Diagenesis of phosphatic hardgrounds in the Monterey Formation: A perspective from bulk and clumped isotope geochemistry

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ABSTRACT

Understanding the authigenesis of carbonate fluorapatite through isotopic geochemistry can yield important information on fundamental geologic processes occurring on continental margins around the world. This is particularly true for phosphatic hardgrounds, which are often found in regions of upwelling, but of which questions remain about the initial formation and subsequent diagenesis. Here, we apply standard isotopes ($\delta^{13}C$, $\delta^{18}O$) alongside the novel clumped isotope (Δ_{47}) used in this study for the first time to reconstruct the temperature of formation of carbonate ions within the lattice of sedimentary carbonate fluorapatite. We investigated phosphatic hardgrounds of Miocene age (12.7–10.8 Ma) sampled at El Capitan State Beach in the Monterey Formation. The range of isotopic signatures observed is between +1.5‰ and +8.0‰ for $\delta^{13}C$ relative to the Vienna Peedee belemnite (VPDB) standard and –9.5‰ and –6.0‰ VPDB for $\delta^{18}O$, and values range between 0.599‰ and 0.615‰ for Δ_{47}. The enriched $\delta^{13}C$ and depleted $\delta^{18}O$ signatures are suggestive of recrystallization within the methanogenic zone. Clumped isotope geochemistry further constrains this transformation as having taken place at a temperature of 61–66 °C ± 5 °C, in line with previous estimates for maximum burial of the Monterey Formation based on the silica phase transition. The calculated $\delta^{18}O$ for the connate fluid shows an expected range for seawater composition for the Miocene, suggesting only minor contribution of silica-derived oxygen to the $\delta^{18}O$ of carbonate fluorapatite. The combined conventional and clumped isotope data set also points out that methanogenesis took place deeper within the sediment in the middle Miocene than at present day within the Santa Barbara Basin. This study furthers our understanding of phosphogenesis and potential links to burial processes in the Monterey Formation, and it shows for the first time that the clumped isotope paleothermometer could be used to understand fundamental geochemical processes in authigenic sedimentary phosphates.

INTRODUCTION

Authigenesis, or the formation of minerals in situ, can potentially record critical geochemical information that helps to unravel fundamental geological processes taking place at the sediment-water interface and/or within the pore network of sediments. An important authigenic mineral within sediments is carbonate fluorapatite, an economical phosphatic ore deposit used in the production of fertilizers (Leather, 1994) and sometimes associated with petroleum source rocks (Isaacs and Petersen, 1987). There is a strong scientific interest in the formation of carbonate fluorapatite because it is intimately linked to biological processes, the evolution of the ocean, and associated biological productivity and its feedback on the carbon cycle and climate (Föllmi, 1996; Cook and Shergold, 2005). Carbonate fluorapatite, also known as sedimentary francolite, contains up to 6 wt% (weight percent) of carbonate ions substituting the phosphate ions within the lattice of the mineral (McClellan, 1980). By analyzing the stable isotopic ratios of both carbon and oxygen within the carbonate ions of carbonate fluorapatite, one can gain information on the formation history and potential diagenesis of phosphates (Shemesh et al., 1983, 1988; Kastner et al., 1990; Leather, 1994).

The goal of this study is to investigate the formation and isotopic composition of phosphatic hardgrounds containing carbonate fluorapatite deposited in the Monterey Formation of California (John et al., 2002). We used conventional stable isotopic analysis ($\delta^{13}C$ and $\delta^{18}O$), and for the first time the novel clumped isotope paleothermometer Δ_{47} (Eiler, 2007) to determine the formation temperature of carbonate fluorapatite. A central question to this paper is whether the $\delta^{13}C$ and $\delta^{18}O$ values of the different carbonate fluorapatites within individual hardgrounds of the Monterey Formation record a range of seawater compositions reflecting deposition over a prolonged period, or diagenetic processes during burial. If the isotopic composition of carbonate fluorapatite is reset during burial, will individual nodules within hardgrounds record a single diagenetic event, or several? How does the stable isotopic composition of hardgrounds in the Santa Barbara Basin compare to other basins along the Californian coast? These questions are broadly relevant to paleoclimate studies in general as the accumulations of phosphatic deposits on continental margins offer a potential archive with which to study the link between biological productivity and climate. Conversely, if carbonate fluorapatites within the Monterey Formation were to reset during burial, they would provide a window into diagenetic processes occurring in the subsurface of a major petroleum source rock. Initial study on the conventional isotopic signature of discrete nodules of carbonate fluorapatite at four different locations along the Californian coast (Lions Head Beach, Mussel Rock Beach, Gaviota Beach, and Naples Beach) by Leather (1994) seemed to suggest that the $\delta^{13}C$ and $\delta^{18}O$ of the associated carbonate content in carbonate fluorapatite recorded diagenetic alteration.

Here, we extend the initial work on the isotopic signature of the phosphates within the Monterey Formation by (1) investigating the isotopic signature of phosphatic hardgrounds in addition to the data existing for individual nodules, thus allowing comparison between the two types of phosphatic occurrences, (2) providing an enhanced data set of $\delta^{13}C$ and $\delta^{18}O$ that helps to constrain the distribution of processes affecting phosphates during burial within different basins along the California margin, and (3) combining the bulk stable isotopes with multiply

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substituted isotopologues (clumped isotopes) to constrain the temperature of phosphate diagenesis. The overall results of our study demonstrate the usefulness of measuring conventional and clumped isotopes on sedimentary carbonate fluorapatite, opening up the possibility of further clumped isotope investigation of authigenic phosphates along continental margins.

GEOLOGICAL SETTING

Monterey Formation

The Monterey Formation in California has been the subject of a wide range of sedimentology, paleoclimate, and diagenetic studies, and it is located in multiple basins along the coast of California (Fig. 1). The basins are filled with similar types of Miocene deposits also found in multiple sites around the Pacific Rim margin (Bramlette, 1946; Isaacs, 1980). Samples from this study come from the El Capitan State Beach, located within the Ventura–Santa Barbara Basin (Figs. 1 and 2). To the north of Santa Barbara Basin lies Santa Maria Basin, and to the south lies the Los Angeles Basin (Fig. 1).

The Monterey Formation was originally deposited at midbathyal marine depth on the continental margin off the coast of California (Isaacs, 2001). It consists of a lower calcareous-siliceous member, a middle carbonaceous marl member, and an upper clayey-siliceous member (John et al., 2002). The studied interval is located within the carbonaceous marl member and includes several phosphatic hardgrounds. The Santa Barbara and Santa Maria Basins have been extensively studied (Pisciotto, 1978; Leather, 1994; Isaacs, 2001; John et al., 2002; Föllmi et al., 2005; Loyd et al., 2012). Total organic carbon content of the middle member of the Monterey Formation at El Capitan State beach varies between 1.2 and 23.2 wt%, with the sedimentation rate varying between 75 m/m.y. in a gray marl unit with no phosphate, to 3 m/m.y. in the condensed phosphatic beds (John et al., 2002).

The Monterey Formation is of broad significance because it contains evidence for the most recent switch between greenhouse and icehouse conditions (Vincent and Berger, 1985; Flower and Kennett, 1993). Study of marine sediments has led to the "Monterey hypothesis," which suggests that increased upwelling during the Miocene caused a rise in productivity and the formation of organic-rich sediments and the associated drawdown of carbon during the middle Miocene (Vincent and Berger, 1985). However, it has also been suggested that the formation of organic-rich sediments and associated condensed phosphatic intervals postdate the Miocene cooling phase (John et al., 2002; Föllmi et al., 2005).

