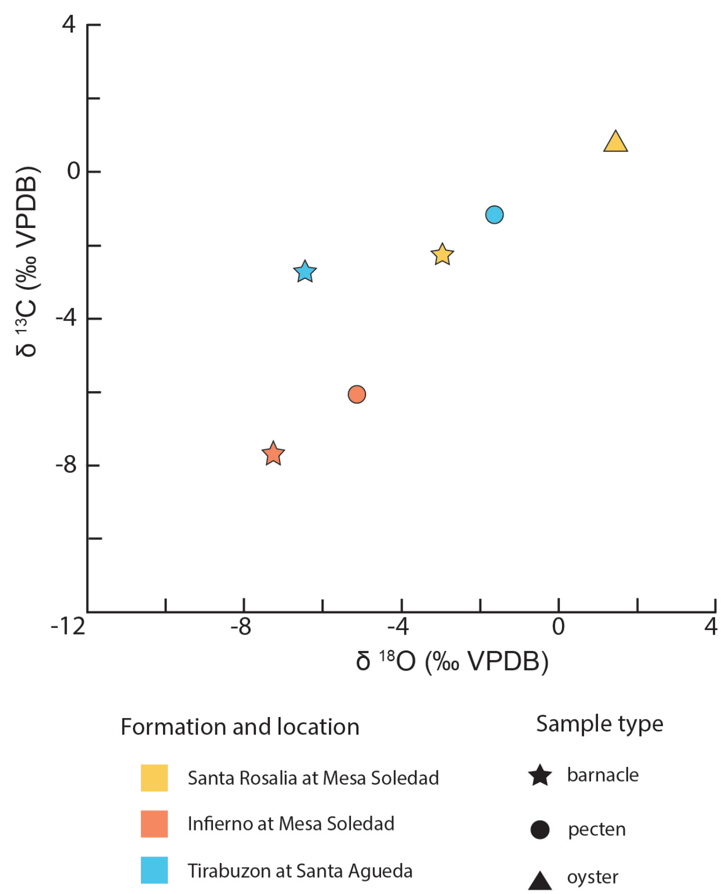

Figure 9. $\delta^{18}O$ and $\delta^{13}C$ data for barnacles and the mollusks they were encrusted onto from the Mesa Soledad and Santa Agueda sites. All barnacle samples show lower $\delta^{18}O$ and $\delta^{13}C$ values compared to the mollusks they were encrusted onto.

Aquatic invertebrates usually record the $\delta^{13}C$ value of DIC and therefore are representative of the environment (Keith *et al*., 1964; Fritz and Poplawski, 1974; McConnaughey *et al*., 1997). For aquatic mollusks, it is generally accepted that they record oxygen isotope values in equilibrium with ambient water. Studies have shown that the $\delta^{13}C$ value in aquatic mollusks is mostly reflective of ambient DIC (Fritz and Poplawski, 1974; McConnaughey and Gillikin, 2008) and when they are not, the deviations are on the order of -2‰ or less (McConnaughey *et al*., 1997; Owen *et al*., 2002). Keith *et al*. (1964) found that environment was more important than species-specific vital effects in mollusks. Fritz and Poplawski (1974) found that vital effects and food have a minimal influence on the $\delta^{13}C$ value in skeletal mollusks.

Current literature on oxygen and carbon isotopes from barnacles are not nearly as robust as mollusks, with many studies concentrating on oxygen isotopes over carbon isotopes (Burgess *et al*., 2010; Detjen *et al*., 2015; Pearson *et al*., 2019). Studies on carbon isotope values in acorn barnacles found that they record values in close equilibrium with ambient DIC (Ullmann *et al*., 2018; Brand *et al*., 1987). Although studies have suggested that metabolic effects (McConnaughey, 2003; Tanaka *et al*., 1986), food source (Tanaka *et al*., 1986; Architiv *et al*., 1997), or elevation within a living range (Craven *et al*., 2008) can affect carbon isotope values in barnacles. The amount that these factors affect $\delta^{13}C$ values in barnacle skeletal carbonate is not well constrained. McConnaughey (2003) argues that metabolic processes contribute very little (>2‰) to the $\delta^{13}C$ value in skeletal carbon. McConnaughey and Gillikin (2008) supports this and claims that skeletal carbonate can be used as a proxy for salinity as freshwater DIC is often isotopically lower than marine DIC, which would be recorded in the $\delta^{13}C$ value of skeletal carbonate. Furthermore, Brand *et al*. (1987) found that the $\delta^{18}O$ and $\delta^{13}C$ values of marine barnacle and mollusk shells were in equilibrium with ambient water.

