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ARTICLE



Unraveling Island Economies through Organic Residue Analysis: The Case of Mocha Island (Southern Chile)

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Abstract

Biophysical conditions played a fundamental role in early human colonization of insular territories, particularly in food-producing societies dealing with limited resources and the challenges of maintaining a sustainable carrying capacity. Studies on past human colonization of small oceanic islands thus offer insights into economic plasticity, ecological impacts, and adaptation of early food-producing groups. On the coast of southern Chile, early evidence is dated to 950 cal BP of island colonization by coastal populations with mainland subsistence systems based on the exploitation of marine resources, along with gathering, managing, and cultivating plants and hunting terrestrial animals. Strikingly, the extent to which these mixed economies contributed to insular colonization efforts is largely unknown. Here we used organic residue analysis of ceramic artifacts to shed light on the subsistence of populations on Mocha Island in southern Chile. We extracted and analyzed lipids from 51 pottery sherds associated with the El Vergel cultural complex that flourished in southern Chile between 950 and 400 cal BP. Chemical and stable isotope analysis of the extracts identified a range of food products, including C_3 and C_4 plants and marine organisms. The results reveal the central role of mixed subsistence systems in fueling the colonization of Mocha Island.

Resumen

Las condiciones biofísicas desempeñaron un papel fundamental en la temprana colonización humana de territorios insulares, sobre todo en sociedades productoras de alimentos que se enfrentaban a recursos limitados y a los desafíos de mantener una capacidad de carga sostenible. Los estudios sobre la colonización humana de pequeñas islas oceánicas en el pasado ofrecen, por lo tanto, información sobre la plasticidad económica, los impactos ecológicos y la adaptación de los primeros grupos productores de alimentos. En la costa del sur de Chile, los primeros indicios de colonización de islas datan de hace 950 años cal aP por parte de poblaciones costeras con sistemas de subsistencia en tierra firme basados en la explotación de los recursos marinos, además de la recolección, manejo y cultivo de plantas, y la caza de animales terrestres. Sorprendentemente, se desconoce en qué medida estas economías mixtas contribuyeron a los esfuerzos de colonización insular. En este trabajo, empleamos el análisis de residuos orgánicos de artefactos cerámicos para elucidar la subsistencia de las poblaciones de la isla Mocha, en el sur de Chile. Extrajimos y analizamos lípidos de 51 fragmentos cerámicos asociados al complejo cultural El Vergel, que se desarrolló en el sur de Chile entre 950 y 400 años cal aP. El análisis químico y de isótopos estables de los extractos identificó una serie de productos alimenticios, incluyendo plantas C_3 y C_4 , así como organismos marinos. Los resultados revelan el papel central de los sistemas mixtos de subsistencia en el impulso de la colonización de la isla Mocha.

Keywords: pottery; organic residue analysis; island colonization; southern Chile; El Vergel; mixed economies

Palabras clave: cerámica; análisis de residuos orgánicos; colonización de islas; sur de Chile; El Vergel; economías mixtas

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The socioecological drivers of early human colonization of oceanic islands have been the subject of a contentious debate in archaeology (Braje et al. 2017; Terrell 2023). Insular biogeographic conditions, distance from mainland enclaves, seafaring technology, and the flexibility of a subsistence economy were some of the interplaying factors conditioning island-colonization efforts (Crowther et al. 2016; Leppard 2014; O'Connor et al. 2019; Takamiya 2006). Over the preceding several decades, genetic, archaeological, and linguistic studies have increased our understanding of these processes in regions such as the west and northeast Pacific Ocean (Horsburgh and McCoy 2017; Lepofsky et al. 2015; McFadden et al. 2021; Potter and White 2009; Walworth 2014). Despite extensive archaeological research along the western coast of South America (Beresford-Jones et al. 2018; King et al. 2018; Reyes et al. 2022; Stothert et al. 2003), large geographic areas of the Chilean coast remain poorly understood.

