An alkenone (U_{37}K') quasi-annual sea surface temperature record (A.D. 1440 to 1940) using varved sediments from the Santa Barbara Basin

Meixun Zhao\textsuperscript{a,}\textsuperscript{*}, Geoffrey Eglinton\textsuperscript{b,c}, Gareth Read\textsuperscript{b}, Arndt Schimmelmann\textsuperscript{d}

\textsuperscript{a}Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA
\textsuperscript{b}Biogeochemistry Centre, Department of Earth Sciences, University of Bristol, Bristol BS8 1TR, UK
\textsuperscript{c}Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, MA 02543, USA
\textsuperscript{d}Department of Geological Sciences, Indiana University, Bloomington, IN 47405-1403, USA

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Abstract
Analyses for C_{37} alkenones (U_{37}K') and total organic carbon (TOC) in a varved core from the depocenter of the Santa Barbara Basin (34°13.5'N, 120°01'W, 590 m water depth) have been made on an approximately 1–2 year basis from A.D. 1440 to 1940. The U_{37}K'-based sea surface temperature (SST) record oscillates around 15.5°C with an amplitude of less than 3°C at approximately interannual, decadal, and centennial frequencies. Historical El Niño/Southern Oscillation (ENSO) events are matched only partially by warmer U_{37}K' SSTs. Three records: our SST, a published Pacific coral d\textsuperscript{18}O, and a published tree-ring temperature anomaly from the California valleys, show no evidence of colder temperatures during the Little Ice Age (ca. 1500 to 1840 A.D.). Significantly, there is a strong centennial-scale cyclicity in the U_{37}K' SST record which approaches 1°C in amplitude. TOC burial and alkenone fluxes are largely controlled by sedimentation rate as expressed in varve thickness. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Molecular stratigraphy; Alkenones; SST; U_{37}K'; Santa Barbara Basin; Varved sediments; Little Ice Age; ENSO; Centennial scale oscillation

1. Introduction
Continuous, high resolution climate records of the past few hundred years are needed for predictive modeling, but few have been reported (e.g. Martinson et al., 1995; Overpeck et al., 1997; Mann et al., 1998). Interpretation of the processes responsible for 20th century warming will benefit from the availability of more records on a decadal to centennial scale. This paper reports a quasi-annual resolution record for the last 500 years of U_{37}K' sea surface temperature (SST) for the Santa Barbara Basin (SBB), off southern California.

* Corresponding author. Tel.: +1-603-646-2150; fax: +1-603-646-3922.
E-mail address: meixun.zhao@dartmouth.edu (M. Zhao).

The Little Ice Age (LIA) is commonly known as a centennial-scale cold climate event, mostly documented in the Northern Hemisphere, that started ca. 1500 A.D. and terminated just before the acceleration of anthropogenic activities (Grove, 1988). Although terrestrial records of LIA climatic variability have been well-documented (Grove, 1988; Bradley and Jones, 1993; Mann et al., 1998), the extent of oceanic changes during the same period is less well known (Dunbar et al., 1994; Keigwin, 1996). A key parameter in any paleo-reconstruction relating climate and oceanography is SST, since heat transfer between ocean and atmosphere is fundamental to the generation of climate. The El Niño/Southern Oscillation (ENSO) phenomenon (Philander, 1990; Diaz and Markgraf, 1992) in the Pacific has dramatically highlighted the importance of changes in SST, since it is clear that ENSO effects and
telecommunications extend from southeast Asia beyond the Americas to Europe, Africa, India and worldwide (Kiladis and Díaz, 1989; Philander, 1990; Charles et al., 1997; Neelin and Latif, 1998).

The surface water circulation is, to a first approximation, westwards in the east Pacific both north and south of the equator (Fig. 1). The ENSO events occur irregularly over periods of 2–11 years, and are characterized by a general warming of the tropical east Pacific waters of roughly one year duration. Thus, the waters off Peru during strong/very strong El Niño events, such as those of 1982 and 1997, show strong positive SST anomalies of up to 5°C as compared with the non-El Niño years. Further to the west and north in the vicinity of the Galapagos Islands, the warmer equatorial waters exhibited somewhat smaller SST anomalies of ca. 3°C. In the Northern hemisphere along the California coast, the SST anomalies are even smaller, for example 1–2°C for the 1982 and 1997/8 ENSO (Rasmusson and Hall, 1983; Neelin and Latif, 1998). Much socio-economic interest attaches to the ENSO climatic pattern. Thus, unusual weather events have been documented intermittently for the east Pacific rim since the initial Spanish occupation (Quinn, 1992). However, more continuous

Fig. 1. Map of the Eastern Pacific region showing the surface currents (modified from Fig. 7.24 in Pickard and Emery, 1982). The location of Puerto Chicama is also shown. Inset A: coring site and the drainage area of the Ventura and Santa Clara Rivers that supply terrigenous materials to the Santa Barbara Basin, offshore southern California. Sediment inputs from the rivers are indicated by small arrows. Surface currents are shown by thick arrows. Inset B: the Galapagos Islands.
proxy records are available in the sediments off the California coast, where the varved deposits in the SBB provide a particularly valuable source of information (Schimmelmann and Tegner, 1991).