Bulk carbonate samples in this study showed both micrite and sparry calcite in thin section (Fig. 4), potentially reflective of some amount of alteration. For marine limestones sparry calcite is usually reflective of alteration or diagenesis but for freshwater limestones the presence of microspar and sparry calcite is not always diagnostic of diagenesis (Andrews, 2006). Because oxygen is a major component of water whereas carbon is merely a trace component, $\delta^{13}C$ values in carbonates are less sensitive to diagenetic overprint compared to $\delta^{18}O$, and it is generally accepted that $\delta^{13}C$ records paleoenvironment conditions at the time of deposition, not of diagenetic conditions (Huck *et al*., 2017; Sharp, 2017). Stable isotopes resulting from neomorphism of original freshwater limestone can be harder to discern than neomorphism of marine limestones, as waters that deposited the original freshwater limestone will be similar to waters involved in neomorphism (Andrews, 2006). Due to the vulnerability of oxygen isotopes to re-equilibrate with diagenetic fluids caution is advised when interpreting $\delta^{18}O$ values from bulk carbonates (Andrews, 2006; Sharp, 2017).

El Morro Boleo Fm. bulk carbonate samples have a narrow range of $\delta^{18}O$ values (-10‰ to -8.5‰), a somewhat larger range of $\delta^{13}C$ values (-4.3‰ to -0.5‰) and collected samples span 4 m of section. The consistency of $\delta^{18}O$ values even though samples were collected from several meters of section could be the result of a diagenetic fluid altering the original calcite (Turi, 1986). A previous study on the depositional environments of deposits at El Morro suggests that tufa deposits located close to the ones in this study were affected by early diagenesis of hydrothermal fluids (Miranda-Alviles *et al*., 2005). Many studies have shown that a high covariance between $\delta^{18}O$ and $\delta^{13}C$ values is evidence of hydrothermal or post-depositional diagenesis (Zheng and Hoefs, 1993; Mitchell *et al*., 1997; Buonocunto *et al*., 2002; Hossain *et al.,* 2013), but the bulk samples in this study have a low covariance between $\delta^{18}O$ and $\delta^{13}C$ values ($r^2 = 0.002$). A trend toward more positive values up section could be evidence for early influence by geothermal fluids (Johnson *et al*., 2009), but oxygen and carbon isotopes from El Morro samples do not become more positive up section.

Dolomite found in sample BA14-1 (Fig. 6C) could suggest brackish water conditions at the time of deposition or evidence of diagenesis (Longman, 1981). Modern dolomite is frequently found as a replacement product, often replacing original aragonite or high-Mg calcite (Scholle and Ulmer-Scholle, 2003). Out of the six El Morro samples, only one showed an XRD pattern representing dolomite (Fig. 6C) and no dolomite crystals were observed in thin section. A previous study on stable isotopes of the Boleo Fm. limestone provides evidence that Boleo Fm. limestones formed in brackish water conditions (Conly *et al*., 2006). Although primary precipitation of dolomite is rare in modern times, because of the lack of dolomite replacement seen in thin section, the infrequency of dolomite in XRD analysis, and the previous work suggesting brackish conditions, the dolomite found in sample BA14-1 is interpreted as original and not a product of diagenesis.

6.2 Paleoenvironmental Interpretations

6.2.1 El Morro

Boleo Fm. deposits at El Morro were previously identified as travertines and stromatolites with tufa facies identified at a location further south from where the samples in this study were collected (Miranda-Alviles *et al*., 2005). Ford and Pedley (1996) define tufa as "the product of calcium carbonate precipitation under a cool water (ambient temperature) regime and typically contains the remains of micro- and macrophytes, invertebrates and bacteria" and travertines as "restricted to all "freshwater" thermal and hydrothermal calcium carbonate deposits dominated by physico-chemical and microbial precipitates, which invariably lack in situ macrophyte and animal remains." Other authors offer simpler definitions such that travertines are freshwater carbonates formed from spring deposits due to inorganic or organic processes (Chafetz and Folk, 1982) or that tufas are freshwater carbonates with dominantly low-Mg calcium carbonate formed through biomediation and/or physico-chemical processes under ambient temperature conditions (Pedley *et al*., 2003). Many others provide a definition for how to classify deposits as tufa or travertine based on water temperature, depositional settings, microorganisms, minerology, or hardness (Jones and Renaut, 2010). Although there is great debate on how to define a deposit as tufa or travertine, for interpretation of El Morro deposits, the Ford and Pedley (1996) definitions will be followed.

