Sourcing archaeological asphaltum (bitumen) from the California Channel Islands to submarine seeps

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A B S T R A C T

Asphaltum, often referred to as bitumen, is a naturally occurring form of petroleum that was used by ancient cultures for thousands of years. Asphaltum deposits are found throughout the world and occur both on land and submerged under water. Ethnohistoric accounts of native Californians suggest that asphaltum from terrestrial seeps was shaped by hand into cakes and traded throughout Southern California and was the only grade of asphaltum used to manufacture plank-canoes. While there are no terrestrial seeps on the California Channel Islands, drift asphaltum exuded from submarine seeps can frequently be found washed up on the shore. It remains unclear to what extent prehistoric island populations relied on this drift asphaltum and whether or not they acquired terrestrial asphaltum through trade. This study combines gas chromatography/mass spectrometry (GC/MS) and liquid chromatography coupled with carbon isotopic analysis in an effort to identify the sources of six archaeological bituminous mixtures from San Nicolas and San Miguel islands. We compare the archaeological asphaltum to four modern samples collected from marine tarballs and a mainland terrestrial seep. Further, we compare our results to a USGS chemometric database to determine if our archaeological samples match extant sources. Our results show that prehistoric peoples on the Channel Islands utilized drift asphaltum from submarine seeps in a variety of technological applications throughout the Holocene. The methods used in our study are globally applicable and can be used to address a variety of broad anthropological questions.

1. Introduction

Asphaltum, also referred to as bitumen, naphtha, rock-oil, and tar, is a naturally occurring form of petroleum. Among different cultures across the world, asphaltum was highly prized and used for a variety of practical, symbolic, and decorative purposes (Boëda et al., 2008; Connan, 1999, 2012; Forbes, 1936; Habu, 2004; Schwartz and Hollander, 2001; Wendt and Cyphers, 2008). In California, asphaltum was used as an adhesive to fasten fishhooks to line, attach projectile points to shafts, haft knife blades to handles, appliqué shell beads to effigies and other artifacts, and repair broken bowls and pestles, among other uses (Alliot, 1970; Gamble, 2008; Gutman, 1979; Heizer, 1943; Hudson and Blackburn, 1987; McCawley, 1996). Some California groups used the substance as body paint and cosmetic, particularly during curing, mourning, and burial ceremonies (Gutman, 1983; Hodgson, 2004). Significantly, asphaltum’s water resisting characteristics made it ideal for waterproofing baskets (Craig, 1966; Hudson and Blackburn, 1983) and caulking sea-going watercraft such as the tomol (ti’at and the tule balsa (Arnold, 2007; Hudson et al., 1978).

Asphaltum fragments, cakes, and other encrusted artifacts are found throughout California Channel Islands archaeological sites, suggesting a long technological heritage. A large chunk of asphaltum was recovered from a stratum dated to between 8400 and 7500 cal BP within the Early Holocene (10,000–7000 cal BP) at Cave of the Chimneys on San Miguel Island (Erlandson et al., 2009; Vellanoweth et al., 2003). On Santa Cruz Island a tarring pebble, an artifact known to have been used prehistorically to melt and apply asphaltum, was found in a shell midden dated to between 6800 and 4800 cal BP (Perry, 2004). The frequency of archaeological
asphaltum increases in Middle Holocene (7000–3500 cal BP) deposits, as the range of asphaltum technologies expanded (Erlandson et al., 2008; Glassow et al., 2007). Direct evidence of water-bottle production in the form of basketry impressions and tarring pebble clusters appears archaeologically as early as 5130 years ago (Bleitz, 1991; Braje et al., 2005; Vellanoweth, 1996) and may have been developed in response to Middle Holocene aridity and an increasing need to store and transport water (Braje et al., 2005; Gamble, 2005). Mixing dishes and other tools used to melt, process, and apply asphaltum also appear in Channel Island deposits dated to this period.

By the Late Holocene (3500–200 cal BP), asphaltum technology in Southern California reached its full florescence (Wärmländer et al., 2011); tarring pebbles and other asphaltum coated artifacts become prevalent in archaeological contexts from places including San Nicolas Island (Brown and Vellanoweth, 2014), San Miguel Island (Rick, 2007), Santa Cruz Island (Arnold and Bernard, 2005) and Pitas Point in Santa Barbara County (Gamble, 1983). The plank canoe is likely to have been invented during the Late Holocene (Arnold, 1995; Arnold and Bernard, 2005; Davenport et al., 1993; Gamble, 2002), and any coastal group involved in the construction and/or maintenance of these craft would probably have required larger quantities of asphaltum than in previous periods (Arnold and Bernard, 2005; Gamble, 2002).