1.1. The Santa Barbara Basin

The SBB lies within a highly productive coastal region of the Pacific Ocean (Soutar and Crill, 1977; Schimmelmann and Tegner, 1991). Its high productivity contributes to high sedimentation rates (3–5 mm year^{-1} in recent years) and high organic carbon content (2–5\%). Oxygen depletion in the bottom water of the depocenter (Sholkovitz and Gieskes, 1971) inhibits bioturbation by macrobenthos and allows for the preservation of millimeter-scale laminae (Soutar and Crill, 1977; Reimers et al., 1990; Thunell et al., 1995). Past variations in paleoceanographic parameters, such as SST, upwelling strength, productivity and intensities of the California Current, could have been registered on an almost annual basis in the sediment record.

SST in the SBB and the Southern California Borderland region in general are influenced by: (1) the colder and relatively nutrient-rich, southward-flowing California Current (Fig. 1), which is strong during spring and summer; (2) the warm and nutrient-poor northward-flowing Davidson Current (Fig. 1), which is strong during winter (Hickey, 1979); (3) the seasonal (mostly spring and summer) upwelling of the cold and nutrient-rich Pacific Intermediate Waters, which is driven by the northerly trade winds caused by the North Pacific high (Thunell and Sautter, 1992). Recent shipboard, buoy and satellite data (e.g. Winant and Hendershott, 1996) show that cold water from the North mixes extensively with the warm coastal waters, creating cyclonic flow within the Basin and numerous eddies. Due to the complex and variable interaction of the currents and the seasonal upwelling, productivity in the SBB surface waters shows a large seasonal variation while SST varies from 10 to 18\°C (cf. Kennedy and Brassell, 1992b). Instrumental SSTs recorded in the SBB by the CalCOFI studies do not show a well-defined seasonal pattern, although satellite temperature estimates and sea level heights reveal a more consistent seasonal cycle in the SBB (Harms and Winant, 1998). During typical ENSO years, the California coastal region experiences weakened upwelling, accompanied by a deeper thermocline, while the warm Davidson current extends northwards and the flow of the cold California current slows, resulting in a generally warmer SST and lower productivity (Hayward et al., 1994).

1.2. Molecular stratigraphy-U_{37}^C, SST

Recent developments in biomarker geochemistry have included molecular tools suitable for high resolution climatic reconstruction (Brassell, 1993). The C_{37} long-chain unsaturated ketones (alkenones) are lipid biomarkers whose biological source is known only from a narrow range of marine microalgae belonging to the class of Haptophyceae (Prymnesiophyceae), of which Emiliania huxleyi is an important contemporary member (Volkman et al., 1980a,b; Marlowe et al., 1990). The U_{37}^C index [C_{37:2}/(C_{37:2}+C_{37:3})], based on the ratio of the C_{37:2} and C_{37:3} alkenones, has been widely used to reconstruct past SST (for example, Brassell et al., 1986; Prahl and Wakeham, 1987; Eglinton et al., 1992; Prahl et al., 1995; Rosell-Mélè et al., 1995; Zhao et al., 1995a; Müller et al., 1997; Villanueva et al., 1998) and the abundances and accumulation rates of the alkenones have been used to estimate haptophyte productivity (e.g. Prahl et al., 1993; Villanueva et al., 1995). Small sample requirements and the ability to achieve high sample throughput with automation of analytical procedures make SST molecular stratigraphy especially suitable for high resolution paleoclimatic applications. This technique has been applied for the estimation of modern and last glacial surface waters of the California Current system (Doose et al., 1997), and for the reconstruction of SBB SST by Kennedy and Brassell (1992a,b) and by Herbert et al. (1998), with an approximate annual resolution record from ca. 1915 to 1990. Additionally, lower resolution SBB U_{37}^C data for the Holocene have been published by Herbert et al. (1995) and Hinrichs et al. (1997) using ODP Hole 893 samples.

The present paper extends and further develops our preliminary report (Zhao et al., 1995b) of a U_{37}^C SST record for a site in the depocenter of the SBB, back into the 15th century. We present 1–2 year resolution molecular records of U_{37}^C SST and alkenone content for the period A.D. 1440 to 1940 and compare them with parallel data of TOC and varve thickness for the same sample set. We have evaluated the variations of the U_{37}^C SST record in the context of past ENSO influences and of the oceanic response to the LIA in the southern California Borderland. The TOC and alkenone fluxes are evaluated as indicators of paleoproductivity/preservation.

2. Methods

2.1. Samples

Box cores were recovered from the depocenter of the SBB in 1987 and 1988 (SABA87-1, SABA87-2, SABA88-1) (Fig. 1). Subcoreing was performed on board ship immediately and the subcores stored for later X-radiography and geochemical/paleontological sampling. Each box core provided three to five cyclindrical cores taken with transparent acrylic tubes (8.3 cm i.d., 75 cm long with sharpened bottom rim; Schimmelmann et al.,
1990). The sediment in the acrylic tubes was then extruded and sectioned with a stainless spatula, layer by layer (1–5 mm). In most cases, distinct dark/light differences marked the boundaries between layers, which were then followed closely to minimize contamination of adjacent layers. One varve normally comprised a dark, clay-rich winter layer together with the adjoining light, carbonate/opal-rich biogenic layer. This sampling procedure ensured annual resolution. Each slice was then documented as containing one to a few varves by comparison with the pre-scanned sediment X-radiograph. Each layer was then freeze-dried and thoroughly mixed for sub-sampling prior to geochemical analysis. Freeze-drying was done immediately after sectioning of samples to minimize the oxidation of sulfides. The samples were then stored under nitrogen until the sulfur study was completed (Schimmelmann and Kastner, 1993). The samples were later stored dry under air at room temperature (20–25°C), prior to analyses for TOC and alkenones. The detailed procedure for TOC analysis is given in Schimmelmann and Tegner (1991). The cores were dated using varve-counts and correlation of varve thickness versus dendrochronological data (Schimmelmann et al., 1990; Schimmelmann and Lange, 1996). The samples used have been set against this scale as A.D. 1440 to 1940. The samples used in this study did not include thin gray “turbidites” or recognizable flood deposits (Schimmelmann and Lange, 1996). These sediment intervals were removed from the stratigraphic framework since they are regarded as effectively instantaneous deposition events. Dating and calculations across the bioturbated Macoma interval (ca. 1840) (Schimmelmann et al., 1992) assumed a constant sedimentation rate. Samples were not obtainable from our core after the 1941 varve due to heavy prior sampling.