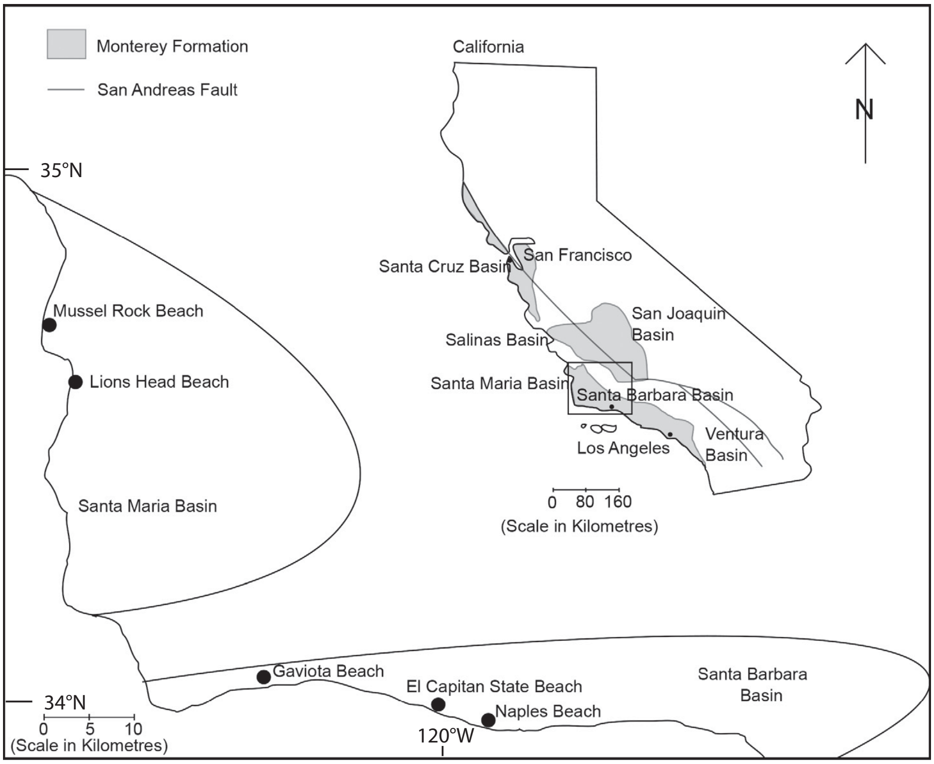

Figure 1. Location of El Capitan State Beach and the locations sampled by Leather (1994). Monterey Formation distribution is modified from Isaacs (2001).

Phosphogenesis

Carbonate fluorapatite generally forms during authigenesis in regions of upwelling and associated high biological productivity (Burnett, 1990), but it has also been shown to form as microscopic inclusions (Berner et al., 1993; Kim et al., 1999; Baturin, 2003) in nonupwelling environments such as the eastern Australian continental margin (O'Brien and Heggie, 1988), Long Island Sound, and the Mississippi Delta (Ruttenberg and Berner, 1993). The key to carbonate fluorapatite precipitation in coastal upwelling regions such as California is the high flux of preserved organic matter to the seafloor, as the phosphorous content of organic matter is released during microbially mediated decomposition (Reimers and Suess, 1983; Loyd et al., 2012) and combines with dissolved inorganic phosphate from the upwelling waters (Reimers et al., 1992; Föllmi, 1996). Phosphate release from iron oxides and hydroxides using redox pumping can also create high phosphate concentrations in pore water (Van Cappellen and Berner, 1988; Schuffert et al., 1998). Since carbonate fluorapatite forms in the upper part of the sediment, near the sediment-water interface, a prerequisite for its precipitation is a high concentration in dissolved phosphate content of the pore water (Boström et al., 1988). Other factors that affect the formation of apatite include pH, alkalinity, and pore-water constituents such as Ca^{2+}, Mg^{2+}, and F^{-} (Glenn et al., 1988; Van Cappellen and Berner, 1991). The first stage of carbonate fluorapatite precipitation is an amorphous precursor (amorphous calcium phosphate), which is then transformed to stable apatite with the addition of fluorine from seawater (Van Cappellen and Berner, 1991; Krajewski et al., 1994; Arning et al., 2009).

In the Monterey Formation, reworking or winnowing of sediment by bottom-water currents or gravity flows after carbonate fluorapatite precipitation has been suggested to physically concentrate the phosphate particles into layers (Burnett, 1977; Glenn and Arthur, 1988; Schuffert et al., 1998; John et al., 2002; Föllmi et al., 2005; Arning et al., 2009). The phosphatic hardgrounds investigated in this study are considered to epitomize this dynamic mode of formation and show evidence of multiple stages of winnowing under current-swept conditions that concentrated coarse nodules into decimeter-thick layers of phosphatic material on the seafloor (Garrison et al., 1987, 1990, 1994; Garrison and Kastner, 1990; Föllmi et al., 1991; John et al., 2002).