2. Terrestrial and submarine asphaltum seeps in Southern California

Natural asphaltum seeps and deposits are widespread in California, particularly in the state’s southern half along the coasts of Santa Barbara, Ventura, and Los Angeles counties (Gutman, 1979; Heizer and Treganza, 1972; Priestaf, 1979). In addition to onshore sources, submarine seeps release asphaltum into the water column, which is carried by ocean currents and wind-driven waves, and deposited in the form of tarballs on beaches and rocky shores throughout coastal and insular California (Fig. 1; Hostettler et al., 2004; Lorenson et al., 2009; Wilkinson, 1972). The richest recorded history of submarine seepage, and one of the most prolific seep fields in the world, is found under the Santa Barbara Channel (Landes, 1973). Chumash ethnographic accounts clearly distinguish between two types of tar (Hudson et al., 1978; Hudson and Blackburn, 1987). In the Chumash languages, malak was the name given to drift asphaltum from submarine seeps while the word woqo was used to describe asphaltum from terrestrial sources.

Chumash informant Fernando Librado stated that malak was not used in the construction of plank canoes and that builders instead relied upon a woqo-based compound called yop. To produce yop, woqo was pounded, boiled, and mixed with pine “pitch” and ochre (Hudson et al., 1978; Hudson and Blackburn, 1987). What Hudson et al. (1978) refer to as “pitch” is technically pine resin collected in its natural state from conifers, not pine tar obtained by heating conifer wood (Connan, 2012).

Although ethnographic sources suggest that asphaltum from terrestrial seeps was utilized in antiquity, debate continues as to the extent to which the Chumash, Takic speaking groups, and other coastal California peoples made use of asphaltum from submarine sources. Arnold (2001), Arnold and Bernard (2005), and Bauville (2011) maintain that “high-grade” asphaltum was only available on the mainland. However, Braje et al. (2005) and Erlandson and Braje (2008) challenge this notion, citing a major seep off the northwest coast of San Miguel Island that regularly washes pure asphaltum ashore in very large quantities. In the supratidal zone of rocky shores, this bitumen hardens into a mineral-like state that can be re-melted and used for a variety of purposes. Ethnographic accounts suggest that asphaltum from these offshore seeps was used for various purposes. Heizer (1943) noted that, on the mainland, bitumen was routinely collected from beaches in addition to being mined at terrestrial tar seeps. In 1853, sea captain George Nidever (1973) observed that Juana Maria, “The Lone Woman of San Nicolas Island,” used drift asphaltum found along the beach to coat the interior of a basketry water-bottle. The distinction between the two types of asphaltum is an important one: on one hand if terrestrial asphaltum was required for certain applications, it would have become a significant and highly desired trade good for island populations. On the other hand, if Islanders could rely primarily, or even exclusively, on marine asphaltum they would maintain a higher degree of resource independence.

In this paper, we present the results of GC/MS, liquid chromatography and carbon isotope analyses of six bitumen samples from three archaeological sites on San Nicolas and San Miguel islands (Fig. 2). We compare the archaeological samples to four modern reference samples: two marine tarballs from San Nicolas Island, one marine tarball from Coal Oil Point in Santa Barbara County, and one from a terrestrial seep near Carpinteria in Ventura County. This study represents a scientific approach to asphaltum sourcing and illustrates the potential of geochemical techniques, especially molecular and isotopic geochemistry, to answer key questions related to the origins of the asphaltum found in archaeological contexts throughout Southern California. Our goal is to shed light on the sources of the asphaltum utilized by the prehistoric Channel Islanders, who had little to no direct access to terrestrial seeps.

3. Sourcing asphaltum

The hydrocarbon composition of petroleum varies between deposits. Since the late 1970s, this fact has allowed researchers to chemometrically fingerprint bitumen from different sources by identifying specific biomarkers using several geochemical analyses (Freeman et al., 1994; Marschner and Wright, 1978; Peters and Moldowan, 1993). The most commonly used classes of biomarkers (Peters and Moldowan, 1993) are steranes and terpanes, which occur in the C\textsubscript{15} alkane fractions. Individual biomarkers can be identified by GC/MS, establishing a chemical fingerprint. Another analytical method is field-ionization mass spectrometry (FI-MS), which allows for the quantification of saturated hydrocarbon rings in the alkanes (Kato et al., 2008).