The combined data collected (*i.e*., stable isotopes, thin sections, XRD) from El Morro bulk carbonates suggest that these deposits are more likely to be considered tufas that were formed when ambient spring waters mixed with shallow marine waters as opposed to travertines formed from thermal or hydrothermal waters. El Morro samples have average $\delta^{18}O$ and $\delta^{13}C$ values of -9.1‰ and -2.7‰, respectively. These values agree with $\delta^{18}O$ and $\delta^{13}C$ values for Quaternary freshwater limestones (Fig 10A). The $\delta^{18}O$ values from El Morro fall in the general range of $\delta^{18}O$ values for calcareous tufa (-12‰ to -3‰) (Gandin and Capezzuoli, 2008). $\delta^{18}O$ and $\delta^{13}C$ values from Jurassic tufa mounds in northern Arizona and southern Utah had average values of -7.0‰ and -3.3‰, similar values to the ones in this study (Parrish *et al*., 2018). Although the reliability of using $\delta^{18}O$ values to discuss paleoenvironment in deep time may be questionable due to diagenetic overprinting, $\delta^{13}C$ values suggest some amount of freshwater influence and agree with $\delta^{13}C$ values reported from tufa deposits in Baringo, Kenya (-4.6‰ to 0.2‰; Johnson *et al*., 2009), Lake Victoria, Kenya (-5‰ to -1‰; Aringo and Kisaaka sites; Beverly *et al*., 2015) and in the Olduvai Basin, Tanzania (-3.7‰ to 0.4‰; Upper Bed II; Ashley *et al*., 2014).

The mean annual temperature in the Santa Rosalía area is 25 °C (Wilson and Rocha, 1955) and precipitation has a mean annual $\delta^{18}O$ value of -5.0‰ SMOW ($\delta^{18}O_{mw}$) (Bowen, 2010). To estimate the value of $\delta^{18}O$ for calcite ($\delta^{18}O_c$) precipitated under modern conditions the Kim and O’Neil (1997) equation was applied:

$$1000\, ln\, \alpha_{(calcite-H_2O)} = 18.0(10^3T^{-1}) - 32.42 \qquad (1)$$

where T is in kelvins and α is the fractionation factor between two substances, in this case the precipitating calcite and water. Under modern conditions, tufa deposits would have $\delta^{18}O_c$ values around -7.3‰, only 1.8‰ lower than the average for the El Morro tufa. For deposits at El Morro to be precipitated from strictly meteoric water in modern times (-5‰ SMOW), they would have to have formed in an average temperature of 34 ºC, 9 ºC warmer than the modern annual mean. However, it is not uncommon for temperatures in Santa Rosalía to reach 35 ºC or more during the summer (Wilson and Rocha, 1955). Although the temperature for this area during the late Miocene is unknown, it is known that the global climate during the late Miocene was warmer than modern times and SSTs in the north Pacific were 5-8 ºC warmer (LaRiviere *et al*., 2012). An average temperature of 34 ºC in the late Miocene may seem a bit high but not improbable. If this carbonate formed in purely marine waters (0‰ SMOW), El Morro deposits would have formed in average temperatures of 63 ºC, ~30 ºC warmer than the modern average maximum temperature for this area and outside of the realm of possibility for this area even during the late Miocene when SSTs were 5-8 ºC warmer.

The presence of ostracods and foraminifera visible in thin section (Fig. 4B, C and E) suggests marine influence at the time of deposition. Although ostracods can be found in a variety of aquatic environments, foraminifera are almost always found in marine to marginal marine environments (Scholle and Ulmer-Scholle, 2003) with very few species found in freshwater environments (Siemensma *et al*., 2017). A hydrothermal origin of these deposits, thereby defining them as travertines, is unlikely as the upper temperature limits for living conditions of ostracods is 50°C and protozoa (of which foraminifera belong to) is around 60 °C (Jones and Renaut, 2010) and the majority of $\delta^{13}C$ values are lower than the typical range for travertines, -2‰ to 8‰, respectively (Gandin and Capezzuoli, 2008).

The combined stable isotope, thin section and XRD data from El Morro samples all leads to the conclusion that El Morro deposits were influenced by both ambient spring and shallow-marine waters. Following the definitions presenting by Ford and Pedley (1996), El Morro deposits are more likely to be considered tufas, as oppose to travertines, as the presence of ostracods and foraminifera rules out that these deposits were formed from hydrothermal waters. El Morro tufa deposits likely formed as ambient spring water entered shallow-marine waters in an estuary setting.