On the Pacific coast of South America, the productive Humboldt upwelling system (3°24′S–54°55′S) has sustained coastal adapted populations since the Late Pleistocene. Throughout the Holocene, coastal communities developed mixed economies with distinct degrees of reliance on marine and terrestrialbased resources (Dillehay et al. 2022; Knudson et al. 2015; Pearsall et al. 2020). In southern Chile the intensification of food production during the Late Ceramic period (950–400 cal BP) led to sedentarism and a remarkable demographic upsurge (Campbell and Quiroz 2015). During this time, farming groups from the El Vergel cultural complex migrated and permanently settled on small offshore islands (Campbell 2015; Campbell and Quiroz 2015). From here, the occupation of Mocha Island, the largest, most isolated island, lying 35 km offshore, is an intriguing case. The proliferation of El Vergel residential sites and the construction of monumental architecture by a large workforce seem to suggest that a dense, complex, and permanently settled society was established here (Campbell 2015; Campbell and Pfeiffer 2017). However, Mocha Island's biogeographic characteristics denote limited terrestrial resources, making for unsuitable conditions for supporting large groups of people (Campbell 2015; Pefaur and Yáñez 1980).

The translocation of domestic plants and tamed camelids is argued to have been a prerequisite for the permanent settlement of Mocha Island by the El Vergel groups (Becker 1997a; Campbell 2015; Godoy-Aguirre 2018; Roa et al. 2015, 2021). Preliminary results on lipid distributions extracted from Mocha Island pottery fragments indicated a preferential use of terrestrial resources, including the exploitation of terrestrial animals (Roa et al. 2021). Carbon (δ^{13} C) and nitrogen (δ^{15} N) stable isotope analyses of El Vergel individuals from Mocha Island suggest a diet largely based on terrestrial resources with only a low contribution of marine proteins (Campbell et al. 2020). The results clearly show the predominance of a mixed diet. ¹³C enrichment in the individuals is attributed to the consumption of locally cultivated maize (Campbell et al. 2020), while marine resources are claimed to have played a marginal role in the foodways and adaptive process of El Vergel farmers—despite the island's location within one of the most productive upwelling systems of the world (Campbell et al. 2020; Roa et al. 2021).

Attributing human bone collagen ¹³C enrichment to the sustained consumption of C_4 plants such as maize is problematic when marine resources are involved because of the possible overlapping of δ^{13} C values (Corr et al. 2005). Moreover, mollusk remains were found at every residential site on Mocha Island, along with marine mammal and fish bones; in some cases, they outnumbered terrestrial animal remains (Power 2013; Roa et al. 2021). The identification of net sinkers and fishing hooks in some sites indicates the use of specialized technology for exploiting local marine resources (Martínez 2013, 2015; Quiroz and Sánchez 2005). The clear evidence for the use of marine commodities and the possible methodological biases suggest that the role of marine products in El Vergel farmers' foodways on Mocha Island is not well understood and needs further assessment.

Here we present the first organic residue analysis from the Pacific coast of South America using single-compound stable carbon isotope composition and molecular evidence extracted from pottery sherds to evaluate the use of marine resources by El Vergel coastal farmers settling on Mocha Island. This analysis enabled us to assess local foodways, the use pottery might have had for processing marine resources, and whether this reflects the adaptive and socioeconomic strategies developed during Mocha Island's colonization.

Mocha Island: Environmental Setting

Mocha Island is an offshore small insular territory of 52 km² that is located 35 km from the mainland (Figure 1). It originates as the highest section of an emerging ridge from the continental plaque, continuously rising above sea level for the last 6,000 years (Melnick et al. 2003; Nelson and Manley 1992). It comprises two main mountain ranges of 390 m asl and is covered by a dense evergreen forest that is surrounded by a coastal plain of beaches and meadows (Bahlburg and Spiske 2015; Prieto 1997). Annual precipitation of around 1,350 mm forms small rivers and lakes supplying the island with fresh drinkable water (Pefaur and Yáñez 1980; Prieto 1997).

The composition of its flora has remained relatively unchanged for the last 2,000 years: it is mainly dominated by evergreen species such as *Aextoxicon punctatum*, *Drimys winteri*, and *Azara lanceolata* and a variety of Myrtaceae (Lequesne et al. 1999). This landscape also contains a range of wild edible plants, mainly *Aristotelia chilensis* (Chilean wineberry), *Fragaria chiloensis* (Chilean strawberry), *Rubus geoides* (wild raspberry), *Gevuina avellana* (Chilean hazelnut), and *Madia sativa* (Roa et al. 2015, 2021).