Archaeological asphaltum has been sourced extensively in the Near East (Connan, 2012; Connan and Deschesne, 1992; Connan and Van de Velde, 2010; Connan, 1999; Harrell and Lewan, 2002;
Schwartz and Stein, 2000) as well as in Mesoamerica (Wendt and Lu, 2006) and Japan (Kato et al., 2008), but few chemical analyses have been carried out on samples from California; however, Gutman (1979, 1983) used porphyrin nickel/vanadium ratios, relative oxidation, sulfur content, and carbon isotope ratios to correlate extant seeps with bitumen from nearby archaeological sites in Santa Barbara, Ventura, and Los Angeles counties. He was only partially successful due to biodegradation and the lack of significant differences in values between seeps in the study. Jacobsen (2012) used GC/MS to identify biomarkers in archaeological asphaltum from Santa Catalina Island and several modern samples in an effort to evaluate whether or not asphaltum was an elite-controlled resource on the island. Qualitative approaches, such as Salwen’s (2011) study have been used to classify asphaltum and understand regional exchange; however, geochemical analyses were not employed.

The United States Geological Survey (USGS) has recently made progress using GC/MS and isotopic studies to analyze petroleum from onshore and offshore seeps, oil wells, and pelagic tarballs in Southern California. The goal of this research has been to link marine tar originating in the Monterey Formation with its various sources and establish a database of their chemometric fingerprints. This work began with Hostettler et al.’s (2004) investigation of tarball accumulation along the shores of the northern Channel Islands, attempting to distinguish naturally versus anthropogenically (i.e. production oils from drilling operations) dispersed specimens. Lorenson et al. (2009) built upon this data, chemometrically classifying 667 samples taken from tarballs, tar residues, seeps, bitumen in rock, and production oils into thirteen families within three tribes. These researchers have built a valuable library of coastal tar fingerprints that makes comparative studies of spatial and temporal asphaltum distributions possible.

4. Materials and methods

Ten samples, six bituminous mixtures from three archaeological sites on San Nicolas and San Miguel islands (Fig. 3), two tarballs from San Nicolas Island, one tarball collected at Coal Oil Point, and one sample taken from a terrestrial seep at Carpinteria State Beach (Table 1), were analyzed for biomarker patterns (steranes and...
terpanes) using GC/MS and isotopic values ($^{13}C$ in $\%_{oo}$ per VPDB) acquired on four chromatographic fractions isolated by liquid chromatography. The three archaeological sites vary considerably in site type, function, and chronology.

4.1. CA-SMI-603 (8400–7500 cal BP)

Cave of the Chimneys (CA-SMI-603) is a multi-component rock shelter located on the northeast coast of San Miguel Island. Within the single 0.5 × 1 m unit (Unit 1) excavated, seven archaeological strata were identified and found to represent discrete depositional phases spanning the Holocene from 8400 to 1000 cal BP (Ainis, 2012; Vellanoweth et al., 2003). The deposits’ diverse faunal assemblage represents a detailed and well preserved record of human maritime subsistence during the over 7000 year span. The asphaltum chunk analyzed in this study (#2834, Fig. 3 and Table 1) was modified with linear impressions and measured roughly 7.5 × 3 cm. It consists of pure bitumen with some white mineral inclusions, perhaps shell fragments. The chunk was found in Stratum VI, dated to about 7690 cal BP. This stratum also contained well-preserved sea grass twined cordage and knots, olivella (Calliclax biplicata) beads, a bone-gorge, and fragments of asphaltum. Vellanoweth et al. (2003) suggest that the asphaltum was likely part of the fishing kit of the Early Holocene inhabitants of the cave, serving to fasten bone gorges to sea grass fishing line.

4.2. CA-SNI-40 (4300 BP–3700 cal BP)

CA-SNI-40 is a Middle Holocene site located near the shore on the northwest end of San Nicolas Island. During the summer field seasons of 2010 and 2011, archaeological investigations directed by Vellanoweth concentrated on a shell midden deposit within a large aeolian dune. Excavations yielded remarkably well-preserved subsistence remains, including black abalone (Haliotis cracherodii) and red abalone (Haliotis rufescens) concentrations, lenses of articulated seabird bones, and a shell and ash feature provisionally interpreted as a baking pit. Among the artifacts associated with this feature are expedient flaked tools, olivella beads, red ochre, a tarring pebble cluster feature, and pieces of asphaltum (Brown and Vellanoweth, 2014). From among these we selected a small fragment of detritus (#2832, Fig. 3 and Table 1) (approx. 2 × 2 × 1.5 cm) for GC/MS analysis (provenience: Locus A, Unit 1, Stratum II). The sample contains mineral fragments (possibly quartz grains), shell fragments, and plant fibers and displays degassing holes. Our second GC/MS sample (#2835, Fig. 3 and Table 1) from CA-SNI-40 was uncovered at a different locus (Locus B, Unit 3A, Stratum 1A) and extracted from the interior of a filled shell (H. rufescens). The surface of the sample was coated in calcareous sand and shell debris, including crushed gastropods and sea urchin (Strongylocentrotus sp.). The two loci from which the samples were culled are roughly contemporaneous and radiocarbon dates for both fall within the site’s 4300–3700 cal BP occupational phase.