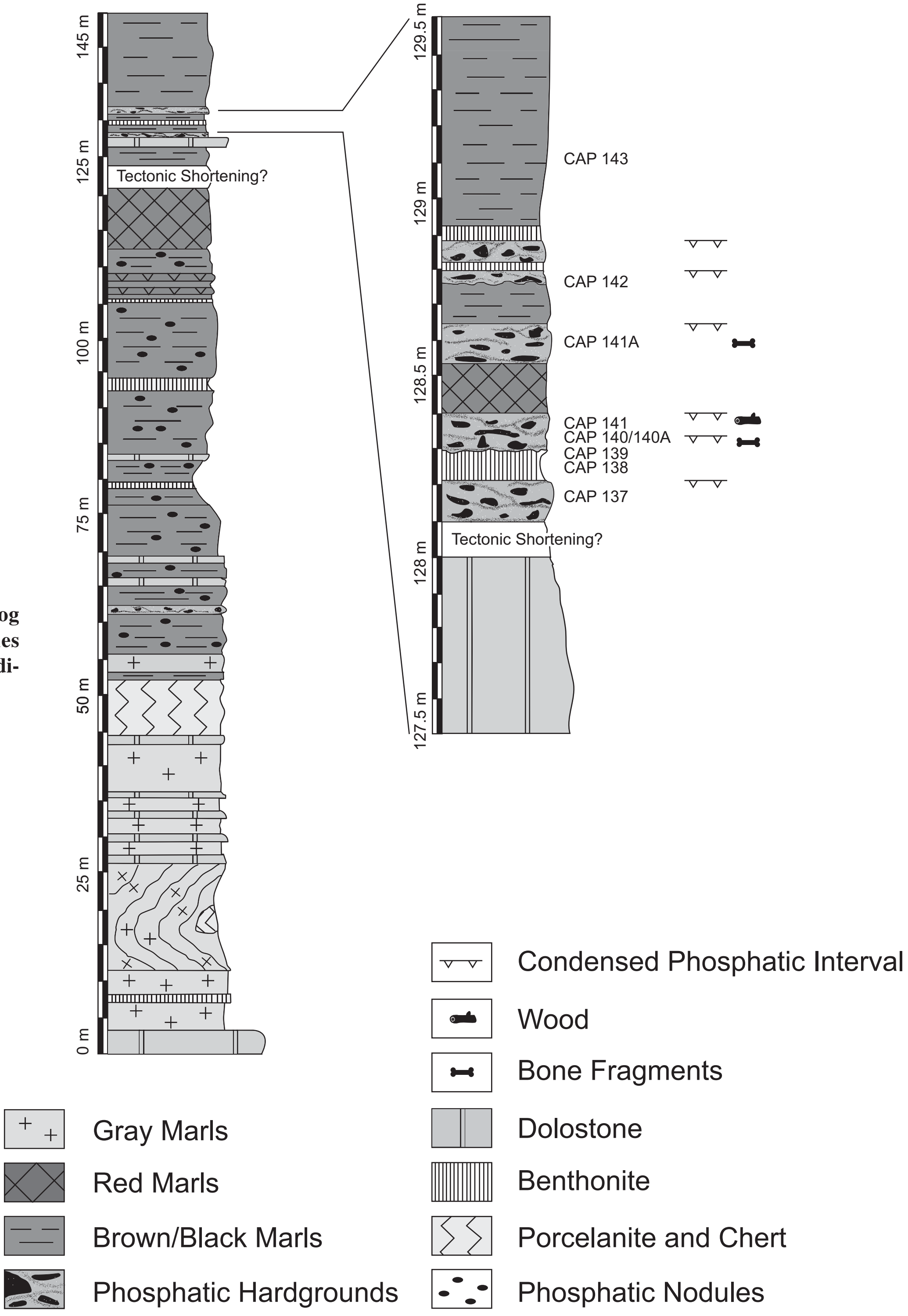

Figure 2. Simplified sedimentary log showing the position of the samples within phosphatic hardgrounds, modified from John et al. (2002).

MATERIALS AND METHODS

Materials

The samples were collected at El Capitan State Beach in the middle member of the Monterey Formation (John et al., 2002; Fig. 2). In total, eight samples were taken from five different stratigraphic horizons in a condensed section of phosphate-rich beds located between 128 and 129 m in the section. The age of the sample was bracketed by nannofossil biostratigraphic markers between 12.69 Ma to 10.82 Ma, with hand sample 137 being the oldest stratigraphic horizon, and 142B being the youngest (John et al., 2002). It is assumed that each hardground represents a significant hiatus. Within each sample, two main types of phosphatic nodules exist, the D-phosphate and F-phosphate (Fig. 3), first described by Garrison and Kastner (1990). F-phosphates are friable and typically are light

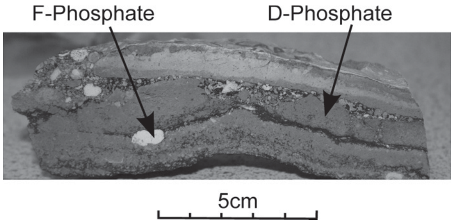

Figure 3. Photograph of sample 142B.

in color; they are interpreted to represent in situ precipitation of carbonate fluorapatite during early diagenesis at the sediment-water interface. D-phosphates are dense, well-lithified nodules or hardgrounds with a dark color or dark external coatings; they are interpreted to represent multiple stages of phosphogenesis and sediment reworking (Garrison and Kastner, 1990). The phosphatic layers vary in composition, with some layers containing small phosphatized particles, whereas others are more homogeneous and less friable. The layers and laminae are generally D-phosphates, although often lighter in color than those described by Garrison and Kastner (1990). There are also white nodules (F-phosphates), which appear to be pure phosphate. F-phosphates nodules are often contained between the darker layers or above the layers of D-phosphate. In places, the F-phosphate nodules appear within the darker D-phosphates. There are some bone fragments within the specimens, which are up to several centimeters in size and can be recognized by their columnar internal structure and light-gray to white rims. These range in color between dark brown to a lighter brown. The phosphatic pebbles are darker in color than the D-phosphates, and they are rounded, with a darker rim around the outside.

Methods

Sample Preparation

Each hand sample was drilled for multiple aliquots so as to sample the gray, more-condensed phosphate layers (D-phosphates), the smaller white phosphate nodules (F-phosphates), and pebbles or bones where present. To prepare the carbonate fluorapatite sample powders for isotopic analysis, we followed procedures described in Zazzo et al. (2004), Leather (1994), and Fox and Fisher (2001). These approaches have previously been shown to successfully remove sedimentary calcium carbonates while preserving the carbonate ions bound within the carbonate fluorapatite. Aliquots of 0.5–1 mg of powdered carbonate fluorapatite were treated with 3% sodium hypochlorite solution for 4 h at 20 °C to remove organic matter (Zazzo et al., 2004). The powders were then centrifuged for 5 min at 4000 rpm, after which the solution was discarded, and the powders were rinsed and centrifuged with distilled water three times before being treated with 0.1 *M* acetic acid–ammonium acetate buffer solution (pH 4.75) for 20 h at 20 °C to remove authigenic carbonates such as calcite and dolomite cements (Bocherens et al., 1996). The samples were then centrifuged for an additional 5 min at 4000 rpm, rinsed in distilled water five times (centrifuging between each rinse), and left to dry for 12–24 h at 50 °C.

X-Ray Diffraction

X-ray diffraction (XRD) analyses were performed at the Natural History Museum of London in order to check for the purity of the carbonate fluorapatite phase and the effectiveness of the cleaning method. Aliquots of 250–500 mg of carbonate fluorapatite treated with the chemical method described in the previous paragraph were analyzed on a Philips PW 1830 diffractometer system using CuKα radiation at 40 kV and 20 mA. The XRD system was fitted with a PW 1820 goniometer. The powders were scanned over a sampling range of 2.5–70° 2θ with a step size of 0.02° 2θ and an integration time of 2 s per step.

Bulk Isotope Analysis ($\delta^{13}C$ and $\delta^{18}O$) of Phosphates

All stable isotope measurements were performed in the Qatar Stable Isotope Laboratory at Imperial College London. For conventional isotopes, aliquots of 220 µg (±40 µg) of treated carbonate fluorapatite were analyzed using a Kiel IV device attached to a Thermo MAT 253 mass spectrometer equipped with a dual inlet system. The Kiel device was run at 70 °C, and the samples were reacted for 45 min to liberate CO_2. Previous studies on apatite used a reaction time of 1–5 h at 50 °C or lower temperature (McCrea, 1950; Banerjee et al., 1986; Koch et al., 1990; Leather, 1994; Zazzo et al., 2004), but carbonate fluorapatite had not been analyzed on a Kiel device before, although hydroxi-apatite from bone samples was measured on a Kiel device at 72 °C for an unreported reaction time (Fox and Fisher, 2001). To check that the short, 70 °C reaction was not introducing any analytical biases, a sample was analyzed using the manual vacuum line for 5 h at 50 °C and compared to the same sample run at 70 °C on the Kiel device. Both results came within one standard deviation of each other, suggesting that the 70 °C reaction on the Kiel device is a valid approach.

All conventional stable isotope values are expressed using the standard per mil notation and reported against the Vienna Peedee belemnite standard (VPDB). Replicate analyses of carbonate standards show a reproducibility of 0.05‰ (1σ) for δ^{13}C and 0.11‰ (1σ) for δ^{18}O, and triplicate analyses of carbonate fluorapatite samples show a sample reproducibility of 0.11‰ (1σ) for δ^{13}C and 0.27‰ (1σ) for δ^{18}O. The standard reproducibility is lower than typically expected for the Kiel device, and this is thought to be due to the longer reaction time, inducing a higher probability of minor leaks on the vial during measurement (a known issue with Kiel devices). In view of the differences that are observed in the isotopic signature of different phosphatic phases, this error is not significant. Sample reproducibility is typically lower than standard reproducibility due to inhomogeneity of samples. The sample run values were corrected based on the standard values of an internal standard (Imperial Carrara Marble). In addition, corrections for the temperature-specific acid fractionation of the associated carbonate in carbonate fluorapatite were done following Passey et al. (2007).