The native fauna comprised various small rodents, birds, reptiles, and amphibian species; no large terrestrial mammals were present before the translocation of mainland animals by humans (Pefaur and Yáñez 1980; Reiche 1903; Saavedra et al. 2003). Local marine fauna are abundant and include mollusks, crustaceans, marine mammals, and different fish species (Báez 1997; Gálvez 1997; Rebolledo 2013; Reiche 1903).

The El Vergel Cultural Complex and Pottery Production

The El Vergel cultural complex consisted of farming groups that cultivated domestic crops, tamed wild animals, and engaged in hunting-and-gathering practices (Becker 1997b; Contreras et al. 2005; Roa et al. 2018). The main characteristic element of the El Vergel cultural complex is its pottery. Decoration using red or black geometric motifs over a white slip surface is a distinctive feature of the El Vergel pottery found in funerary contexts (Adán et al. 2005; Aldunate 1989; Bahamondes et al. 2006). Large ceramic containers were common, some of which functioned as funerary urns; however, these containers were also found in residential settings (Bullock 1970; Gordon 1978; Navarro and Aldunate 2002). Ethnographic investigations within the Mapuche people, descendants of the El Vergel cultural complex, described the use of similar large containers for culinary purposes, mainly the storage and preparation of fermented maize or wheat beverages known as *chicha* or *muday* (Alvarado 1997). Other types, such as nondecorated monochrome vessels and pots with a red slip surface, are frequently found in residential sites (Adán et al. 2005; Quiroz 2001). These pots correspond to various vessel types such as jars, cooking pots, mugs, and dishes, presenting specific morphological characteristics that denote a long-standing pottery tradition in southern Chile (Adán et al. 2005; Aldunate 1989; Dillehay 1990; López 2017; Palma 2013).

On Mocha Island, diagnostic elements found in residential sites confirm the presence of the El Vergel cultural complex (Campbell 2020; Campbell and Pfeiffer 2017; Roa et al. 2021). Its population comprised autonomous communities with equal access to local and exotic resources (Campbell 2020). Camelids or *chilihueque*, the name for local guanaco (*Lama guanicoe*), were translocated from the mainland and exploited at every residential site for fur and meat (Becker 1997a; Roa et al. 2021; Westbury et al. 2016). Domesticated crops, specifically quinoa (*Chenopodium quinoa*), maize (*Zea mays*), and beans (*Phaseolus vulgaris*), were cultivated along with gathering wild local plants (Roa et al. 2015, 2021; Rojas and Cardemil 1995). The presence of mollusks, marine birds and mammals, and fish remains at every residential site confirms generalized access to coastal foraging, hunting, and fishing, mainly nearshore fishing (Gálvez 1997; Martínez 2014, 2015; Power 2013; Rebolledo 2013; Roa et al. 2021).

Materials and Methods

We selected 51 pottery sherds chronologically associated with the Late Ceramic period from three residential sites located at different points of the island (Table 1). These sherds comprised polished, smoothed, and eroded monochrome pottery fragments from the rim, neck, body, and base (Supplemental Table 1). Only samples with a thickness greater than 7.25 mm were selected. The

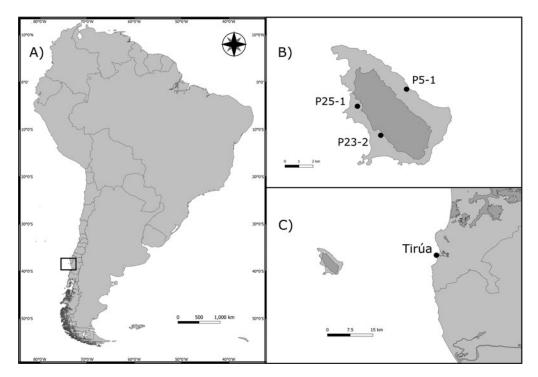


Figure 1. (A) Mocha Island in South America; (B) archaeological sites at Mocha Island; (C) Mocha Island facing the coast of Chile.