4.3. CA-SNI-25 (540–385 cal BP)

Known as the Tule Creek Site, CA-SNI-25 is a large Late Holocene village site situated on a series of marine terraces overlooking San Nicolas Island’s north shore. Directly below CA-SNI-25 lies Corral Harbor, a small protected cove where drift asphaltum can be found adhering to the rocks. In 1930, Malcolm J. Rogers reported numerous house depressions, the remains of communal structures, and two cemeteries at the site. He excavated several burials and

Table 1

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Location</th>
<th>Provenience</th>
<th>Age</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>2830</td>
<td>CA-SNI-25</td>
<td>East Locus; Unit 7A1, Stratum II</td>
<td>592–495 cal BP</td>
<td>Waste/detritus</td>
</tr>
<tr>
<td>2831</td>
<td>CA-SNI-25</td>
<td>South Locus; Unit 60, Stratum 1</td>
<td>481–384 cal BP</td>
<td>Waste/detritus</td>
</tr>
<tr>
<td>2832</td>
<td>CA-SNI-40</td>
<td>Locus A; Unit 1, Stratum II</td>
<td>4321–3719 cal BP</td>
<td>Cached/Filled Shell</td>
</tr>
<tr>
<td>2833</td>
<td>CA-SNI-25</td>
<td>East Locus; Unit 7A1, Stratum 2</td>
<td>523–453 cal BP</td>
<td>Cached/Filled Shell</td>
</tr>
<tr>
<td>2834</td>
<td>CA-SMI-603</td>
<td>Cave Deposit; Unit 1; Stratum VI</td>
<td>7480–8450 cal BP</td>
<td>Modified Chunk</td>
</tr>
<tr>
<td>2835</td>
<td>CA-SNI-40</td>
<td>Locus B; Unit 3A, Stratum 1A</td>
<td>4321–3701 cal BP</td>
<td>Cached/Filled Shell</td>
</tr>
<tr>
<td>2836</td>
<td>San Nicolas Island</td>
<td>Northeastern edge of the island</td>
<td>Modern</td>
<td>Tarball</td>
</tr>
<tr>
<td>2837</td>
<td>Carpinteria</td>
<td>Carpinteria State Beach</td>
<td>Modern</td>
<td>Terrestrial Source</td>
</tr>
<tr>
<td>2838</td>
<td>San Nicolas Island</td>
<td>Northwestern edge of the island</td>
<td>Modern</td>
<td>Tarball</td>
</tr>
<tr>
<td>2839</td>
<td>Coal Oil Point</td>
<td>Near UC Santa Barbara</td>
<td>Modern</td>
<td>Tarball</td>
</tr>
</tbody>
</table>
made surface collections of ground stone and other artifacts (Rogers, 1930). Recent, large scale, open-area excavations directed by Vellanoweth focused on a domestic midden whose earliest strata date about 5000 cal BP (Martz, 2008) and a special use area by Vellanoweth focused on a domestic midden whose earliest bitumens from the Near East in Connan and Deschesne (1992) and identical to those reported for GC/MS analysis of archaeological materials, testifying to the villagers’ participation in regional trade networks (Cannon, 2006; Kendig et al., 2010).