2.2. Alkenones

Aliquots of 0.2 to 0.3 g of sediment (dry weight) were used for alkenone analyses. Sulfur was removed from the samples by adding ca. 0.2 g of ‘activated’ copper granules to the sediment before extraction. The copper had been activated with 0.5–2.0 M HCl for 1 h, rinsed with double distilled water, methanol (MeOH) and dichloromethane (DCM) before drying with N₂. After adding an internal standard (C₃₆ n-alkane), the samples were extracted (three times) with ultra-clean solvents (CH₂Cl₂/CH₃OH, 3/1 by vol.). Extractions were carried out using a semi-automated BenchMate robot workstation (Zymark Corp.), which handled the weighing of sediments, addition of internal standard, and the addition and transfer of liquid phases. The total extracts were purified by solid phase extraction using silica gel cartridges (500 mg Bond Elute, Varian), using the BenchMate. Solid phase extraction eliminates polar and large molecules, to avoid the injection of total extracts from the very organic-rich SBB samples which cause the deterioration of the resolution of the gas chromatography (GC) columns. The cleaned extracts were derivatized with 40 µl of N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) and alkenone contents were measured using a Varian 3400 GC fitted with an autosampler and a 50 m capillary column (Chrompack CP-Sil 5, 0.32 mm i.d., 0.25 µm film, H₂ carrier gas). GC data were acquired and processed using VG Minichrom software. Abundances of individual compounds were calculated by comparing their peak areas with those of the internal standard (C₃₆ n-alkane). SST was calculated from the U³⁷/S³⁷ index using the Prahl et al. (1988) calibration: SST (°C) = (U³⁷/S³⁷ – 0.039)/0.034. Alkenone contents (per dry weight) are expressed as the total of C₃₇:2 and C₃₇:3. A few of the sediment samples lacked sufficient amounts of sediment for alkenone analysis. The analytical error is about ±0.3°C in SST. In the SBB extracts, an unknown compound (possibly the C₃₆ methyl ester) often co-elutes with, or elutes very close to, the C₃₇:3 alkenone peak, under some chromatographic conditions. Since integration of this peak with the C₃₇:3 peak is undesirable (inclusion results in a slightly lower SST estimate), we took special care to make sure that these peaks were completely separated and that the integration of the alkenone peaks was accurate. The alkenone data will be submitted to the World Data Center-A for Paleoclimatology in Boulder, CO.

2.3. Burial flux calculation

The burial flux of the alkenones (ng cm⁻² year⁻¹) was calculated from contents in dry sediment (corrected for salt content) and from varve thickness data. The same procedure was also used to calculate TOC burial flux (Schimmelmann and Tegner, 1991). Since each sample can contain sediment deposited over several months to over 3 years, single point flux calculations can be misleading. This problem has been minimized by smoothing the data over five samples, where stated.

3. Results

Varve thickness (Fig. 2A; Schimmelmann and Lange, 1996) varied from 1 to 5 mm per year. The thickness varied between 1 to 3 mm from A.D. 1440 to 1640 and then increased to 5 mm and stayed generally high until 1730, but with major high frequency oscillations. The next 120 years are noted for thinner varves. Varve thickness was relatively large (3 to 4 mm) from 1860 to 1940, but also with major variations.

TOC contents (Fig. 2B) range from 2.2 to 3.8% by weight. The TOC record for the period 1840–1940 has been reported in Schimmelmann and Tegner (1991). The record shows many high frequency oscillations, notably
near 1475, 1600, 1760, 1840, 1870 and 1910 A.D. These TOC oscillations seem to be characterized by higher values followed by a sudden drop and a gradual return to reach the next maximum. From the mid-1700s to the mid-1800s, the oscillations decrease in frequency and amplitude.

Alkenone content (Fig. 2D) varied by a factor of 7 over the 500-year period, with a maximum of about 8 µg g⁻¹ and a minimum of 1 µg g⁻¹. The record reveals many oscillations on interannual, decadal and centennial timescales.

U³⁷ SST (Fig. 2F) varied by 3°C (14–17°C) over the 500-year period from A.D. 1440 to 1940. Of the 499 points, 83% fall in the range of 15 to 16°C, though numerous small SST oscillations on the order of 1–2°C occur over 3–4-year intervals. SST is generally lower around the turns of the centuries, while the higher SSTs are approximately midway.

The TOC burial flux (Fig. 2C) and the alkenone burial flux (Fig. 2E) are similar in general trend, except for the interval from 1840 to 1860. They resemble closely the plot of varve thickness (Fig. 2A), unlike the original content data (Fig. 2B and D). This underlines the dominance of the varve thickness in the burial flux calculation, at least qualitatively.