Site	Number of Samples	Laboratory Code	Excavation Unit	Material	Таха	¹⁴ C Age BP	Median Probability cal yrs BP
P5-1	17	UB-26214 UB-26216 UB-26215	05.02.03	Kernel	Zea mays	552 ± 26	530
			05.02.03	Bone (Phalange)	Camelidae	605 ± 26	554
			05.02.03	Cobb	Zea mays	635 ± 25	607
P23-2	15	UB-29290 UB-29289	23.03.01	Kernel	Zea mays	1108 ± 28	961
			23.03.01	Seed	Phaseolus vulgaris	679 ± 25	603
P25-1	19	UB-29287 UB-29288	25.03.04	Kernel	Zea mays	644 ± 35	605
			25.03.04	Kernel	Zea mays	661 ± 30	606

Table 1. ¹⁴C Dates from Associated Material.

Source: Data from Campbell and Pfeiffer (2017:Supplemental Tables 10-15).

identification of soot marks in some of them potentially indicates their exposure to fire. Based on these characteristics, the selected fragments likely represent cooking pots and large containers, mainly used for processing food resources (Albán et al. 2013).

To obtain molecular and δ^{13} C references of local resources, cooking experiments were conducted using seven nontempered replica vessels (Bondetti et al. 2020; see Supplemental Table 2 and Supplemental Text 1). Each commodity was cooked in a specific container, with no mixing between resources.

Organic Residues Analysis

A small section of the inner surface of the 51 pottery fragments was cleaned before drilling 2–3 mm into the potsherds to obtain 1 g of pottery powder for acid extraction (AE). A one-step acidified

methanol protocol was followed (Craig et al. 2013). A blank was included as a control to assess contamination throughout the extraction process. An internal standard (*n*-tetratriacontane (C_{34}): 10 µg) was incorporated in each tube. Methanol (4 mL) and sulphuric acid (800 µL) were added and the mixture was subsequently sonicated and centrifuged before being placed on a heating block for four hours at 70°C. Three successive extractions using *n*-hexane allowed the lipids' separation before their neutralization using potassium carbonate. Subsequently, lipids were concentrated and resuspended in *n*-hexane at appropriate dilution for gas chromatography-mass spectrometry (GC-MS) analysis. An internal standard (*n*-hexatriacontane (C_{36}): 10 µg) was added at the end of the extraction to infer lipid yield and concentration.

Another 1 g was prepared from nine potsherds and subjected to solvent extraction (SE). The extraction procedure followed a protocol similar to that described by Colonese and coworkers (2017). Lipids were extracted by sonication from the ceramic powder using dichloromethane:methanol DCM:MeOH 2/1 v/v three times. A blank was also prepared to assess contamination. After the centrifugation, the liquid fraction was transferred into clean and labeled hydrolysis vials, and their content was evaporated to complete dryness under a gentle stream of nitrogen. One aliquot of the sample was resuspended in 50 µl of *n*-hexane and derivatized by adding four drops of N, O-bis (trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane (BSTFA+TMCS, 99:1). Samples were placed on a heating block for one hour at 70°C and then dried under a gentle stream of nitrogen. Subsequently, samples were resuspended in *n*-hexane for their analysis by GC-MS.

Seven acid extracted samples were also derivatized with BSTFA+TMCS, 99:1, to identify very longchain fatty alcohols. Samples were transferred from their respective GC-vial inserts by adding 100 μ l of *n*-hexane into each vial and transferring it into a clean hydrolysis vial (x3). Samples were dried and resuspended in 50 μ l of hexane, and four drops of BSTFA+TMCS, 99:1, and a flush of nitrogen were added before they were placed on a heating block at 70°C for one hour. Samples were concentrated and then transferred to a new GC-vial with a conical insert for their analysis within 48 hours.

Around 1 g of pottery powder was obtained from each of the seven replica vessels used in the cooking experiments. An extraction protocol using acidified methanol was also followed.

Lipid extracts were screened and quantified using an Agilent 7890B high-temperature gas chromatograph (Agilent Technologies, Cheadle, Cheshire, UK) equipped with a flame ionization detector (HT-GC-FID). A 100% Dimethylpolysiloxane DB-1 column (15 m \times 320 µm \times 0.1 µm; J&W Scientific, Folsom, California, USA) was used. A splitless injector was used to inject 1 µL of acidextracted samples into the GC at 300°C. The carrier gas was helium, with a constant flow rate of 2 mL min⁻¹. The temperature of the oven was set at 100°C for two minutes and then increased to 20°C min⁻¹ up to 325°C, holding for three minutes.