One asphaltum sample (#2833, Fig. 3 and Table 1) from East Locus was taken from an interior-stained abalone shell found in the northeastern section of the excavation in Unit 8K, Stratum II. The asphaltum had fragments of shell nacre adhering to its ventral surface and a white mineral, probably quartz, on its dorsal surface. Another sample (#2830, Fig. 3 and Table 1) in East Locus was collected from Unit 7A1, Stratum II, in the southwestern part of the locus. The sampled detritus had visible minerals, possibly quartz, and marine carbonates from unidentified species. A third sample (#2831, Fig. 3 and Table 1) from Tule Creek was taken from the area designated South Locus, some 13 m south of East Locus. Less extensively investigated than East Locus, the depositional circumstances which produced South Locus are not clearly understood. While the two loci were formed concurrently, South Locus is of a distinctly different character and appears to represent more ephemeral use. The high density of cores suggests that South Locus may have been a lithic production area (Richard B. Guttenberg and William E. Kendig pers. comm. 2013). A roughly 3 cm fragment of asphaltum detritus was tested from South Locus (Unit 60, Stratum I). The sample was crumbly, partially carbonized, displayed degassing holes and had minerals (probably quartz), plant fibers, and shell debris cemented into its matrix.

4.4. Modern reference samples

For comparison, four modern reference asphalt samples were collected and subjected to GC/MS analysis. Two pelagic tarballs were collected from the shores of San Nicolas Island. One of these (#2836, Table 1) was recovered from the northeast side of the island at Corral Harbor, directly below the Tule Creek Site. The other (#2838, Table 1) came from the northwest side of the island near Lost Indian Cave (CA-SNI-551). Another two samples were collected on the mainland at Carpinteria (Ventura County) and Coal Oil Point (Santa Barbara County). The former (#2837, Table 1) was collected with the aid of a hammer and chisel from an indurated asphaltum mound capping an active terrestrial seep on Carpinteria State Beach. The Coal Oil Point sample (#2839, Table 1) was taken from a beached tarball most likely exuded from the massive submarine seep located just offshore. To broaden our comparative data set and support the information obtained from our modern samples, we cross-referenced the chemicometrical values of our archaeological samples with the USGS database (see Hostettler et al., 2004; Lorenson et al., 2005) discussed above.

4.5. Laboratory methods

The laboratory methods employed in this study are effectively identical to those reported for GC/MS analysis of archaeological bitumens from the Near East in Connan and Deschesne (1992) and Connan et al. (2006). All archaeological and modern samples were subjected to the same analytical procedure conducted at GeoMark Research Ltd. The dichloromethane extract was deasphalted using n-hexane. The deasphalted fraction was separated into saturated hydrocarbons, aromatic hydrocarbons, and resins using gravity flow column chromatography employing a 100–200 mesh silica gel support activated at 400 °C prior to use. Hexane was used to elute saturates, methylene chloride to elute the aromatic hydrocarbons and methylene chloride/methanol (50:50) to elute the NSO fraction. Following solvent evaporation the recovered fractions were quantified gravimetrically. The C15 saturated hydrocarbon fraction was subjected to molecular sieve filtration (Union Carbide S-115 powder) after the technique describe by West et al. (1990). An aliquot of the total alkane fraction was not fractionated by silicilite in order to preserve access to the n-alkanes.

GC/MS of the C15 branched and cyclic hydrocarbon fractions was performed using an Agilent 7890A (split injection) interfaced to a Agilent 5975C mass spectrometer. The HP-2 column (50 m × 0.2 mm, 0.11 μm film thickness) was temperature programmed from 150 °C to 325 °C at 2 °C/min and held for 10 min. The mass spectrometer was run in the selected ion mode (SIM), monitoring ions m/z 177, 191, 205, 217, 218, 231 and 253 amu for branched and cyclic alkanes. For the aromatic fraction, m/z 133, 178, 184, 192, 198, 231, 245 and 253 amu were acquired.

To determine the absolute concentration of individual biomarkers, a deuterated internal standard (d4-C29,29,29,29) was added to the C15 branched/cyclic hydrocarbon fraction. Response factors (RF) at 221 for the deuterated standard to hopane (m/z 191) and sterane (m/z 217) authentic standards were found to be 1.4 for terpanes and 1.0 for steranes. Concentration of individual biomarkers were determined using the following equation: Conc. (in ppm) = (Ht biomarker)/(ng standard)/(Ht standard) (RF) (mg B/C fraction).

The C15 saturates, C15 aromatics, asphaltenes and resins of the asphaltum samples were analyzed for their respective stable carbon isotope (δ13C, VPDB) compositions. Approximately 200–300 μg of each sample is loaded and sealed in a tin cup (Costech, Valencia, CA). Samples are placed in sequence in an autosampler mounted on a Costech elemental analyzer interfaced through a Conflo III valve with a Thermo Delta V Plus isotope ratio mass spectrometer (Thermo Fisher Scientific, West Palm Beach, FL). The δ13C values are reported in per mil (‰) relative to the VPDB standard (uncertainty ±0.1‰).