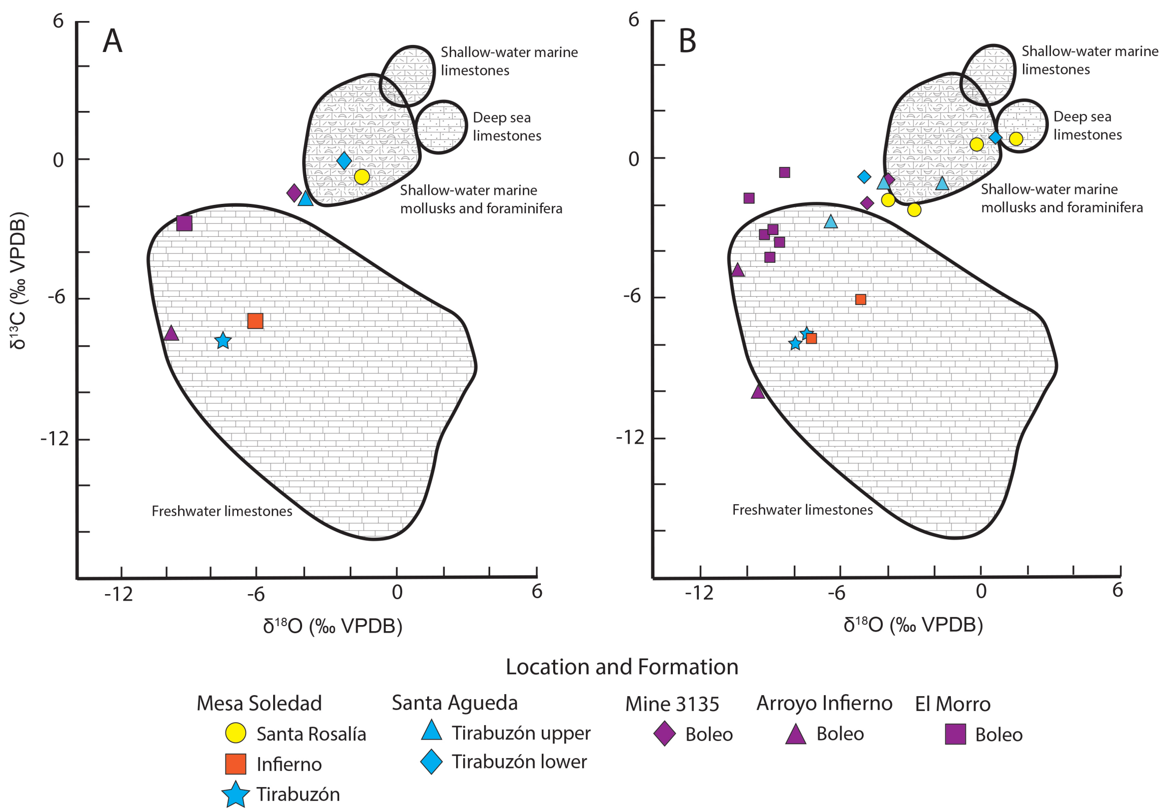

Figure 10. Cross-plots of $\delta^{18}O$ and $\delta^{13}C$ values from samples in this study compared to the general distribution of $\delta^{18}O$ and $\delta^{13}C$ data in Quaternary carbonates (modified from Boggs, 2009). A) Average $\delta^{18}O$ and $\delta^{13}C$ data for samples collected within a formation at a given site. B) $\delta^{18}O$ and $\delta^{13}C$ values from all samples shown by site and formation.

6.2.2 Arroyo Infierno

Previous studies on the Boleo Fm. limestone denote it as a marine limestone (Wilson and Rocha, 1955; Ochoa-Landín *et al*., 2000). Conly *et al*. (2006) recorded $\delta^{18}O$ and $\delta^{13}C$ values of -11.0‰ to -4.5‰ and -6.0‰ to 4.4‰, for limestones of the Boleo Fm. In this study, average $\delta^{18}O$ and $\delta^{13}C$ values of fossils collected from the Boleo Fm. limestone at Arroyo Infierno are -9.9‰ and -7.5‰, respectively. These $\delta^{18}O$ and $\delta^{13}C$ values are significantly more negative than what is commonly reported for shallow-water marine mollusks, with $\delta^{18}O$ values between -4‰ to 3‰ and $\delta^{13}C$ values between -4‰ to 1‰ (Anderson and Arthur, 1983) and instead reflect isotopic fractionation in predominantly freshwaters (Fig. 10A). Although the low oxygen values could suggest a temperature effect or possible diagenesis, these factors would not account for the low value of carbon, suggesting that these values are more characteristic of precipitation in predominately freshwater. The source of freshwater could be explained by waters from a fluvial source. A study on fossil shells collected near the mouth of the Colorado River in the Gulf of California had minimum $\delta^{18}O$ values of -8.8‰ (Dettman *et al*., 2004), 1.1‰ more positive than the average for Arroyo Inferno samples.