4. Discussion

4.1. U³⁷ SST in the Santa Barbara Basin

The U³⁷ SST technique has been used successfully in the Eastern Pacific region in a number of studies. However, problems with the interpretation of the significance of small differences in the U³⁷ values include the obvious ones of seasonality (the timing of the coccolithophore bloom), the depth of maximum production, and the nutrient availability. A recent paper by Epstein et al. (1998) based on isothermal culture experiments with a single clone has shown that extreme nutrient variation can affect U³⁷ SST by several degrees.

Very recently, Herbert et al. (1998) have published a substantive evaluation of the method using a latitudinal transect (23 to 40°N) along the Californian Margin, using core top samples, which included some from the SBB. They have convincingly demonstrated that U³⁷ measurements on individual varves from laminated sediments may be expected to give an average temperature for each quasi annual interval. Indeed, Kennedy and Brassell (1992a,b) had already presented U³⁷ SST results for a core from the SBB for the period 1915 to 1988, and a second record from almost the same site.

Fig. 2. Geochemical time-series of varved sediments from the Santa Barbara Basin with ca. 1–2 year resolution, A.D. 1440 to 1940. (A) Annual varve thickness (mm, Schimmelmann and Lange, 1996); (B) TOC content (% of dry, salt-free weight, Schimmelmann and Tegner, 1991); (C) a 5-point moving average of TOC burial flux (mgC cm⁻² year⁻¹); (D) the alkenone content (µg g⁻¹ dry, salt-free weight); (E) a 5-point moving average of alkenone burial flux (ng cm⁻² year⁻¹); (F) U³⁷ sea surface temperature (SST, °C). The thick line in Fig. 2F is a 50-point (ca. 50-year) moving average of SST to show the centennial scale oscillations. Data gaps result either from the presence of turbidites and flood deposits, or are due to insufficient sample for individual measurements. Dashed intervals in flux calculations bridge gaps that result from the exclusion of gray turbidites and flood deposits that do not constitute regular varves. These layers were not included in the burial flux calculation, because they contained unusual amounts of terrigenous materials in flood-related pulses not relevant to the SBB oceanography. F, flood layer of 1605, T, turbidite of 1738, M, Macoma layer of 1840 A.D.
covering a similar time period has now been described in the paper by Herbert et al. (1998) The \( U_{37}^{K} \) SST data in the present paper are also derived from a core from this site, but for a much longer time span (A.D. 1440 to 1940). Comparing the data for the 20th century in each of the three records (Table 1 and Fig. 3) gives us some measure of the reliability of \( U_{37}^{K} \) SST molecular stratigraphy based on varve counting; all these studies used the same equation: SST (°C) = \( (U_{37}^{K} - 0.039)/0.034 \).

In Fig. 3C, there is only a short time interval (A.D. 1919 to 1941) where all three sets of \( U_{37}^{K} \) SST values are available. It is evident that there are small differences in average SST between the three records, with ours being almost 0.5°C higher than those of Herbert et al. (1998) and almost 1°C higher than those of Kennedy and Brassell (1992a,b). These differences may have their origin in analytical methodology and sampling site location. The records despite being quite different in detail, do show some general similarities. Small differences may be caused by the difficulties inherent in varve chronology, such as the dissection and counting procedures. The accuracy of varve dating is ±2 years above 1840 (the Macoma Event; Schimmelmann et al., 1992), but as much as ±5 years below 1840 (Schimmelmann and Lange, 1996). The three curves display a warm maximum around 1941, which is a well-known ENSO event.

Table 1

<table>
<thead>
<tr>
<th>Cores</th>
<th>Location</th>
<th>Age range (A.D.)</th>
<th>( U_{37}^{K} ) SST(^b) (°C)</th>
<th>( C_{37} ) alkenones (µg g(^{-1}))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBB 88-9, 10a, 10b</td>
<td>34°14’N, 120°01’W</td>
<td>1915–1988</td>
<td>14.3</td>
<td>6</td>
<td>Kennedy and Brassell, 1992a,b</td>
</tr>
<tr>
<td>SBBX-1</td>
<td>34°13’N 120°03’W</td>
<td>1918–1995</td>
<td>14.8</td>
<td>4.5</td>
<td>Herbert et al., 1998</td>
</tr>
<tr>
<td>SABA 87-1, 87-2, 88-1</td>
<td>34°13.6’N 120°01’W</td>
<td>1900–1941</td>
<td>15.3</td>
<td>4</td>
<td>Zhao et al., 1995b and this paper</td>
</tr>
</tbody>
</table>

\( ^a \) Water depth is 590 m for all cores. SST is calculated using the following equation: SST (°C) = \( (U_{37}^{K} - 0.039)/0.034 \).

\( ^b \) These are the average SSTs for the common period: 1919–1941.