5. Results

Stable isotope values for the various fractions separated by liquid chromatography are listed in Table 2. As has been previously observed in archaeological bitumen from the Near East, our archaeological samples are highly enriched in asphaltites as a result of the prolonged oxidation to which they have been exposed (Connan, 2012). The modern tarballs and terrestrial seep sample, influenced mainly by biodegradation and evaporation, still contain higher percentages of the other hydrocarbon fractions. We observed a high degree of homogamy in our archaeological samples relative to the modern samples. While it is possible that this homogamy results from prolonged oxidation, it is likely that the archaeological asphaltites were formed in a similar depositional environment. This does not necessarily mean that they originate from a single source, simply that they derive from sources with the same geochemical characteristics. Plotting the ratios of δ13Casph. to δ13Caro. (Fig. 4) and δ13Casph. to δ13Cresins (Fig. 5) provides further insight regarding the sources of our samples. The δ13Casph. to δ13Cresins values of our archaeological samples constitute a cluster along with both of the San Nicolas Island tarballs, while the tarball...
Table 2
Title: Gross compositional data of archaeological and modern samples.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>EOM%</th>
<th>Gross composition of EOM</th>
<th>δ¹³C (%/VPDB)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Sat.%</td>
<td>Aro.%</td>
<td>Sat. + aro.%</td>
</tr>
<tr>
<td>2830</td>
<td>50.8</td>
<td>2.6</td>
<td>2.3</td>
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<tr>
<td>2831</td>
<td>23.2</td>
<td>2.5</td>
<td>3.4</td>
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<td>2832</td>
<td>35.3</td>
<td>2.6</td>
<td>1.6</td>
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<td>66.3</td>
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<td>4.2</td>
<td>23.6</td>
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<td>90.7</td>
<td>10.6</td>
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</tr>
<tr>
<td>2839</td>
<td>18.9</td>
<td>16.1</td>
<td>25.2</td>
</tr>
</tbody>
</table>

Fig. 4. Title: Ratios of δ¹³C sat. to δ¹³Caro.

Fig. 5. Title: Ratios of δ¹³C asp. to δ¹³Cresins.
from Coal Oil Point and the onshore seep sample from Carpinteria express ratios well outside of this cluster. This result makes clear that none of our archaeological asphaltums were imported from Carpinteria or derived from the same source as the Coal Oil Point tarball.

The terpane fingerprints of our samples are characterized by prominent C_{28} terpane, the 28, 30- Bisnorhopane (BNH), part of a complete series of tricyclopolyrenanes from C_{20} (20/3) to C_{30} (30/3) and the 27β-hopane family (from C_{20} to C_{35}) (Fig. 6). BNH is believed to derive from chemoautotrophic bacteria and is typical of source rock deposited under anoxic conditions. Its presence, not surprisingly, indicates an origin in the Miocene Monterey formation, the geologic source of California’s petroleum deposits. As will be seen below, the high levels of BNH in our samples caused an echo in the sterane series. Among other molecules present are: Tm (17α-22, 29, 30-trisnorhopane), Ts (18α-22, 29, 30-trisnorhomohopane), 18α(H)-oleanane (Olean), and Gammacerane (GA). Molecule 18α(H)-oleanane, which is indicative of higher-plant input, is low in our archaeological samples and San Nicolas Island tarballs yet significant in the onshore seep at Carpinteria. The high levels of this molecule serve to further distinguish the terrestrial source from the archaeological asphaltum.

While the sterane fingerprints of our archaeological samples are fairly homogenous, they can be classed into two types (A and B) (Fig. 7) with a third type (C) expressed in the onshore seep at Carpinteria and San Nicolas Island tarball #2. Type C is enriched in diasteranes (27Sdia and 27Rdia) indicating an origin in shale. Type A, expressed in samples #2830 (detritus, CA-SNI-25), #2831 (modified chunk, CA-SMI-603), #2832 (detritus, CA-SNI-40), and #2834 (filled H. rufescens, CA-SNI-25) and #2835 (filled H. rufescens, CA-SNI-40), displays elevated 24-nor-cholestan and 27-nor-methylcholestan (Fig. 8). Here too, the BNH echo exerts an influence on C_{29}ββR. The norsterane values in Type B may represent the signature of its source rock. Molecule 24-nor-cholestan may derive from 24-nor-cholesterols found in marine eukaryotes. A high concentration of this norsterane seems associated with diatom rich siliceous Oligo-Miocene sediments (Holba et al., 1998). It is also possible that the enhanced 24-and 27-norsteranes result from biodegradation, whereby specific molecules were eliminated from both specimens (Lorenson et al., 2009). This possibility cannot be objectively evaluated at this time.