A splitless injection was also used to inject 1 μ L of solvent-extracted samples at 350°C. The temperature of the oven was set at 50°C for two minutes and then increased 10°C min⁻¹ up to 375°C, settling for 10 minutes.

Acid-extracted and solvent-extracted samples were analyzed using an Agilent 7890A series chromatograph attached to an Agilent 5975C inert XL mass selective detector with a quadrupole mass analyzer (Agilent Technologies). The column used was a methylpolysiloxane (5%-phenyl) DB-5ms ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$; J&W Scientific). Samples were injected (1 µL) using a splitless injector at 300°C. Helium was used as the carrier gas, at a constant flow rate of 2 mL min⁻¹. The temperature of the oven was set at 50°C for two minutes and then rose 10°C min⁻¹ to 325°C, where it settled for 15 minutes. The mass spectrometer ionization energy was 70 eV, obtaining a spectrum by scanning ions between m/z 50 and 800.

Preliminary results using HT-GC-FID indicated the possible presence of triacylglycerols in some samples (Roa et al. 2021). We used high-temperature gas chromatography-mass spectrometry (HT-GC-MS) to assess their presence in the pots. TMS solvent extracts were analyzed using a Perkin Elmer Clarus 690 gas chromatograph coupled to a SQ8-T mass spectrometer. The column was a DB5-HT column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.1 \mu \text{m}$). Helium was used as the carrier gas at a constant flow rate of 1mL min⁻¹. The temperature of the oven was set at 50°C for two minutes and then increased to 10°C min⁻¹, reaching a maximum temperature of 375°C held for 15 minutes.

The identification of isoprenoid acids and ω -(*o*-alkylphenyl) alkanoic acids (APAAs) as aquatic biomarkers was performed using a GC-MS equipped with a 50% cyanopropyl-methylpolysiloxane DB-23 column (60 m × 0.25 mm × 0.25 µm; J&W Scientific) as in the study by Shoda and coworkers (2017). A splitless injector was used to inject 1µL of the acidified methanol extracts into the GC at 300°C. Helium was used as the carrier gas, with a flow rate of 1.5 mL min⁻¹. The temperature of the oven was set at 50°C for two minutes and then rose 10°C min⁻¹ to 100°C, after which it increased 4°C min⁻¹ up to 140°C then 0.5°C min⁻¹ up to 160°C, and finally by 20°C min⁻¹, reaching 250°C where it settled for 20 minutes. The mass spectrometer was operated in single ion monitoring (SIM) mode to achieve higher sensitivity of target compounds. Selected ions allowed the identification of the three main isoprenoid acids (m/z 74, 101, 171, and 326 for phytanic acid; m/z 74, 88, 101, and 312 for pristanic acid; and m/z 74, 87, 213, and 270 for 4, 8, 12-trimethyltridecanoic acid [4, 8, 12-TMTD]), and APAAs of carbon length C₁₆-C₂₂ (m/z 74, 105, 262, 290, 318, 346).

MSD Chemtation F.01.03.2357 software was used to compute the GC-MS results. Compounds were identified according to retention time and mass spectrum and by comparison with the National Institute of Standards and Technology (NIST) library. Peaks were integrated using Agilent Mass Hunter Quantitative Analysis software version B.07.01/ Build7.1.524.0 for GC-MS.

GC-c-IRMS and Single-Compound δ^{13} C Analysis

We selected 49 samples for δ^{13} C analysis of the main alkanoic acids— $C_{16:0}$ and $C_{18:0}$ —based on a minimal alkanoic acid quantity needed for injection. These samples were analyzed using a Delta V Advantage Isotope Ratio Mass Spectrometer (Thermo Fisher Scientific, Bremen, Germany), coupled to a Trace Ultra 1310 Gas Chromatograph (Thermo Fisher) with a GC IsoLink II interface (with a CuO combustion reactor held at 850°C). The column was an ultra-inert fused-silica DB-5 ms UI (60 m × 0.25 mm × 0.25 µm; J&W Scientific), into which 1 µl of each sample was injected for analysis. Ultra-high-purity grade helium was used as the carrier gas with a flow rate of 2 mL min⁻¹, from which a small part of the flow was diverted to an ISQ mass spectrometer (Thermo Fisher) for parallel acquisition of molecular data. The temperature of the oven was set at 50°C for 0.5 min, and then increased 25°C min⁻¹ to 175°C and then 8°C min⁻¹ until it reached 325°C and then settled for 20 minutes.