Fig. 3. Comparison of sea surface temperature records. (A) instrumental SST record from Puerto Chicama, Peru, A.D. 1936–1981 (Shen et al., 1992); (B) the instrumental SST anomalies from the western coast of USA, A.D. 1900–1985 (Schimmelmann et al., 1995). (C) the Santa Barbara Basin \( U_{37}^{K} \) SST (solid line: this paper using SST scale on the left, A.D. 1900–1941; dotted line: data from Kennedy and Brassell (1992a,b) using SST scale on the right, A.D. 1914–1982, dashed line: data from Herbert et al. (1998), using SST scale on the right, A.D. 1919–1985); the two SST scales are used to show the rough parallelism of the \( U_{37}^{K} \) SST records, despite the systematic offset of 1°C, which may have its origin in analytical methodology and sampling site location. Documented strong and very strong ENSO events (Quinn, 1992) are indicated by shaded vertical bars.
The situation appears to be similar for the period 1942 to 1985 where only the Kennedy and Brassell (1992a) and Herbert et al. (1998) records can be compared. Once again, the Herbert et al. data are systematically warmer than the Kennedy and Brassell data by 0.3 to 0.5°C.

The SBB $^{37}$SST records for the 20th century are of special interest in terms of historical ENSO events. Although the ENSO events are characterized by a general warming of the tropical east Pacific waters, not every event has been registered in the SST off the California Borderland. This can be seen by comparing the instrumental SST record of 1936 to 1982 from Puerto Chicama off Peru (Fig. 3A), which has been demonstrated to record ENSO accurately (Shen et al., 1992), with the West Coast instrumental SST anomalies (Barnett, 1985; Schimmelmann et al., 1995) (Fig. 3B). Although the two instrumental SST records show some common features, major differences do exist. For example, the 1965 and the 1972 strong ENSO events were both recorded with a SST maximum at Puerto Chicama, but with SST minima in the West Coast SST record. An increase in upwelling or the strengthening of the cold California Current could have accounted for the lower West Coast SST. Recent studies of the circulation patterns of the Santa Barbara Channel show that this region is influenced by cold cyclonic eddies that spin off the California Current and are not necessarily associated with ENSO or La Niña events. The AVHRR satellite images clearly show the variable, complex and especially changing nature of SST maps for this region (Winant and Hendershott, 1996; Harms and Winant, 1998). Nevertheless, the availability of the varved sedimentary record renders this a prime site for the study of annual to decadal climate variability.

Kennedy and Brassell (1992a,b) concluded that there was a reasonable correlation of major, historically recorded 20th century ENSO events with increased $^{37}$SST for the relevant varves in the SBB sedimentary record. However, while the strong 1972 ENSO event matches with a $^{37}$SST maximum in their record for the SBB (Fig. 3C), the West Coast SST anomalies (Fig. 3B) and the CalCOFI SST records show a minimum (Kennedy and Brassell, 1992b; Schimmelmann et al., 1995). Again, in the record of Herbert et al. (1998), there is no major change of $^{37}$SST around 1972. In making their comparison with instrumental SST (Scripps Pier data set), Herbert et al. (1998) remarked that after 1965 the two records correlate poorly, except during the strong ENSO event of 1982–1983.

The Kennedy and Brassell (1992a) paleo-SST reconstruction prompted the present study of $^{37}$SST record for the SBB back in time beyond the LIA. We have compared our SST record with Quinn’s (1992) ENSO events for the period of 1840 to 1920, because confidence in varve chronology is higher above 1840. For this period, only five of the 12 strong/very strong historical ENSO events coincide with significant temperature increases within ±1 year. The other ENSO events have no apparent SST responses. There are several possible reasons for these discrepancies. Firstly, a small mismatch between an ENSO event and a SST maximum can simply be due to errors in the chronologies of the records. Secondly, the historical ENSO record is based mostly on South American historical data (Quinn, 1992). The warming effect of tropical waters often takes several months to 1 year to become apparent in the SST. Thirdly, not every ENSO event would be expected to cause a SST increase along the west coast, and indeed, the strong 1965–1966 and 1972–1973 El Niño events did not (Schimmelmann et al., 1995). Finally, the present result is from one site only. We do not know how dependent the SST record is on the precise location of the site, bearing in mind the strong SST gradient within the basin (Harms and Winant, 1998). In the Santa Monica Basin, two cores 15 km apart afforded $^{37}$SST records which differed by as much as 4°C. Gong and Hollander (1999) ascribed the SST differences to selective oxidative degradation of the alkenone pair in theoxic bottom sediments compared with the anoxic sediments at the basin depocenter. However, the spatial complexity and variability of the thermal structure of the waters in this region may also play an important role.

There is a more general, biologically- and ecologically-related problem inherent in attempting to match ENSO events with alkenone SST records. This is the uncertainty in the precise meaning of the $^{37}$SST estimates in relation to the timing and location in the water column of the alkenone production. Thus, in upwelling areas, coccolithophorids do not necessarily bloom at the time of maximum upwelling. Coccolithophorid production usually does not coincide with that of the diatoms, which are typically the main source of marine organic matter. In fact, coccolithophorids may bloom just after the main bloom crashes (Mitchell-Innes and Winter, 1987). The ecological situation will reflect competition for nutrients, as well as other factors. But, in any case the temperature recorded by the alkenone production will not necessarily be that of the time of the main upwelling. This biological aspect to the use of $^{37}$SST was extensively discussed during a recent workshop (Eglington et al., 2000), and several recent papers also bear on these issues. Bentaleb et al. (1999) carried out time course filtration studies in the Northwest Mediterranean at 5 and 30 m water depth during well-defined thermocline conditions. Analysis of the suspended particles showed that the alkenones were synthesized at the depth of highest primary productivity, thus recording the temperature of those layers. Additionally, also in the Northwest Mediterranean basin, Sicre et al. (1999) examined sediment trap debris collected over annual
periods and found high alkenone fluxes in both fall and spring. The $U_{37}^{K}$ SST values correlated well with the seasonal temperatures of the major production depth (50 m for spring and 30 m for fall). However, Ohkouchi et al. (1999) have suggested that in the central Pacific Ocean, the depth of alkenone production is mainly controlled by the response of the haptophyte producers to the nutrient supply (e.g. nitrate) from deeper waters. Hence, at these sites, the $U_{37}^{K}$ SST measured in the underlying sediments may reflect the temperature of thermocline waters significantly deeper than the surface mixed layer. We conclude that alkenone SST estimates are not readily related to a single parameter, such as the water temperature at a specific depth and season. In effect, they will reflect some time and spatial averaging of the complex pattern of ocean surface temperatures created by insolation, upwelling cells, current movements and wind strength. This lack of a facile one-to-one relationship must apply to other proxies as well, but medium to longer term trends (10 to 100 years) can still be useful climate records despite the short-term noise (Weaver et al., 1999).