Common $\delta^{13}C$ values for fluvial carbonates are between -12‰ and -4‰ (Arenas-Abad *et al*., 2010). The $\delta^{13}C$ values from Arroyo Infierno are within that range. Common $\delta^{18}O$ values for fluvial carbonates are between -8‰ and -5‰ (Arenas-Abad *et al*., 2010), higher than the $\delta^{18}O$ values for samples at Arroyo Infierno but studies of fluvial carbonates recording more negative $\delta^{18}O$ values do exist (Pazdur *et al*., 1988; Andrews *et al*., 1997; Dettman *et al*., 2004). The stratigraphically lowest sample from Arroyo Infierno had a $\delta^{13}C$ value of -10.1‰ and the stratigraphically highest sample had a $\delta^{13}C$ value of -4.8‰, whereas the $\delta^{18}O$ values remain fairly constant (between -10.3‰ and -9.4‰). This could potentially be explained by changes in vegetation, with C_3 vegetation dominating during deposition of the lowest sample and C_4 vegetation dominating during deposition of the highest sample. Additional samples would need to be collected to test this.

Sea-surface temperatures 5-8 ºC warmer during the late Miocene would affect the $\delta^{18}O$ value of carbonates precipitating from marine waters (0‰ SMOW). This would decrease $\delta^{18}O$ values by about 1-2‰, a significant amount, but not significant enough to account for the negative values recorded in these samples. This increase in temperature would also not explain the negative $\delta^{13}C$ values and suggests the influence by freshwaters (likely fluvial). The $\delta^{18}O$ and $\delta^{13}C$ values from Arroyo Infierno and at least some from Conly *et al*. (2006) are consistent with fluvial-influenced carbonates. This finding conflicts with previous studies claiming a marine origin for the limestone of the Boleo Fm. (Wilson and Rocha, 1955; Ochoa-Landín *et al*., 2000).

6.2.3 Mine 3135

Samples from the Boleo Fm. above manto 4 at Mine 3135 consist of two mollusks collected from a fossiliferous sandstone with average $\delta^{18}O$ and $\delta^{13}C$ values of -4.4‰ and -1.4‰, respectively. The average $\delta^{13}C$ value falls within range for shallow-water marine mollusks and the average $\delta^{18}O$ value falls just outside of accepted values (minimum of -4.0‰) for shallow-water marine mollusks (Fig. 10A; Boggs, 2009). These mollusks likely still lived and grew in a shallow water setting with lower values of $\delta^{18}O$ and $\delta^{13}C$

recording the influx of freshwater, which has previously been interpreted as fluvial (Conly *et al*., 2006).

Similar $\delta^{18}O$ values to the mollusks at Mine 3135 are reported by Rodriguez *et al*. (2001) from aragonite mollusk shells collected at the mouth of the Colorado River in the Gulf of California, where isotopically lower fluvial water from the Colorado River mixed with isotopically higher marine waters in the Gulf of California, resulting in mollusks having average $\delta^{18}O$ values between -4.3‰ to -3.1‰. In order to properly compare the $\delta^{18}O$ values for aragonite shells from Rodriguez *et al*. (2001) to the $\delta^{18}O$ values of calcite shells in this study, some conversions and assumptions must be made as aragonite is enriched in $\delta^{18}O$ compared to calcite at different temperatures. Rodriquez *et al*. (2001) used mollusks that are reported to grow in temperatures ranging from ~17 °C to ~31 °C, average 24 °C. At 24 ºC, aragonite is enriched in $\delta^{18}O$ by ~0.6‰ relative to calcite (Anderson and Arthur, 1983). Assuming an average temperature of 24 °C, the $\delta^{18}O$ averages from Rodriguez *et al*. (2001) would have been between -4.9‰ to -3.7‰ if calcite shells had been analyzed. The converted calcite range includes the average and individual sample $\delta^{18}O$ values at Mine 3135.

The increased depletion in $\delta^{18}O$ compared to $\delta^{13}C$ could also be reflective of an increase in water temperature. An increase in water temperature would decrease the value of $\delta^{18}O$ but not $\delta^{13}C$, as oxygen isotope fractionization is temperature dependent whereas carbon isotope fractionization is relatively insensitive to temperature (Sharp, 2017). Currently, water in the Gulf of California is relatively warm, reaching average maximum temperatures of 31 °C in the summer (Reynolds *et al*., 2007). Sea-surface temperatures in the late Miocene are estimated to have been 5-8 ºC warmer than they are today (La Riviere *et al*., 2012). The late Miocene SST increase in waters that are already fairly warm is likely reflected in these deposits with additional input of freshwater leading to negative $\delta^{13}C$ values and further lowering $\delta^{18}O$ values.

The negative $\delta^{13}C$ values could partially be explained by the decrease of marine DIC from 7.8 to 6.2 Ma, when the global average of $\delta^{13}C$ decreased by 0.5‰ (Hodell *et al*., 1994). Although the absolute age of these specimens is unknown, they were collected from a siliciclastic deposit estimated to have been deposited between 7.1 to 6.2 Ma, a length of time included in the global decrease of marine DIC. It has been suggested that the decrease of marine DIC was due to erosion of organic material during a global sea-level drop (Vincent *et al*., 1980). The negative $\delta^{13}C$ values from Mine 3135 could potentially be due to fluvial waters eroding continental organic material into shallow-marine waters, as this was happening globally.