Clumped Isotope Analysis (Δ_{47}) of Phosphates

Previous work on clumped isotopes in phosphates has focused on applications to bioapatite in vertebrae (Eagle et al., 2010) and tooth enamels of sauropods dinosaurs (Eagle et al., 2011). The Eagle et al. (2010) study did a thorough testing of the effects of their cleaning procedure on modern rhinoceros teeth, using different reaction times between the powdered bioapatite sample and a 3% H_2O_2 solution. The results showed no adverse effect on clumped isotope measurement (results fell within 1 standard deviation of the expected temperature of 37 °C). The samples in the Eagle et al. (2010) study were also washed with 0.1 *M* acetic acid and buffered to pH 2.8 or pH 4.6, which proved sufficient at removing diagenetic carbonates and also did not impact the clumped isotope composition of the teeth. Finally, reasonable growth temperatures for phosphates were obtained in the Eagle et al. (2010) paper when applying calibrations originally derived for calcite, suggesting a universal calibration exists for clumped isotopes.

Although our study is the first of its kind to focus on sedimentary phosphate, our sample preparation protocols are similar to those of Eagle et al. (2010), with similar pH and acetic acid concentrations, and thus we can be confident that the carbonate fluorapatite has not been impacted by the cleaning procedure and is yielding reasonable temperature estimates. An aliquot of 150 mg of carbonate fluorapatite was used for each replicate analysis. The aliquots were reacted at 90 °C with 105% phosphoric acid in a reaction vessel that was evacuated for 30 min on a manual vacuum line, and typically

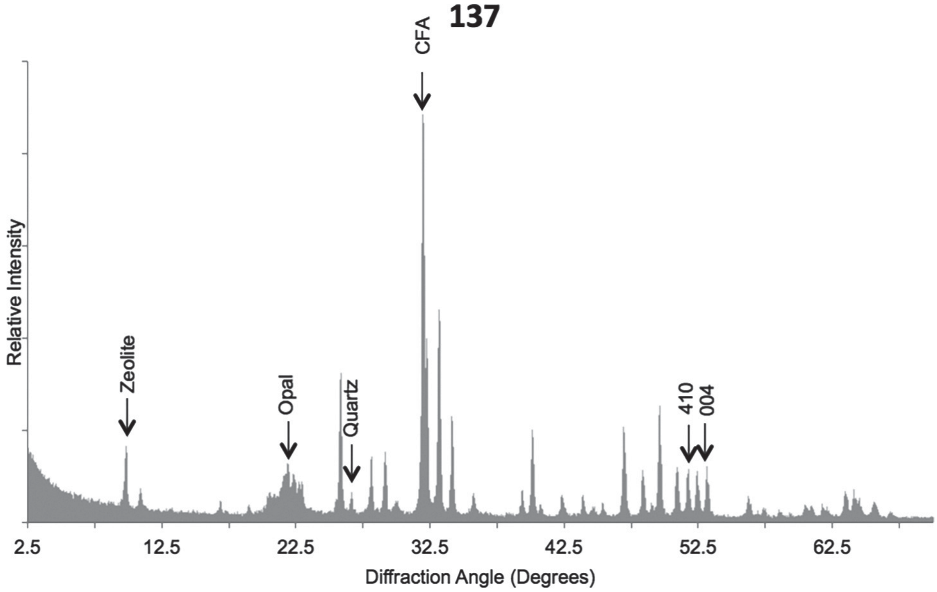

Figure 4. X-ray diffraction (XRD) profile of sample 137 showing the minerals with their associated peaks of highest intensity. CFA—Carbonate-fluorapatite.

reached pressures of 10^{-1} to 10^{-2} mbar before the acid digestion was started. At 90 °C, carbonate fluorapatite was reacted for 20 min in the continuously stirred reaction vessel. The reactant CO_2 was cleaned using a procedure analogous to that of Dennis and Schrag (2010) and further described for the laboratory at Imperial College in Dale et al. (2014). Briefly, the CO_2 liberated by the phosphoric acid reaction was continuously trapped, water was separated from the gas using a dry-ice ethanol–cooled glass trap, and the CO_2 gas was then passively passed through a glass trap filled with silver wool and another trap densely packed with Poropak Q (filled length: 13 cm, inner diameter: ~8 mm) held at –35 °C. The purified CO_2 gas was afterward transferred to one of two mass spectrometers for analysis (mass spectrometer “Pinta” and “Nina”; Table DR1[1]). Mass spectrometric analyses were performed on a MAT 253 and followed the procedures described by Huntington et al. (2009) and Dennis et al. (2011). The sample gas was measured against an Oztech reference standard ($\delta^{13}C$ = –3.63‰ VPDB, $\delta^{18}O$ = –15.79‰ VPDB). Heated gases (1000 °C), water-equilibrated gases (25 °C), and two carbonate standards (Carrara Marble and ETH3) were measured regularly to transfer the measured values into the absolute reference frame (Dennis et al., 2011; Table DR1 [see footnote 1]). Sample measurements were rejected based on elevated 48 and 49 signals, and each sample was analyzed until at least 2–3 replicates were deemed uncontaminated (Table DR1 [see footnote 1]). The Δ_{47} values were linearity-corrected using heated gas data (Huntington et al., 2009) and corrected for isotope fractionation during phosphoric acid digestion using the correction of 0.069‰ for phosphate (based on Guo et al., 2009). The Δ_{47} values are reported in the absolute reference frame of Dennis et al. (2011), and the equation of Passey and Henkes (2012) was used to calculate the temperature of formation of the carbonate fluorapatite.

RESULTS

XRD Results

The XRD spectra of three samples of the D-phosphate (representing all three stratigraphic horizons sampled) contain almost pure carbonate fluorapatite (Fig. 4); this has been compared to the XRD analysis of synthetic carbonate fluorapatite produced by Regnier et al. (1994). In all three samples, there is a trace amount of quartz, and in samples 137 and 142A, there are traces of both zeolite and opal-CT. Figure 4 shows the low relative abundances of the other minerals within the samples. There are no traces of calcite or dolomite, implying that the carbonate associated with carbonate fluorapatite is the only possible source for CO_2 during orthophosphoric acid digestion.

Using the equations derived by Schuffert et al. (1990), which relate the spacing of the 004 and 410 XRD reflections to the associated carbonate content of the carbonate fluorapatite, the weight percentage of carbonate within the carbonate fluorapatite was calculated as 4.8% (±0.3%) for samples 137 and 142A and 4.3% (±0.3%) for sample 141A.

Conventional Stable Isotope Results

Both the $\delta^{13}C$ and $\delta^{18}O$ values of carbonate fluorapatite vary over a wide range of values and across stratigraphic horizons (Fig. 5). Samples 141 and 141A both contain lower values of $\delta^{13}C$ and $\delta^{18}O$ when compared to samples 137 and 142A and 142B. The range of $\delta^{13}C$ values in samples 137, 142A, and 142B is from 4.9‰ to 7.7‰, and the range in $\delta^{18}O$ values is between –9.3‰ and –6.3‰. However, the range in $\delta^{13}C$ for samples 141 and 141A is 1.3‰–5.2‰ and the $\delta^{18}O$ range is between –7.5‰ and –6.3‰. There is no clear trend observed in the isotopic composition of the different phases of the phosphate, i.e., between D-phosphate, F-phosphate, and phosphatic layers (Fig. 6).