The above comparisons show that, although the $U_{37}^{K}$ SST record is of some value in ENSO reconstruction, SST maxima are not conclusive measures of ENSO events. Indeed, correlation between $U_{37}^{K}$ SST maxima and individual paleo-ENSO records for much older sediments is even more problematic, due to the increased uncertainties in the true dates of the varves and of the historically-reconstructed ENSO events. Indeed, McCaffrey et al. (1990) remarked in their study of a core off the Peru margin, that while the $U_{37}^{K}$ SST signals of individual ENSO events were substantially attenuated in the sediments, a cluster of $U_{37}^{K}$ SST maxima would indicate a period of frequent and intense ENSO activity, e.g. the warm period of 1865–1885, which is also seen in our record.

4.2. $U_{37}^{K}$ SST record during the Little Ice Age

Recent paleoclimate reconstructions indicate that the Little Ice Age was not global (Bradley and Jones, 1992a, 1993; Mann et al., 1998). Most regions experienced colder periods, but there is geographic variability (Bradley and Jones, 1993). The late 1500s and the early 1600s were cold in both North America and Europe, but this interval was very warm in China and Asia. The most profound cooling period in China occurred in the mid-1600s (1650–1670), but was coeval with one of the warmest decades in North America. Although the unsmoothed SBB $U_{37}^{K}$ SST for individual varves has varied by as much as 3°C during the last 500 years (Fig. 2F), there is no recognizable “cool period” associated with the Little Ice Age, the average $U_{37}^{K}$ SST for each century being rather consistent (ca. 15.5°C). Thus, the difference in average SST between the coldest century (18th) and the warmest century (19th) is only 0.2°C. This region’s oceanic response to global LIA cooling appears to have been minimal. Rather, it seems quite clear from the 50-year averaged SST record (Fig. 2F) that the dominant features are centennial scale oscillations involving decadal scale cooling and warming. On the decadal timescale, the warmest decade (1651–1660) is 1.6°C warmer than the coldest one (1899–1908) (Table 2). As far as the sub-decadal SST variability is concerned, the relatively warmer 18th century is characterized by rather stable SST, while the 16th, 17th and the 19th centuries exhibit larger $U_{37}^{K}$ SST oscillations.

We observe similar long-term trends in the Santa Barbara Basin $U_{37}^{K}$ SST (Fig. 4B) and in the annual air temperature anomalies from the California Valleys (Fritts, 1991) (Fig. 4C); for example, the major warmings around 1655 and 1865. These similar trends are suggestive of forcing mechanisms involving ocean-atmosphere interaction. However, there are significant differences in both the timing and amplitude of the temperature changes in the two records. For example, the major cooling in the $U_{37}^{K}$ SST starting from ca. 1870 reached a temperature minimum around 1903, while the tree-ring air temperature minimum was around 1913. The age uncertainty of 2–5 years for the SBB samples (Schimmelmann and Lange, 1996) may partially explain this time offset, while different response times of the systems to the internal or external forcing may also be important (Stuiver and Braziunas, 1993). Although ocean and atmospheric systems are coupled, it is not unusual for the ocean to witness warming or cooling events a few years after the atmospheric expression (Crowley and Kim, 1996). In addition, the SBB SST is strongly influenced by upwelling events and these are not necessarily recorded in a tree-ring record. Also, volcanic eruptions often cause short-term cooling of the atmosphere, whereas the ocean’s thermal inertia limits short-term SST excursions (Portman and Gutzler, 1996).

The $U_{37}^{K}$ SST record for the SBB is also compared with the sea surface temperature proxy record reconstructed using coral $\delta^{18}O$ values from Urvina Bay, Galapagos Islands in the Eastern Equatorial Pacific (Fig. 1 and 4A; Dunbar et al., 1994). Coral $\delta^{18}O$ values during the Holocene mainly record SST, with more negative $\delta^{18}O$ values indicating warmer SST. Again, there is no clear evidence of LIA cooling in the coral record, but there is some correlation between the long term trends in the SBB $U_{37}^{K}$ SST and the coral $\delta^{18}O$ records. Starting from 1600, both show warm periods in the mid-1600s, mid-1700s and mid-1800s, followed by cooling into the early 1900s. However, the major cold event of the early 1900s in the SBB record is matched only by a weak excursion in the coral $\delta^{18}O$ record. On the other hand, a ~1°C cooling of the Sargasso Sea during the LIA was deduced from foraminiferal isotope data (Keigwin, 1996).
The spectral output (10–1000 years) for $U_{37}^{K}$ SST in the SBB, in terms of decadal and centennial periodicities, is shown in Fig. 5. For the subdecadal periodicities, the major peaks are 3–4 and 6 years (Zhao et al., 1995b). These peaks are within the frequency band of the ENSO variability (Anderson, 1992; Dunbar et al., 1994). On the decadal scale, periodicities of 12–13 and around 20 are significant. For the centennial scale, SST has a strong peak in the region of 100 year periodicity.