Eluted compounds were ionized in the mass spectrometer through electron impact. The intensities of ions m/z 44, 45, and 46 were recorded to automatically compute the ${}^{13}C/{}^{12}C$ ratios of each peak in the extracts. The software used for the computation were Isodat (Thermo Fisher Scientific) and LyticOS (Isoprime, Cheadle, UK). Computation was based on the comparison with the repeatedly measured standard reference gas (CO₂). Calculated $\delta^{13}C$ values are presented in parts per mil (‰), relative to the Vienna PeeDee Belemnite (V-PDB) international standard.

Batches were calibrated using a linear calibration curve (average $R^2 = 0.996 \pm 0.002$ in 16 batches) based on expected versus measured δ^{13} C values of *n*-alkanes and *n*-alkanoic acid esters from international standards (Indiana A7 and F8-3 mixtures). The accuracy of the instrument was determined on *n*-alkanoic acid methyl esters of known isotopic composition (Indiana F8-3, 18 measurements). The mean and standard deviation of these compounds were $-29.89 \pm 0.1\%$ for $C_{16:0}$ (reported mean value vs, V-PDB $-29.90 \pm 0.03\%$) and $-23.41 \pm 0.06\%$ for $C_{18:0}$ (reported mean value vs. V-PDB $-23.24 \pm 0.13\%$). The precision was based on a laboratory standard mixture regularly injected between samples (108 measurements). Alkanoic acids mean \pm SD values were $-30.70 \pm 0.15\%$ for $C_{16:0}$ methyl ester and $-26.44 \pm 0.15\%$ for $C_{18:0}$ methyl ester. After this analysis, values were corrected for the methylation of the alkanoic acids that occurred during acid extractions. Corrections were performed using a mass balance formula to compare the values with a standard mixture of $C_{16:0}$ and $C_{18:0}$ fatty acids of known isotopic composition, which was already included in each batch during the acid extractions. Modern references were adjusted according to the atmospheric δ^{13} C variations between the Early Holocene Epoch and the present to better interpret the archaeological data (Hellevang and Aagaard 2015).

Results

Lipid concentrations from the acid extracted fraction ranged from 3 to $360 \ \mu g \ g^{-1}$, with a mean of 57.4 $\ \mu g \ g^{-1}$ Only one sample (P25-1.19) yielded lipids below the interpretable limit of >5 $\ \mu g \ g^{-1}$

(Evershed 2008) and was excluded from further analysis (Supplemental Table 3). Lipid profiles exhibited a mixture of aliphatic compounds comprising a distribution of saturated fatty acids ($C_{8:0}-C_{30:0}$), monounsaturated fatty acids ($C_{14:1}-C_{24:1}$), fatty alcohols ($C_{12}-C_{32}$), α , ω -dicarboxylic acids (C_8-C_{14}), and branched and linear fatty acids $C_{15:0}$ and $C_{17:0}$. Overall, from the lipid distributions and biomarker identification it was possible to distinguish between the processing of aquatic and plant commodities in the El Vergel pots.