Our modern samples from Coal Oil Point and Carpinteria, and our archaeological sample from San Miguel Island, were collected within the USGS study area and can be classified into the tribes established by Lorenson et al. (2009). These tribes constitute a geological reference to the various source rocks in the Monterey Formation: shale (Tribe 1), marl (Tribe 2), and carbonate (Tribe 3). Though San Nicolas Island lies southwest of the limits of the USGS study area, we were able to correlate the values for the tarballs and archaeological samples with Lorenson et al.’s tribes. We plotted values for our samples in relation to specific biomarker parameters in four diagrams: BNH/Hopane vs. Ts/Tm (Fig 9a), Oleanane/
Hopane vs. BNH/Hopane (Fig. 9b), C24/C22 Tricyclic Terpanes vs. C22/C21 Tricyclic Terpanes (Fig. 9c) and Oleanane/Hopane vs. Ts/Tm (Fig. 9d). Archaeological asphaltum constitutes a cluster also encompassing San Nicolas tarball #1 (#2836). This cluster appears within the Tribe 2 marl range, at the boundary with the Tribe 3 carbonate population, implying that these asphaltums derive from a single source or sources with the same geological characteristics. Reference samples from Carpinteria, Coal Oil Point, and San Nicolas Island tarball #2 (#2838) are outliers from this cluster. The values for the Carpinteria sample best match the Tribe 1 shale as supported by the significant diasterane levels referred to above. The Coal Oil Point (#2839) and San Nicolas Island #2 (#2838) tarballs, while within the Tribe 1 marl, trend towards the shale end of the spectrum and are clearly distinct from our archaeological samples and San Nicolas Island tarball #1 (#2836).

Further, we were able to correlate our archaeological sterane fingerprints (Types A and B) with Lorenson et al.’s intra-tribal families. Type A corresponds to either Family 32 or 212, and Type B clearly fits into Family 22. Family 32 drift tars are widely dispersed from Santa Rosa Island north to Point Reyes, Marin County. Based on this northerly distribution, Family 32 tars seem to originate from offshore seeps near the north of Point Conception. Lorenson et al. collected several Family 212 tars from offshore seeps and tarballs at Coal Oil Point as well as from offshore seeps at Point Conception. Drift tars of this family are distributed along a broad swath of coastline from Redondo Beach in Los Angeles County to Angel Island in San Francisco Bay, and their specific source remains uncertain (Lorenson et al., 2009). Family 22 tars are more narrowly distributed and most of the samples analyzed by Lorenson et al. come from tarballs beached near Point Conception. The family was also identified in submarine seep tars from east of Point Conception (Lorenson et al., 2009). Since the USGS study area does not extend south of the northern Channel Islands, we cannot be certain whether our bitumen samples originate from the same sources as Lorenson et al.’s data set or from unstudied submarine seeps with similar geochemical characteristics.

6. Discussion

The hydrocarbon and carbon isotopic fingerprints of the archaeological asphaltum samples analyzed in this study correspond to San Nicolas Island tarball #1 (#2836) and bear a strong resemblance to several bitumen families issuing from submarine seeps in the general vicinity of Point Conception (Lorenson et al., 2009). The California current, guided by the prevailing northwesterlies and associated swells, flows southward along the coast; it passes Point Conception, flows west of San Miguel Island, and then passes the windward shore of San Nicolas Island (Fig. 2). Here the current loops around the leeward coast, contributing to the
Southern California Eddy. This is a possible route by which the sampled asphaltum was carried and deposited upon both the northeast (#2836) and northwest (#2838) shores of the island. The course of this current also explains why both San Miguel and San Nicolas islands may receive tarballs from the submarine seep field near Point Conception and/or seeps located off the northwest coast of San Miguel Island. Because the large expanse of seafloor extending from the northern Channel Islands south past San Nicolas Island remains geochemically unstudied, we cannot at present say with certainty that the bitumens from this study did not originate from a submarine seep in this area.