Several systems are widely-held to be candidates for climate forcing mechanisms, including the Earth’s internal dynamics, coupled atmosphere-ocean interactions, and astronomical factors such as solar activity (Rind and Overpeck, 1993; Wallace, 1995; Schimmelmann et al., 1998). Several authors (Anderson, 1992; Friis-Christensen and Lassen, 1991; Crowley and Kim, 1993, 1996; Lean et al., 1995) have proposed that sunspot activity is the most likely driving force for terrestrial climate cycles at the decadal level (e.g. 11 years), although the forcing mechanism remains obscure. Indeed, the Maunder minimum (A.D. 1645–1705) in sunspot numbers (Foukal, 1990), which has been proposed as one of the causes for the LIA in Europe and

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Table 2
The eight warmest and coldest 10-year $U_{37}^{K}$ SST averages from 1440–1940 in the Santa Barbara Basin

![Fig. 4. Comparison of three temperature proxy records A.D. 1600 to 1940. (A) coral δ18O (‰, PDB) record from Urvina Bay in the Eastern tropical Pacific Ocean (Dunbar et al., 1994). More negative values correspond to warmer SST; (B) $U_{37}^{K}$ sea surface temperature (°C) from the SBB. (C) annual atmospheric temperature anomaly expressed as departure from the 1901–1970 mean instrument data reconstructed using tree ring width and density from the California valleys (Fritts, 1991). All data are plotted as 5-point running averages.](image-url)
North America, is almost coeval with one of the warmest 50 years in our SBB SST record (A.D. 1631–1680; Fig. 2F). However, other workers (Latif and Barnett, 1994; Schlesinger and Ramankutty, 1994; Chang et al., 1997) have claimed that there is a decadal variation in tropical ocean-atmosphere interactions that could be responsible for SST oscillations in the tropical Atlantic and Pacific. Large volcanic eruptions have also been recognized as a major cause of short-term atmospheric and continental cooling (Hammer et al., 1980; Bradley and Jones, 1992b; Briffa et al., 1998; de Silva and Zeylinski, 1998). At this stage, with the results from one long-term, quasi-annual SST record, we cannot discriminate between the effects of local variability in the physical oceanography of the Santa Barbara Channel (Harms and Winant, 1998) and those of the more regional to global processes outlined above. This situation will be improved by more paleo-SST records from the SBB.

4.3. Preservation records of TOC and alkenones

The sedimentary content of TOC and of individual organic compounds is influenced by a variety of biogeochemical factors, notably primary productivity (Eppley and Peterson, 1979), water column remineralization, sedimentation rate and bottom-water oxygen concentration (Müller and Suess, 1979; Pedersen and Calvert, 1990; Hedges and Keil, 1995; Hartnett et al., 1998). Nevertheless, the contents and burial fluxes (mass accumulation rates) of TOC have been used as measures of total marine productivity (Müller and Suess, 1979; Stein et al., 1989; Sarnthein et al., 1992) and those of alkenones as proxies for haptophyte productivity (Prahl et al., 1993; Villanueva et al., 1995). The SBB alkenone content profile (Fig. 2D) shows large variations from 1 to 8 µg g⁻¹ (dry sediment), similar to the early 20th century record of Kennedy and Brassell (1992a,b). TOC (Fig. 2B) and alkenone contents show some similarity in general trends over the last 500 years. The burial flux data for TOC (Fig. 2C) and for alkenones (Fig. 2E) correlate better with each other, but not well with the content profiles. This is understandable, since they are calculated using varve thickness, which can account for a major part of the variances of both data sets.

With regard to the relationship between SST and TOC content in an upwelling region, the prevailing hypothesis is that an increase in upwelling, with accompanying decrease in SST, would cause an increase in surface productivity and hence in sedimentary TOC. A direct visual comparison of the 10 year smoothed records for these two parameters (Fig. 6) indicates some parallelism in long-term trends, together with several major disagreements (e.g. ca. 1650 and 1850 A.D.). However, an X–Y plot of Uclide SST versus TOC (Fig. 7B) does not reveal any meaningful relationship. One could argue that burial flux is a better measure of surface production than content, since it is calculated using annual varve thickness and hence takes account of the effects of sedimentation rate and of terrigenous dilution. If the TOC burial flux is mainly controlled by primary productivity, then it should have a reasonably good inverse correlation with SST, since both are influenced by the upwelling of cold and nutrient-rich waters: stronger upwelling would induce higher TOC burial flux and lower SST. However, comparison of these records does not support this hypothesis (Fig. 2). For example, the TOC flux maximum from 1640 to 1680 AD is correlated with a SST maximum and an X–Y plot of SST vs. TOC burial flux shows no meaningful relationship (Fig. 7C). Thus, primary productivity does not seem to be the main factor controlling TOC burial flux to the SBB sediments. Similarly, there is no significant correlation between SST and alkenone burial flux, supporting the results of Kennedy and Brassell (1992b). However, Herbert et al. (1998) observed, qualitatively, that alkenone content appeared to correlate inversely with SST for the time span of 1919 to 1994, but our longer term data (Fig. 7A) show no relationship.