Clumped Isotope Results

The Δ_{47} results for three samples from different hardgrounds gave values of 0.599‰ ± 0.011‰ for sample 137, 0.613‰ ± 0.012‰ for sample 142A, and 0.615‰ ± 0.012‰ for sample 142B. Clumped isotope measurements were challenging, with failure rates of 50% (Table DR1, showing the replicates with contamination parameters suggesting a clean sample [see footnote 1]). The reproducibility of replicates with no traces of contaminant was very good, however, with 1 standard error of 0.01‰. The resulting temperatures for cleaned aliquots were 61 °C ± 5 °C for samples 142A and 142B and 66 °C ± 5 °C for sample 137. As shown in Figure 7, these are all within 1 standard deviation of each other, which suggests that the temperature of (re)equilibration of carbonate fluorapatite for these three horizons was similar.

DISCUSSION

Carbonate Content of Carbonate Fluorapatite

Carbonate fluorapatite is known to gradually recrystallize with increasing depth, as shown by McArthur (1985), Glenn et al. (1988), Shemesh (1990), and Föllmi et al. (2005). The relationship of increasing crystallinity and decreasing carbonate content with increasing depth of burial could lead to isotopic exchange and alteration of the $\delta^{18}O_{phosphate}$. As the phosphate content of the carbonate fluorapatite is generally accepted to

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[1] GSA Data Repository item 2015165, containing all sample results (part A) and reference frame material for both mass spectrometers (part B), is available at http://www.geosociety.org/pubs/ft2015.htm or by request to editing@geosociety.org.

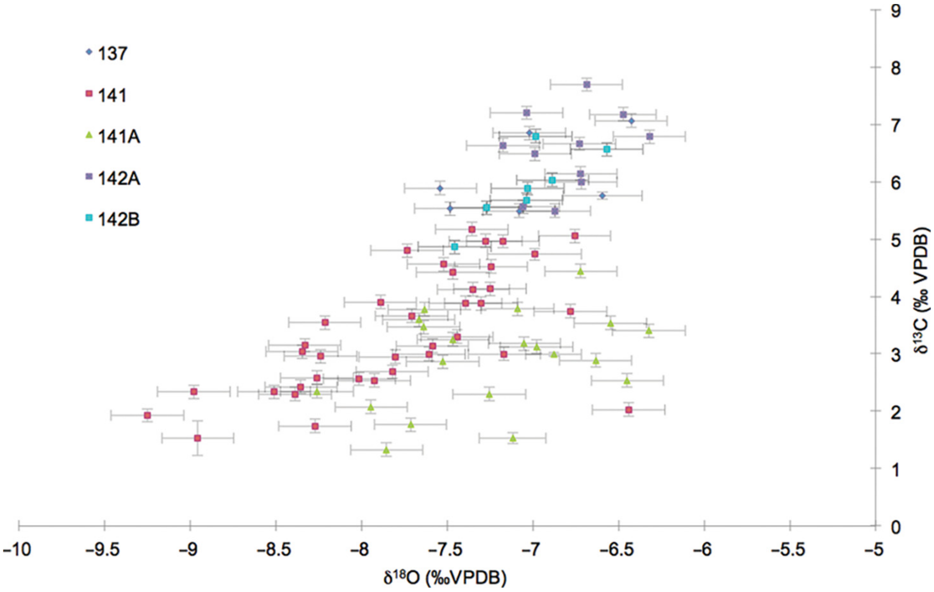

Figure 5. Plot showing δ^{18}O vs. δ^{13}C of carbonate fluorapatite samples in the studied stratigraphic horizons. The error bars represent ±1σ (the standard deviation) of the homogeneity of the samples; VPDB—Vienna Peedee belemnite.

be more refractory than the substituted associated carbonate measured here (Schoeninger and DeNiro, 1982; Shemesh et al., 1988; Iacumin et al., 1996), the associated carbonate ion is likely to also be altered during burial recrystallization. The carbonate content of the carbonate fluorapatite in this study, determined from the XRD results of the samples, is between 4.3 and 4.8 wt% (±0.6%), which suggests a decrease in the substitution of CO_3^{2-} within the mineral lattice due to a burial depth of around 1 km, if compared to the data of Gulbrandsen (1970) and Claypool et al. (1978) presented by McArthur (1985), who concluded that the carbonate content of carbonate fluorapatite starts at 5 wt% and decreases by around 0.3 wt% per km of burial. This estimate of 1 km of burial is of course dependent on a number of assumptions, notably on the initial content of carbonate ions within carbonate fluorapatite, and it relies on the heat flux in the Santa Barbara Basin being similar to the study of McArthur (1985). However, based on isotopic data, Shemesh (1990) concluded that the Monterey Formation experienced a wide range of diagenetic conditions that vary spatially, i.e., different subbasins or outcrops could have experienced very different conditions. Thus, the 1 km burial for the El Capitan Basin section is plausible, and this spatial variation in maximum burial across basins could lead to significant variation in the isotopic signatures being observed at different locations within the Monterey Formation.

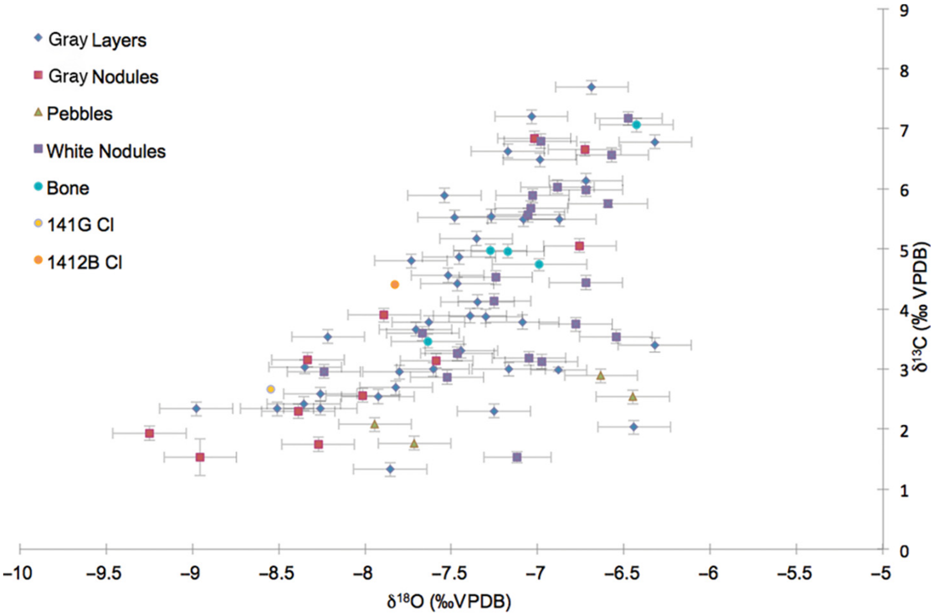

Figure 6. Plot showing the δ^{18}O vs. δ^{13}C of the different types of phosphate sampled. Gray nodules and layers are D-phosphates, and the white nodules are F-phosphates. The error bars represent ±1σ (the standard deviation) of the homogeneity of the samples; VPDB—Vienna Peedee belemnite.