6.2.4 Santa Agueda

Samples collected from the lower calcareous sandstone of the Tirabuzón Fm. at Santa Agueda have average $\delta^{18}O$ and $\delta^{13}C$ values of -2.2‰ and 0.0‰, respectively. These isotopic values suggest carbonate precipitation in a shallow-water marine environment (Fig. 10) similar to the 55-90 m water depth range suggested by Wilson (1985), but likely shallower than the 200-500 m water depth Carreno (1982) and Shroat-Lewis (2007) suggest. A study by Keigwin (2001) on water temperatures in the Gulf of California found that between 200-500 m water depth temperatures were between 10-15 °C and 18-27 °C between 0-100 m. If formed strictly from marine waters (0‰ SMOW), with no freshwater source lowering the $\delta^{18}O$ and $\delta^{13}C$ values, samples from the lower section would have formed in water temperatures about 25 °C on average (Kim and O'Neil, 1997). During the Pliocene SSTs were 3-5ºC warmer, this temperature increase would decrease $\delta^{18}O$ values by ~1‰. However, even after accounting for the temperature increase during the Pliocene and the ~1‰ decrease in $\delta^{18}O$ values it would cause, lower Tirabuzón Fm. $\delta^{18}O$ values would still be within the 0-100 m range, further supporting Wilson (1985) claim that the Tirabuzón Fm. formed in water depths between 55-90 m or potentially shallower.

However, $\delta^{18}O$ and $\delta^{13}C$ data from these samples only represents the conditions at the time of shell growth, not of final depositional environment. It is possible that these organisms lived in a shallow-water marine environment and were later transported into a deeper environment. The two samples collected from the lower calcareous sandstone for stable isotope analysis are not sufficient enough to rule out the possibility of transportation. Additional samples would need to be collected for further analyses to better estimate water depth of this section.

Samples collected from the upper conglomerate of the Tirabuzón Fm. at Santa Agueda have average $\delta^{18}O$ and $\delta^{13}C$ values of and -4.1‰ and -1.7‰, respectively. These $\delta^{18}O$ and $\delta^{13}C$ values are ~2.0‰ lower than values for the lower calcareous sandstone. This decrease in both $\delta^{18}O$ and $\delta^{13}C$ values suggests a greater freshwater input, either from increased fluvial waters or precipitation, and an increase in temperature further lowering $\delta^{18}O$ values. As mentioned, the 3-5 ºC temperature increase during the Pliocene would result in samples having $\delta^{18}O$ values ~1‰ lower compared to Quaternary carbonates. This increase in SSTs during the Pliocene is likely reflected in the upper conglomerate. The upper conglomerate of the Tirabuzón Fm. at Santa Agueda was likely deposited in a beach environment where the introduction of fresh waters into shallow-marine waters resulted in the negative $\delta^{18}O$ and $\delta^{13}C$ values and warmer SSTs further lowered $\delta^{18}O$ values of these samples.

Although average $\delta^{18}O$ and $\delta^{13}C$ values are lower for the upper conglomerate than the lower calcareous sandstone, samples from both sections have average $\delta^{18}O$ values between -4‰ to 3‰ and $\delta^{13}C$ values between -4‰ to 1‰, consistent with a shallow-water marine environment (Anderson and Arthur, 1983). The transition from a calcareous sandstone to conglomerate is characteristic of a change from a shallow marine to beach environment that occurred as local sea level fell, and the shoreline regressed. Lower calcareous sandstone fossil $\delta^{18}O$ and $\delta^{13}C$ values indicate a marine environment shallower than 100 m and upper conglomerate fossil $\delta^{18}O$ and $\delta^{13}C$ values indicate a beach environment influenced by freshwater and warmer SSTs.

6.2.5 Mesa Soledad

Mesa Soledad is the only site with samples collected from multiple formations: the Tirabuzón, Infierno and Santa Rosalía. Samples collected from a fossiliferous sandstone within the Tirabuzón Fm. have average $\delta^{18}O$ and $\delta^{13}C$ values of -7.6‰ and -7.8‰, similar to a fossiliferous limestone within the Tirabuzón Fm. with $\delta^{18}O$ and $\delta^{13}C$ values of -11.0‰ and -7.7‰ (Conly *et al*., 2006). Previous studies of the Tirabuzón Fm. suggest an offshore marine environment (Wilson, 1985; Shroat-Lewis, 2007). The isotopic values from the Tirabuzón Fm. at Mesa Soledad are too negative to indicate an offshore marine environment, which tends to be positive or near zero in offshore marine carbonates