Hartnett et al. (1998) have suggested that oxygen exposure time, which effectively incorporates environmental variables other than primary productivity, controls sedimentary organic matter (OM) preservation. Oxygen exposure time is determined mainly by the bottom water O₂ concentration and the sedimentation rate. For the SBB, bottom water O₂ is very low (< 0.2 ml/l) at present (Sholkovitz and Gieskes, 1971; Reimers et al., 1990), but no direct measure of past O₂ concentrations exists. However, varve thickness, which records the annual sedimentation rate, is another factor...
Fig. 6. Comparison of $U^{137}_{15}$ SST (°C) vs. TOC content (%) for the period A.D. 1445 to 1935. Data are smoothed over 10 years to reveal underlying trends.

Fig. 7. X–Y plots of the 5-year means of the selected geochemical time series for the period A.D. 1440–1940. (A) $U^{137}_{15}$ SST (°C) vs. alkenone content (μg g$^{-1}$); (B) $U^{137}_{15}$ SST (°C) vs. TOC contents (%); (C) $U^{137}_{15}$ SST (°C) vs. TOC burial flux (mgC cm$^{-2}$ year$^{-1}$); (D) varve thickness (mm) vs. TOC burial flux (mgC cm$^{-2}$ year$^{-1}$).
which should be considered in relation to the preservation of OM in the SBB. The dark laminae (predominantly terrigenous detrital clays) are formed during the winter months, when increased precipitation and river runoff transport more terrigenous materials to the basin and the supply of biogenic materials is less, due to decreased productivity (Hülsemann and Emery, 1961; Thunell et al., 1995). Conversely, the light laminae (mostly silica from diatoms) are formed during the spring/summer months when the supply of biogenic debris reflects upwelling-induced surface productivity. If bottom-water $O_2$ concentration is constant, an increase in varve thickness will reduce oxygen exposure time and therefore increase TOC burial flux. Thus, a simple $X-Y$ plot of annual varve thickness vs. TOC burial flux (Fig. 7D) gives a moderately good correlation ($r^2 = 0.56$), suggesting that, indeed, varve thickness is a quantitatively significant factor in controlling TOC preservation in the SBB, in accord with our earlier qualitative observation based on Fig. 2A and C. There is an element of circularity here in that varve thickness is a dominant factor in calculating burial flux, but nevertheless the result in Fig. 7D reflects the sedimentary mechanism controlling TOC burial flux.

Increased varve thickness can result from an increased supply of terrigenous material due to more river runoff, an increased production of biogenic materials due to enhanced upwelling, or a combination of both processes. For an increase in surface productivity, there is more OM supply to the sediment/water interface which will cause more deep-water $O_2$ depletion, and more supply of biogenic inorganic materials to increase varve thickness. These two processes work together to reduce the $O_2$ exposure time of the OM and hence increase preservation of TOC. The major increases in TOC burial fluxes from 1680 to 1740 and from 1880 to 1910 seem to be such situations, since lower SSTs in the 1880s to 1910 may indicate increased upwelling. An increase in varve thickness caused by higher terrigenous flux would also increase the supply of terrigenous OM by small amounts. Any increase in TOC burial flux would be largely the result of a shortened time of exposure to oxygen caused by a higher rate of sedimentation. The higher TOC burial fluxes for the periods of 1640–1670 and 1850–1880 may be such examples, since these periods are characterized by warmer SST (less-upwelling) and higher rainfalls in California.

We thus propose, in accord with the work of Hartnett et al. (1998), that TOC burial flux in the SBB is mainly controlled by sedimentation rate, which in turn controls oxygen exposure time. Studies of the behavior of other marine productivity proxies, such as diatom fluxes, are needed, together with any links between varve thickness, local run-off and precipitation in the catchment region. A means to estimate paleo-bottom water $O_2$ concentration would also be of great value.

5. Conclusions

Our results illustrate the benefits for molecular stratigraphy which accrue from the analysis of individual varves in a sediment core. Coupled with the enhanced ability for rapid micro-analysis resulting from partial automation, such cores make it possible to derive molecular proxy records of approximately annual resolution, appropriate for studies of climate change, especially in the Holocene.

We have reached the following general conclusions for the 1440–1940 sedimentary record obtained from the depocenter of the Santa Barbara Basin. We emphasize that these are based on a single core record and that their relevance for the whole basin needs to be determined by studies of additional cores.

1. The $U^{137}_S$ SST record displays interannual (3–4 year) and interdecadal (12–13 year) variability of 1 to 3°C, which may be caused in part by ENSO-type ocean-atmospheric interactions. However, individual increases in SST do not correlate well with historical ENSO records, probably as a consequence of variable interplay of the oceanic currents in the basin.

2. There is a strong centennial-scale cyclicity in the $U^{137}_S$ SST record which approaches 1°C in amplitude.

3. There was no significant cooling in SST during the Little Ice Age period, in agreement with a coral record from the Equatorial Eastern Pacific (Dunbar et al., 1994) and a tree ring record from the California Valleys (Fritts, 1991).

4. The TOC and alkenone burial fluxes do not correlate well with the SST record, but do correlate well with the varve thickness. We suggest that the TOC burial fluxes in the SBB reflect preservation efficiency dominated by oxygen exposure time as controlled by sedimentation rate (cf. Hartnett et al., 1998).

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## References