Isotopic Composition of the Carbonate Fluorapatite at El Capitan State Beach

The Miocene seawater curve is well defined by studies of the isotopic composition of benthic foraminifera: The value of δ^{13}C in the Miocene ranges between –1‰ and +1.5‰, and specifically between +0‰ to 1‰ (Woodruff and Savin, 1991) for the studied interval (12.7–10.8 Ma). Carbon isotopes are, however, heavily impacted by local fluxes between the organic and sedimentary carbon reservoirs, and Flower and Kennett (1993) reported benthic foraminiferal δ^{13}C values between –0.5‰ and –2.5‰ at the Naples Beach section, less than a kilometer away from our study area. Previous work has shown that carbonate fluorapatite precipitates in isotopic equilibrium with the dissolved inorganic pool (DIC) of the pore water, and thus that carbonate fluorapatite δ^{13}C will be representative of pore-water (or marine) values (Glenn et al., 1988). The positive δ^{13}C values (+1.5‰ to +8‰) and the negative δ^{18}O values (–9.5‰ to –6‰) we measured in the associated carbonate in the carbonate fluorapatite of hardgrounds thus suggest that the isotopic signature observed results from diagenetic alteration. The δ^{18}O of minerals reflects both the isotopic composition of the parent fluid and the temperature of formation or the temperature in which isotopic reequilibration was reached during diagenesis (Zazzo et al., 2004). A higher temperature causes a greater depletion in δ^{18}O. Hence, the depleted δ^{18}O of the associated carbonate of the carbonate fluorapatite (–9.5‰ and –6‰) suggests diagenetic reequilibration of the carbonate fluorapatite, since the measured values are much lower than the δ^{18}O signature of benthic foraminifera at Naples Beach (Santa Barbara Basin) in the Miocene, i.e., –0.5‰ to 2‰ (Flower and

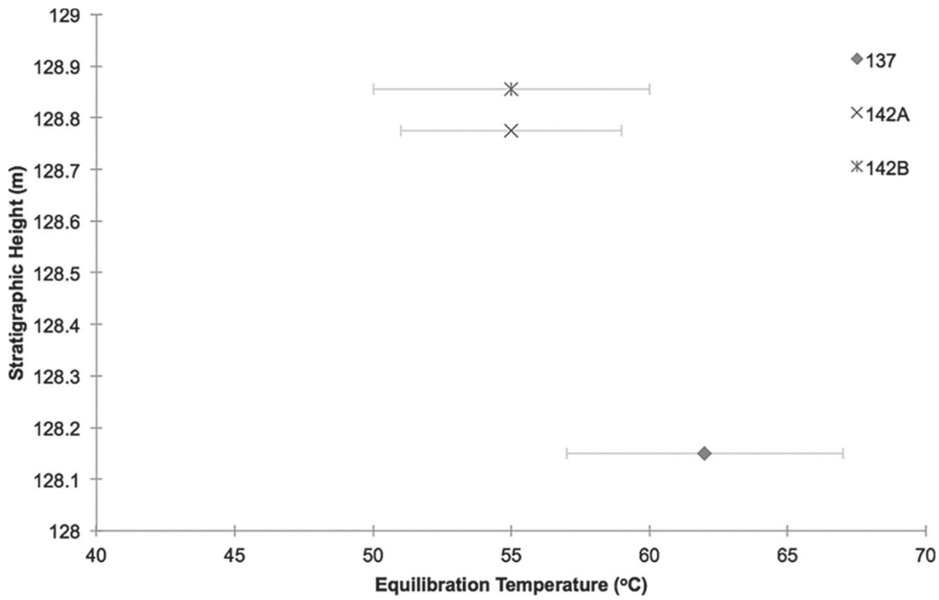

Figure 7. Plot showing the stratigraphic height of the samples vs. the temperature of equilibrium calculated from the average Δ_{47} for each stratigraphic horizon from three repeated analyses. The error bars represent ±1σ (the standard deviation) of the calculated temperature.

Kennett, 1993; Leather, 1994; Lear et al., 2000). Using the formula from Kim and O'Neil (1997), and the clumped isotope–derived temperatures (average of 63 °C), the calculated formation water δ^{18}O is ~1‰ relative to Vienna standard mean ocean water (VSMOW; Table DR1, range of calculated water of –1‰ to +2‰ SMOW [see footnote 1]). This implies very little contribution of oxygen exchanged from the diatomite and opal-CT of the Upper Monterey Formation, as these would drive the δ^{18}O of connate waters to higher values (Behl and Garrison, 1994). We conclude that the carbonate fluorapatite within phosphatic hardgrounds recrystallized in an open system surrounded by largely marine pore water, although we cannot exclude the possible contribution of minor amounts of silica-derived waters to the pore system.

The δ^{13}C of associated carbonate in carbonate fluorapatite has been analyzed at many locations around the world and generally shows negative values (Kolodny and Kaplan, 1970; McArthur et al., 1986; Shemesh et al., 1988). Recent work by Loyd et al. (2012) on carbonate concretions in the Monterey Formation, however, shows positive to highly positive δ^{13}C values. Enriched δ^{13}C values are interpreted to result from recrystallization within a zone of fermentation (Curtis et al., 1977; Hudson, 1977; McArthur et al., 1980; Loyd et al., 2012), where methanogenesis occurs. During the formation of methane, the lighter ^{12}C is preferentially included in the methane due to kinetic isotopic fractionation. Methane derived from thermal methanogenesis has average values of –49‰ (Vinogradov and Galimov, 1970), and bacterial methane has an average composition of –75‰ (Claypool et al., 1973). The enriched δ^{13}C at El Capitan State Beach suggests that the carbonate fluorapatite recrystallized within the zone of methanogenesis, at the same time as carbonate concretions (Fig. 8). This zone extends from between 2 and 100 m to around 1 km of burial (Nissenbaum and Kaplan, 1972; Curtis et al., 1977; Hennessy and Knauth, 1985), depending on the thermal gradient and protolith composition. The data are thus consistent in suggesting that the carbonate fluorapatite reached a maximum diagenetic zone of the lower bacterial methanogenesis zone. In this lower part of the zone, the depleted CO_2 formed by the thermocatalytic decarboxylation of organic matter reduces the δ^{13}C of the CO_2, and hence the HCO_3^-, which is recorded by associated carbonate, relative to the maximum that would be expected in the methanogenic zone.

No correlation is apparent between δ^{13}C or δ^{18}O and the type of phosphate that was measured (i.e., nodule, bone, or layers; Fig. 6). However, stable isotopes clearly show that although marine water was the main connate fluid, the carbonate fluorapatite was also reequilibrated during diagenesis because the variation in δ^{13}C and δ^{18}O between hardgrounds is too great to be related solely to initial differences in isotopic signature during the 2 m.y. of hardground deposition (John et al., 2002; Fig. 5). A complication in interpreting the data is that recrystallization would affect all the different phases of phosphate at the same time, but with variable effects depending on the initial isotopic composition of the nodules, the rock-water ratio within individual hardgrounds (a function of porosity and permeability of each hardground), the burial temperature reached at the time of recrystallization, and the density of the individual carbonate fluorapatite crystals. This explains why individual hardgrounds, although only separated by a few meters of stratigraphy, plot in distinct fields in δ^{18}O versus δ^{13}C plots (Fig. 5). Samples 137 and 142 (A and B) generally show a less-depleted δ^{18}O signature correlated with a more-enriched δ^{13}C signature than samples 141 and 141A. Interestingly, samples 137 and 142 (A and B) are the highest and lowest hardground recovered in the stratigraphy, respectively, suggesting some lithologic control on the pattern observed. There may have been more active methanogenesis to deplete the pore water in ^{12}C for samples 141 and 141A, which in turn may have been related to a greater availability of organic matter surrounding these hardgrounds during recrystallization. However, it could also have been related to a low fluid flow through the beds located in the center of the phosphatic hardgrounds interval, which would reduce the influx of isotopically depleted carbon dioxide from the decarboxylation zone below. A final possibility is that each hardground records the isotopic signature of the pore water at the stage and temperature when recrystallization stopped. However, we discard this option on the grounds that previous work shows that the recrystallization of carbonate fluorapatite occurs throughout burial, with recrystallization continuing to much greater depths than found within this study (McArthur, 1985), and that the clumped isotope temperatures measured in our study are within error of each other.