The context in which our asphaltum samples were produced suggests that ancient islanders collected, processed, and used locally available drift asphaltum for a variety of purposes. At CA-SMI-603, the modified asphaltum chunk (#2834) had linear impressions evident on one side, suggesting it had been utilized for the application to a primary product. The chunk was found in the same stratum as sea grass twined cordage and a bone-gorge that may have been used in the production of fishing tackle (Vellanoweth et al., 2003). The two samples analyzed from CA-SNI-40 were found at different stages of asphaltum production and in contexts that yield information about their use. The sample extracted from the asphaltum-filled abalone shell (#2835) suggests long term storage, while the asphaltum detritus (#2832) was found in context with other encrusted artifacts such as a tarring pebble and an interior-stained abalone dish. From the samples analyzed at CA-SNI-25, the interior-stained abalone shell (#2833) was in a clear transitory stage of asphaltum utilization. Additionally, the asphaltum detritus (#2830) was located in the same unit and stratum of at least seven tarring pebbles, fragments of interior-stained abalone shells, and in close proximity to applicators with asphaltum residue (Brown, 2013). From South Locus, the asphaltum detritus’ (#2831) depositional context and general characteristics, such as degassed holes, represent degraded material from its processing and application.

Since Gutman’s pioneering efforts, new analytical techniques have opened up an avenue to explore asphaltum sources readily available to islanders and mainlanders from coastal and island shores. Today, modern tarballs are found widely dispersed along the coastal shoreline of California, from San Francisco down to San Diego and on both the northern and southern Channel Islands (Lorenson et al., 2009). As our study shows, asphaltum issuing from submarine seeps was a viable source to island populations for thousands of years, and was perhaps used by other coastal mainland groups as well. This new evidence allows us to broaden our understanding of Native American use of asphaltum from submarine seeps, and call into question the assumption that no “high-

Fig. 9. Title: Biomarker Parameters in Four Diagrams. Caption: 9a) BNH/Hopane vs. Ts/Tm; 9b) Oleanane/Hopane vs. BNH/Hopane; 9c) C_{24}/C_{22} Tricyclic Terpanes vs. C_{22}/C_{21} Tricyclic Terpanes; 9d) Oleanane/Hopane vs. Ts/Tm. Average values of parameters for archaeological and source samples calculated on numerous samples by Lorenson et al. (2009).
grade asphaltum sources are located on the Channel Islands (see Braje et al., 2005; Erlandson and Braje, 2008).

If the Nicoleño and proto-Chumash of San Miguel Island were able to utilize asphaltum issuing from submarine seeps for all their needs, they could maintain some degree of autonomy from mainland groups. Brown’s (2013) analysis shows that inhabitants of CA-SNI-25 utilized asphaltum for small-scale activities such as fishhook manufacturing and basketry construction, which supported villagers’ daily life on San Nicolas Island. Other island groups, who utilized asphaltum in similar ways, may not have needed to rely on mainland asphaltum exchange. Island peoples may have exclusively used asphaltum washed up on the island’s shores, in contrast to terrestrial sources located on the mainland. If this is the case, islanders could reserve their trade capital for commodities not locally available, and maintain resource independence for small-scale activities that required asphaltum use. It is likely that local asphaltum sources were adequate for much of the Holocene, but not for scale activities that required asphaltum use. It is likely that local asphaltum sources were adequate for much of the Holocene, but not for the more intensive needs of Late Holocene peoples, especially after the tomato/tlat became widely used.

The possibility that island people gathered or traded asphaltum from the mainland cannot be ruled out by this study. The Nicoleño’s close linguistic relatives, the Gabrieleno, are ethnographically known to have used asphaltum in the Tahitian language in the Taka family, who’s homelands encompass the San Gorgonio Pass and the desert interior beyond, where no bituminous seeps exist (Bean, 1972). It remains an open question whether this trade between linguistic relatives was also extended in a westerly direction, across the waters of the Bight to the southern Channel Islands. Our research is ongoing and we intend to test many more archaeological samples before drawing definitive conclusions about the direction and flow of asphaltum trade.

7. Conclusion

Archaeologists today have more advanced tools than ever to address questions regarding the use of asphaltum by ancient cultures around the globe. Using geochemical analytical techniques, we better understand the use of asphaltum from various sources, and can discover the origin of these sources in the archaeological record. In this study, we have found an alternative marine source utilized by native islander’s for thousands of years. These data add to our knowledge about the use of asphaltum on the California Channel Islands and new exploitable resources of asphaltum in the Bight region. Using an interdisciplinary methodology and collaborative research involving a variety of datasets, the prospects of asphaltum sourcing on a global scale are substantial. Many of the world’s cultures utilized this important resource in the past, and the techniques that we apply here can be used in other regions of the world as well. Much more can be learned about the use and production of asphaltum from an island and mainland perspective that will continue to add to our knowledge of asphaltum use in antiquity.

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