(Anderson and Arthur, 1983). Neither are they reflective of a shallow-water marine environment (Fig. 10). However, even if these isotopic values are more typical of freshwater limestones, the presence of Echinoidea body fossils indicates that the Tirabuzón Fm. at Mesa Soledad formed in a marine environment. Conly *et al*. (2006) suggests that the Tirabuzón Fm. formed in a brackish environment, with $\delta^{18}O_{mw}$ and $\delta^{13}C_{HCO3^-}$ values of ~-9‰ and ~-10.0‰ (at 25 ºC), respectively. Due to the similar isotopic values between the fossiliferous limestone in Conly *et al*. (2006) to the fossiliferous sandstone in this study, the samples in this study likely formed in brackish water conditions where fluvial waters entered shallow-marine waters in the Gulf of California.

Samples from the Infierno Fm. at Mesa Soledad have average $\delta^{18}O$ and $\delta^{13}C$ values of -6.2‰ and -6.9‰, slightly more positive (1.4‰ and 0.9‰) than average $\delta^{18}O$ and $\delta^{13}C$ values for the Tirabuzón Fm. at Mesa Soledad. To date, there are no published studies on stable isotopes from the Infierno Fm, but the values in this study suggest that these deposits also formed in a brackish environment similar to the Tirabuzón Fm.

It is unlikely that increased SSTs during the Pliocene was a dominate factor for the negative $\delta^{18}O$ values of Pliocene deposits at Mesa Soledad. Instead the early to middle Pliocene Tirabuzón Fm. and the late Pliocene Inferno Fm. at Mesa Soledad were influenced by $\delta^{18}O$ and $\delta^{13}C$ low freshwaters entering a shallow-marine setting.

Carbon isotopes from Pliocene deposits at Mesa Soledad provide clues that this area was not dominated by arid or semi-arid vegetation like the modern environment (Wilson and Rocha, 1955). Freshwater carbonates that precipitate from areas dominated by C_3 vegetation have more negative $\delta^{13}C$ values (-8‰ or less) whereas carbonates that precipitate from areas that are predominantly C_4 vegetation have more positive $\delta^{13}C$ values (-6‰ to -2‰) (Andrews, 2006; Beverly *et al*., 2015). The average $\delta^{13}C$ values, -7.8‰ for the Tirabuzón Fm. and -6.9‰ for the Infierno Fm., from Pliocene deposits at Mesa Soledad do not suggest that there was a strong C_4 presence in this area and instead this area was predominantly C_3 vegetation. Providing evidence that the Baja California peninsula was not more arid during the warmer than modern Pliocene.

Above the Inferno Fm. at Mesa Soledad is the Santa Rosalía Fm. The Santa Rosalía Fm. has average $\delta^{18}O$ and $\delta^{13}C$ values of -1.4‰ and -0.7‰, respectively. These values agree with deposition in a shallow-water marine environment (Fig. 10A). Values from individual samples are plotted on Figure 10B. One of the 4 samples from the Santa Rosalía Fm. have $\delta^{18}O$ and $\delta^{13}C$ values of 1.5‰ and 0.7‰, more characteristic of deeper or colder waters. However, it is not particularly unusual to find mollusks with values of this kind in shallow intertidal waters (Schone *et al*., 2006). The Santa Rosalía Fm. is the youngest (~1 Ma) of all marine formations in the SRB and stable isotope values from this formation show some of the highest values in this study. At Mesa Soledad, there is a clear trend toward increasing $\delta^{18}O$ and $\delta^{13}C$ values up section, indicating an environmental change through time, with Pliocene deposits recording a freshwater influence that ultimately diminished by the time the Pleistocene Santa Rosalía Fm. formed.

6.3 Implications for Miocene and Pliocene Paleoclimate

Stable oxygen and carbon isotopes from late Miocene and Pliocene deposits in the SRB show the influence of freshwater at the time of deposition. The modern climate of the Santa Rosalía area is relatively arid, receiving on average ~13 cm of precipitation a year

(Wilson and Rocha, 1955). Due to the paucity of precipitation in Santa Rosalía and the surrounding area, there are no major fluvial systems. Although the amount of precipitation the Santa Rosalía area received during the late Miocene and Pliocene is beyond the scope of this study, our paleoenvironmental interpretations suggest that during the late Miocene and Pliocene this area had fluvial sources and therefore, had more precipitation than present day.

The source for most of the increased precipitation is likely from the North American monsoon. The 5-8ºC SSTs increase during the late Miocene (LaRiviere *et al*., 2012) and the 3-5ºC SSTs increase during the Pliocene (Winnick *et al*., 2013) along with opening of the Gulf of California intensified the North American monsoon (Chaplin, 2008). We hypothesize that a prolonged and intensified North American monsoon resulted in a paleoclimate much wetter than present day. This finding agrees with Molnar and Cane's (2007) hypothesis that warming during the late Miocene-Pliocene lead to a wetter climate in the western US, similar to modern El Niño summers. The prolonged and intensified North American monsoon during the late Miocene and Pliocene resulted in spring and fluvial waters that either directly formed or influenced carbonates within the Santa Rosalía Basin.