Diagenetic Grade

The enriched δ^{13}C signal combined with the depleted δ^{18}O signal suggest that the samples measured from El Capitan State Beach were fully recrystallized within the methanogenic zone. In modern ocean sediments, the methanogenic zone extends to around 250 m below the seafloor (Sivan et al., 2007), but the data collected from the study of the multiply substituted isotopologues suggest that the temperature of recrystallization was around 57 °C, which suggests a deeper burial and possibly a higher geothermal gradient as was demonstrated for the nearby Santa Maria Basin (45–60 °C/km; Williams et al., 1995). Previous work in the North Sea has shown that there are thermophilic

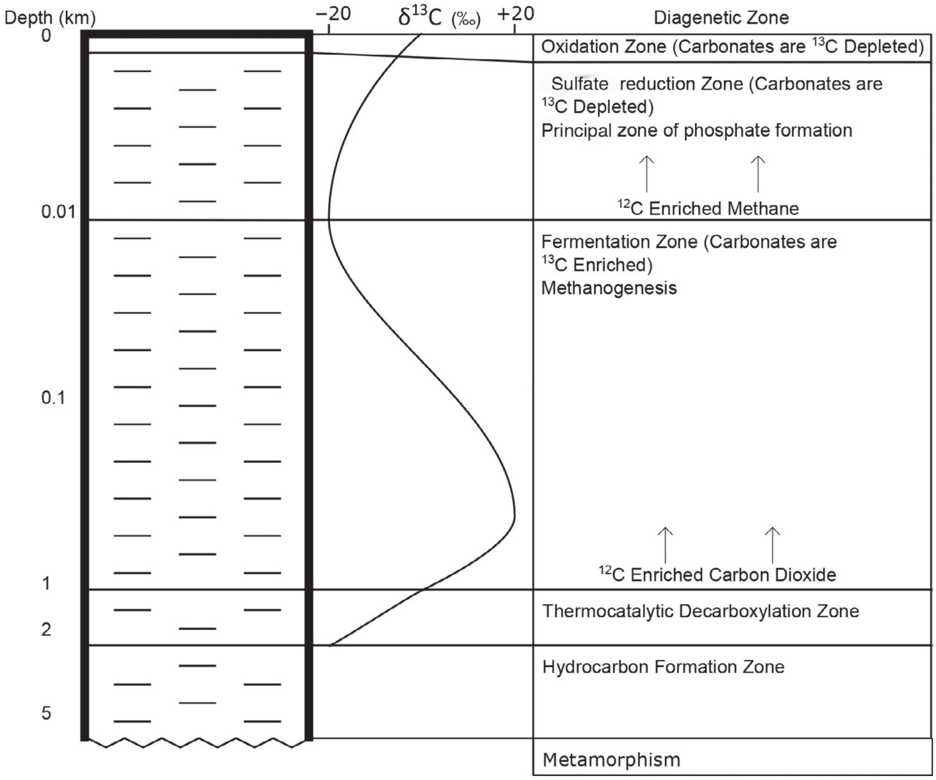

Figure 8. Zones of diagenesis and modeled δ^{13}C of the pore water in a marine environment. Diagenetic zones are modified from Curtis et al. (1977) and Tourtelot (1979). The δ^{13}C profile is modified from Claypool and Kaplan (1974) and Hennessy and Knauth (1985).

methanogens capable of producing methane within a temperature range from 17 °C to 62 °C, with an optimum temperature at 60 °C (Nilsen and Torsvik, 1996), which supports work in the Santa Clara Avenue oil field in the Monterey Formation and other locations showing bacterial methanogenesis occurring up to temperatures of 80 °C (Carothers and Kharaka, 1980; Morad, 1998; Orphan et al., 2000). This, combined with the high organic matter content, as documented by John et al. (2002), suggests that the methanogenic zone may have extended to greater depth in the Miocene in this region than in current sediments. Rock-Eval analysis showed a signal consistent with type II kerogen (marine origin; John et al. 2002), which can start producing oil at temperatures around 80 °C, often with closely coupled biogeochemical cycling of carbon and sulfur by thermophilic microbes (Orphan et al., 2000; Head et al., 2003; Berndmeyer et al., 2012).

Previous work undertaken by Isaacs (1982) and Keller and Isaacs (1985) proposed the use of silica phase transitions as a geothermometer. This suggested that within the Santa Barbara Basin in the Monterey Formation, and for rock composed of 30%–80% biogenic or diagenetic silica not dissimilar to the hardgrounds investigated here, the phase transition from opal-A to opal-CT and then to quartz occurred at two distinct temperature ranges of 43–49 °C and 65–85 °C. The XRD spectrum produced in this study when combined with the clumped isotope temperature fits well within these two ranges, as the opal peak is narrower and well defined, pointing to opal-CT rather than quartz (Jones and Segnit, 1971; Elzea et al., 1994). This suggests that the two geothermometers, clumped isotopes and opal phase transitions, can be used to classify the maximum temperature that the formation reached during diagenesis (in this case, 61–66 °C, concurrent with the silica thermometer estimate of >43 °C and <85 °C).

Comparison of the Isotopic Composition of El Capitan State Beach with Other Areas in the Monterey Formation

Leather (1994) sampled four different locations in two basins in the Monterey Formation, and our data set approximately doubles the available data for this region. This offers an opportunity to study regional trends in carbonate fluorapatite diagenesis. The data from Leather (1994) significantly differ from ours (Fig. 9), so we assessed the possibility of experimental bias. It has only recently been shown that the fractionation factor of associated carbonate is not the same as the fractionation factor of calcite (Passey et al., 2007), which was previously used (Kolodny and Kaplan, 1970). However, analysis of the two differing fractionation factors at the temperature measured shows a variation of around 0.01‰, which is one order of magnitude less than the reproducibility of triplicate samples analyzed. Furthermore, a direct comparison of the method used in Leather (1994) versus the 70 °C reaction on a Kiel device yielded no differences (see Methods). This suggests that the observed differences in the samples are real, rather than bias linked to the method.

The phosphates studied by Leather (1994) were not found within hardgrounds, but were small nodules or laminae of phosphate found within phosphatic calcareous mudstones sampled over a much wider stratigraphic range compared to the focus on discrete hardground layers within this study. Phosphates in hardgrounds are probably more susceptible to diagenetic transformations, as was demonstrated for organic biomarkers preserved within the Monterey Formation by Berndmeyer et al. (2012). The hardground-hosted carbonate fluorapatite may thus more faithfully reflect the diagenetic conditions reached by the sediments. Moreover the samples studied by Leather (1994) have a purity of only 50%–95% carbonate fluorapatite, although it seems unlikely that this would have impacted the range in δ^{13}C and δ^{18}O observed here.

The results from Leather (1994) clearly show that there are three separate groups of isotopic compositions within the carbonate fluorapatite (Fig. 9). The δ^{13}C and δ^{18}O values measured within the Santa Barbara Basin contain all three separate clusters: The average value of the phosphates measured at El Capitan State Beach is 4.1‰ for δ^{13}C and 7.4‰ for δ^{18}O. The associated carbonates measured at Naples Beach show a trend of enrichment in δ^{13}C compared to depletion in δ^{18}O, with a range of values between –2.6‰ and 3.8‰ for δ^{13}C and between –4.1‰ and 0.1‰ for δ^{18}O. The δ^{13}C and δ^{18}O values of the associated carbonate of the carbonate fluorapatite at Gaviota Beach are clustered around –5.9‰ and –3.5‰, respectively.