The El Vergel Pottery and Its Use for Processing Aquatic Organisms

Four El Vergel pots (8%) had a full range of aquatic biomarkers comprising at least one of the three main isoprenoid acids (4, 8, 12-trimethyltridecanoic acid, pristanic, or phytanic acid), and a homologous series of C_{18} , C_{20} , and, in one sample, C_{22} APAAs. These biomarkers are established indicators for the processing of aquatic resources (Evershed et al. 2008; Lucquin et al. 2016). APAAs are only formed by the protracted heating $\geq 200^{\circ}$ C of $C_{18:x}$, $C_{20:x}$, and $C_{22:x}$ unsaturated fatty acids that are found in plants and terrestrial animals but mainly in aquatic commodities (Supplemental Figure 1; Bondetti et al. 2020; Evershed et al. 2008; Hansel et al. 2004) and therefore must be derived from cooking events. The ratio between the two phytanic acid diastereomers, 3S, 7R, 11R, 15–phytanic acid (SRR), and 3R,7R,11R,15–phytanic acid (RRR), helps discriminate between ruminant and aquatic products. A high contribution of the SRR–diastereomer (i.e., 76% ± 16.6) is likely derived from aquatic animal tissue (Supplemental Table 4; Lucquin et al. 2016). An SRR–phytanic acid diastereomer contribution higher than 70% in three of these four samples further supports an aquatic origin. The absence of freshwater commodities on the Island during the Late Ceramic period likely reflects a marine origin for the aquatic resources.

Molecular Evidence for Terrestrial Commodities

Plant commodities were the most representative resources identified in the El Vergel pots. Nineteen samples (38%) had a distribution of even over odd-numbered very long-chain fatty acids and odd over even-numbered middle- and long-chain alkanes, characteristic of the epicuticular wax of plant leaves and stems (Diefendorf et al. 2011; Dove and Mayes 2006; Dunne 2021). Very long-chain fatty alcohols with an even over odd-numbered carbon chain distribution, characteristic of plant commodities (Dove and Mayes 2006), and plant sterols were identified in several samples.

Several pots (n = 16, 32%) contained APAAs with 18 carbon atoms (APAA-C₁₈) but lacked the C₂₀ and C₂₂ ω -(o-alkylphenyl) alkanoic acids. APAA-C₁₈ can form from a wide range of plant and animal products, but the distribution of isomers (A-I) can provide further discrimination (Supplemental Figure 2; Bondetti et al. 2020). Samples in Figure 2 had an APAA-C₁₈ E/H isomer ratio, possibly reflecting (1) cereals, fruits, and non-leafy vegetables; (2) terrestrial and aquatic animals; and (3) leafy plants (Bondetti et al. 2020; Dolbunova et al. 2023). Mixing cereals, fruits, and non-leafy vegetables with leafy plants may produce an intermediate E/H ratio similar to an animal origin (Bondetti et al. 2020). Only one of six samples with intermediate E/H values had a complete set of aquatic biomarkers; the rest lacked any evidence for processing aquatic or terrestrial animal products. The identification of plant epicuticular wax lipid distributions in four of these samples might indicate a plant origin.

Three samples with a full set of aquatic biomarkers had high APAA- C_{18} E/H ratios similar to those found in heated local reference samples of cereals, fruits, and non-leafy vegetables (Figure 2). This evidence may indicate the use of aquatic and plant products in the same container.

A palmitic over stearic acid ratio (P/S) ≤ 1 identified in 46% of the samples may indicate that terrestrial animals were exploited in the El Vergel pots (Romanus et al. 2007). However, the higher solubility of C_{16:0} compared to C_{18:0} may alter the P/S ratio in animal tissue (Whelton et al. 2021). Monoacylglycerols and diacylglycerols were present in a small number of solvent-extracted samples, whereas no triacylglycerols were identified. A distribution of C_{15:0} and C_{17:0} branched and linear fatty acids was found in most of the El Vergel samples. Their presence is associated with bacterial lipids from the rumen of polygastric animals (Evershed et al. 2002). However, they can also be linked to soil bacteria contamination, making them unspecific to ruminant fat (Dudd et al. 1998). An

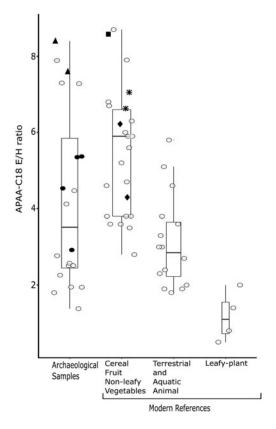


Figure 2. Boxplots of the APAA– C_{18} E/H ratio of Mocha Island samples. Black circles represent samples with a full set of aquatic biomarkers. The black triangles are samples showing ¹³C enrichment of their residues consistent with a C₄ origin. Black square, asterisks, and diamonds correspond to modern references for Chilean hazelnut, maize, and quinoa, respectively. References are based on Bondetti and others (2020) and this study (see Supplemental Table 5).