7. Conclusion

Analysis of mineralogy, petrography, and stable isotopes from bulk carbonate samples at El Morro suggest that these tufa deposits formed in a brackish environment as ambient spring waters entered shallow-marine waters. Stable oxygen and carbon isotopes from fossils collected at Arroyo Infierno record values characteristic of carbonate precipitation in freshwaters, likely fluvial, as these deposits have $\delta^{18}O$ values too negative to be caused by realistic changes in SSTs during the Miocene. The low $\delta^{18}O$ values of mollusk samples collected at Mine 3135 is likely the result of warmer SSTs during the late Miocene but with some amount of freshwater carrying eroded organic material into the shallow-marine waters of the Gulf of California, leading to negative $\delta^{13}C$ values and further lowering $\delta^{18}O$ values. The Tirabuzón Fm. at Santa Agueda is the only section of Pliocene deposits to have $\delta^{18}O$ and $\delta^{13}C$ values characteristic of a shallow-water marine environment, inconsistent with previous studies that suggest an offshore marine environment. At Santa Agueda, the shift to coarser sediment and lower $\delta^{18}O$ and $\delta^{13}C$ values up section suggests a seaward migration of the shoreline. Like the late Miocene Boleo Fm. deposits, Pliocene deposits at Mesa Soledad also have $\delta^{18}O$ and $\delta^{13}C$ values suggesting a freshwater influence. $\delta^{13}C$ values are consistent with freshwater carbonates mostly influenced by C_3 vegetation. This finding suggests that either the Santa Rosalía area had not undergone the expansion of C_4 dominated vegetation by the Pliocene or that even though the climate was warmer, it was still wet enough to sustain C_3 vegetation. The Mesa Soledad section is the only section with samples that span multiple formations and there is a trend toward higher $\delta^{18}O$ and $\delta^{13}C$ values up section, evidence for drying out of the climate from the Pliocene to Pleistocene. Current models predict that as the global climate warms the southwestern US and northern Mexico will become drier, but our findings suggest that when the climate was 3-4 ºC warmer during the latest Miocene and Pliocene the region was wetter than modern times. This suggests that as temperatures increase in this region due to anthropogenic climate change, more precipitation is likely due to an intensified and prolonged North American monsoon.

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9. Appendices

Appendix 1. Raw $\delta^{18}O$ and $\delta^{13}C$ data

Sample	δ ^{18}O (‰VPDB)	δ ^{13}C (‰VPDB)	Location	Formation
17-11-15 Pecten	-3.96	-1.82	Mesa Soledad	Santa Rosalía
17-11-10 Pecten	-0.24	0.58	Mesa Soledad	Santa Rosalía
17-11-10 Barnacle	-2.83	-2.29	Mesa Soledad	Santa Rosalía
17-11-10 Oyster	1.49	0.74	Mesa Soledad	Santa Rosalía
17-10-07 Pecten	-5.13	-6.08	Mesa Soledad	Infierno
17-10-07 Barnacle	-7.24	-7.72	Mesa Soledad	Infierno
17-10-01 Pecten	-7.84	-7.99	Mesa Soledad	Tirabuzón
17-10-01 Oyster	-7.37	-7.57	Mesa Soledad	Tirabuzón
16-18-14 Oyster	-4.15	-1.15	Santa Agueda	Tirabuzón upper
16-18-14 Barnacle	-6.42	-2.75	Santa Agueda	Tirabuzón upper
16-18-14 Pecten	-1.64	-1.15	Santa Agueda	Tirabuzón upper
BA17-2 Pecten	0.65	0.87	Santa Agueda	Tirabuzón lower
BA16-1 Oyster	-4.96	-0.85	Santa Agueda	Tirabuzón lower
BA17-1B Oyster	-4.84	-1.97	Mine 3135	Boleo
BA17-1B Pecten	-3.89	-0.92	Mine 3135	Boleo
BA18-2 Pecten	-10.34	-4.84	Arroyo Infierno	Boleo
BA18-4 Bivalve	-9.43	-10.08	Arroyo Infierno	Boleo
BA14-2	-8.50	-0.51	El Morro	Boleo
BA14-1	-9.32	-3.32	El Morro	Boleo
BA12-5	-9.12	-4.32	El Morro	Boleo
BA12-4	-9.02	-3.07	El Morro	Boleo
BA12-3B	-10.01	-1.66	El Morro	Boleo
BA12-1	-8.75	-3.63	El Morro	Boleo