It is likely that the three different isotopic signatures in different sample locations within the Santa Barbara Basin (Fig. 9) reflect different diagenetic zones in which partial reequilibration of the isotopic signature of the carbonate fluorapatite occurred, thus masking the early formation signature as observed at El Capitan State Beach. The Naples Beach data show a trend of enrichment in δ^{13}C compared to depletion in δ^{18}O. This suggests that the sampled area

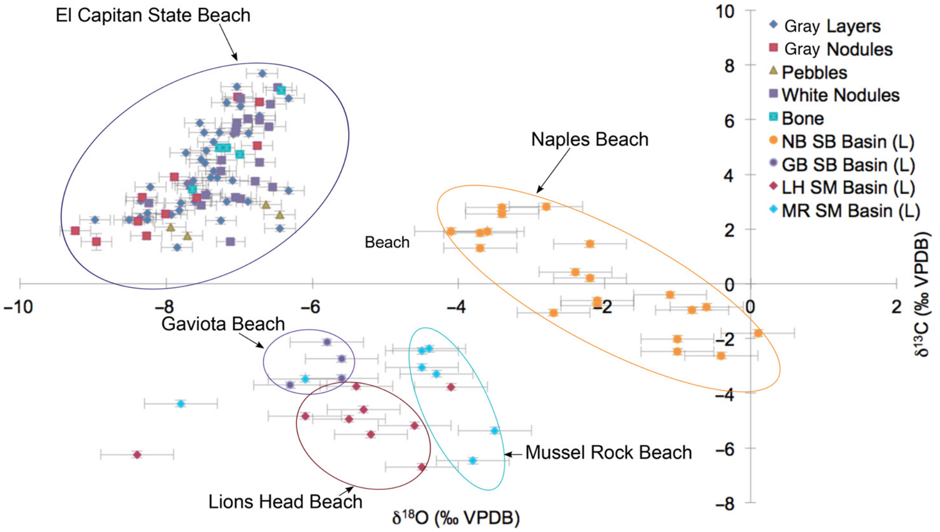

Figure 9. Plot showing δ^{18}O vs. δ^{13}C of different sampled locations within the Monterey Formation. Naples Beach and Gaviota Beach are both located in the Santa Barbara Basin (SB), whereas Lions Head Beach and Mussel Rock Beach are located in the Santa Maria Basin (SM). The (L) stands for data collected by Leather (1994). The error bars represent ±1σ (the standard deviation) of the homogeneity of the samples; VPDB—Vienna Peedee belemnite. Gray nodules and layers are D-phosphates, and the white nodules are F-phosphates.

was at the top of the methanogenic zone, with the increasing depth (decreasing δ^{18}O) leading to enrichment in δ^{13}C. However, the samples from Gaviota Beach show a negative δ^{13}C trend, combined with negative δ^{18}O. This suggests that these samples were formed deeper, at increased temperature of burial when compared to Naples Beach to the east (Fig. 8). The Santa Barbara Basin shows a progressive increase in diagenetic grade from east to west, as shown by the study of silica phase changes (Isaacs, 1980, 1983). This agrees with the data from Shemesh (1990), showing that samples from Gaviota Beach had a high crystallinity index due to deeper burial. Hence, the regional diagenetic gradient of the Monterey Formation can explain the higher diagenetic grade of the El Capitan State Beach section compared to the Naples Beach section, as it is located to the west. However, our oxygen isotopic data also show that this diagenetic gradient does not completely control the δ^{18}O of phosphatic nodules.

The δ^{13}C and δ^{18}O values measured in the Santa Maria Basin show less difference between different sections. The Lions Head Beach data are clustered around –5.5‰ and –5.2‰ for δ^{13}C and δ^{18}O, and the Mussel Rock Beach data are clustered around –4.5‰ and –4.1‰ for δ^{13}C and δ^{18}O. The isotopic signatures of both of these sites are similar to the Gaviota Beach samples. It has been suggested that these locations within the Santa Maria Basin were deeply buried with a high geothermal gradient (Pisciotto, 1978; Leather, 1994), which would support the fact that the carbonate fluorapatite samples from this location have reached the zone of decarboxylation, located between 1 and 2 km depth (Fig. 6). This would have led to the depleted δ^{13}C signatures observed in the Santa Maria Basin. Zaback and Pratt (1992) concluded that the Santa Maria Basin was sediment starved, which can lead to an upward migration of the diagenetic zones, including the decarboxylation zone. One puzzling observation is that in the carbonate fluorapatite of the sections at Gaviota, Mussel Rock, and Lions Head Beach, all located westward of El Capitan State Beach and probably more deeply buried, the δ^{18}O is more positive than the one measured in our study, but the δ^{13}C is more negative. Hence, there is an apparent contradiction between what the δ^{18}O indicates (cooler temperature of precipitation than at El Capitan State Beach), and the known regional burial history. As mentioned already, it is possible that the diagenetic pathway taken by phosphatic hardground is very different than the pathway taken by the carbonate fluorapatite nodules measured in the Leather (1994) study, thus explaining the apparent contradiction. However, it is also possible that an important factor that controls the δ^{18}O of carbonate fluorapatite at greater burial is the effect of silica diagenesis impacting pore-water chemistry. The sections at Gaviota Beach and Mussel Rocks were more deeply buried and lie within the quartz zone. We suspect that with increasing burial at these westward locations, silica-derived waters with more positive δ^{18}O values liberated during diagenesis were being supplied to the sediment, thus pushing the carbonate fluorapatite δ^{18}O to more positive values during recrystallization (Behl, 1992).

CONCLUSION

For the first time, we applied the clumped isotope paleothermometer to sedimentary carbonate fluorapatite, and comparisons with previous work on silica phase transitions within the Santa Barbara Basin validate the use of this novel geochemical approach to reconstructing the thermal and diagenetic history of this type of material. This study also confirms that the stable isotopic composition of the phosphatic hardgrounds within the Monterey Formation reflects a late diagenetic, rather than authigenic, history of the carbonate fluorapatite. The different occurrences of carbonate fluorapatite investigated all show signatures recording diagenetic recrystallization, and, hence, little information linked to the relative ages of the different phases is retained. All carbonate fluorapatite recrystallized within the methanogenic zone, which is shown by the enriched δ^{13}C and the elevated temperature of recrystallization documented through the use of clumped isotopes. However, the middle Miocene methanogenic zone is proposed to have extended to a greater depth than currently within the Santa Barbara Basin, probably due to the high sedimentary organic content linked to high productivity in this upwelling region. The distinct isotopic signatures observed between different hardgrounds suggest that specific conditions, such as density of the carbonate fluorapatite, initial stable isotopic composition of the phosphate, and rock-water ratio, all impacted the stable isotopic signature of the carbonate fluorapatite during recrystallization. In addition, we suggest that for deeply buried locations westward of El Capitan State Beach, the silica-bond water expelled during silica recrystallization drove the δ^{18}O of connate waters to more positive values. We conclude that the investigation of phosphatic hardgrounds and phosphatic nodules does not directly yield information on paleoceanographic signatures, for instance reflecting the middle Miocene cooling event, but rather that carbonate fluorapatite will faithfully record burial temperatures and diagenetic processes. The novel use of clumped isotopes to measure a recrystallization temperature of the carbonate fluorapatite thus adds valuable constraints to the depth and temperature at which diagenetic transformations occurred, and this approach can be used on sedimentary phosphates occurring in other continental margins.

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