SRR-diastereomer contribution below aquatic values may indicate the processing of ruminants in only one El Vergel pot (Lucquin et al. 2016). Cholesterol was detected in some samples in small amounts; however, we cannot ascertain its archaeological origin due to the absence of clear bio-hydrogenated and oxidation derivatives (Hammann et al. 2018).

Single-Compound Stable Carbon Isotope Analysis

To further identify the commodities' origin, we measured the stable carbon isotope values of the palmitic ($\delta^{13}C_{16:0}$) and stearic ($\delta^{13}C_{18:0}$) alkanoic acids extracted from the pots and then compared these values to modern and archaeological references of marine, C₃ plants, maize, and ruminant animals, including South American camelid *Lama glama* (Supplemental Tables 6 and 7).

Most pots (74%) had $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values plotting within the ranges for C₃ plants. Three of the four samples showing a complete set of aquatic biomarkers were more depleted in ¹³C relative to marine references, plotting close to C₃ plant values (Figure 3). The E/H ratios of these samples coincided with the use of cereals, fruits and non-leafy vegetables, probably indicating that plants and aquatic products were used in these pots.

It is likely that maize was processed in some pots with high δ^{13} C values relative to C₃ plant references (Figure 3). Extracts from these pots had high APAA-C₁₈ E/H ratios coinciding with cereals, fruits, and non-leafy vegetables; a high P/S ratio; and a fatty alcohol distribution characteristic of plant commodities. The identification of C₃₂ alcohol in a high relative abundance can be associated with panicoid grasses like maize (Reber and Evershed 2004). Although C₃₂ was found in low abundance in one sample, its association with panicoid plants is debatable (Supplemental Figure 3). The different δ^{13} C values in these samples might indicate the incorporation of other commodities, possibly C₃ plants, in varying proportions.

Nine samples had $\Delta^{13}C_{(C18:0-C16:0)}$ offsets coinciding with ruminant carcass fat references (Copley et al. 2003; Dolbunova et al. 2023). These samples yielded plant lipids and some aquatic biomarkers;

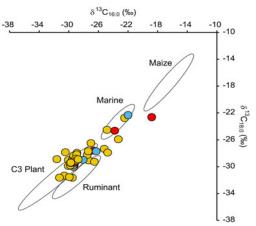


Figure 3. Scatterplot of compound-specific δ^{13} C analysis of the main alkanoic acids (X-axis = $\delta^{13}C_{16:0}$; Y-axis = $\delta^{13}C_{18:0}$) extracted from the El Vergel pots. Blue circles indicate the four samples with a full range of aquatic biomarkers. The red circles highlight samples with a high APAA-C₁₈ E/H associated with cereals, fruits, and non-leafy vegetables (Bondetti et al. 2020). The 68% confidence ellipses are based on reference values published in the literature and from this study (see Supplemental Tables 6 and 7). (Color online)

however, they lacked compounds typically documented in ruminant fats, such as SRR% <64 and acylglycerol distributions. They possibly reflect the mixing of plant and animal products that can result in low $\Delta^{13}C_{(C18:0-C16:0)}$ values (Cramp et al. 2019; Hendy et al. 2018; Taché et al. 2021). To investigate further, we applied a simple linear mixing model based on averaged $\delta^{13}C$ values of modern reference endpoints, adopting a progressive 10% increment (Figure 4). The hypothetical mixing lines indicate the possible use of marine and terrestrial animal products or C₃ and C₄ plants in these pots.

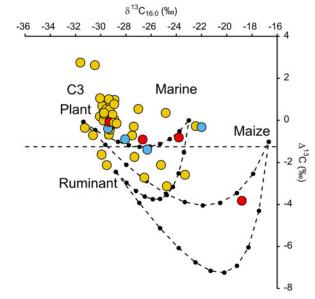
Discussion

Organic residues from pottery artifacts demonstrated that local marine products were certainly part of the El Vergel farmers' foodways, which aligns with other evidence of marine resources exploitation on the island, such as faunal remains and fishing gear (fishhooks and net sinkers). This coastal adaptation gave the inhabitants access to a rich source of animal protein, compensating for the lack of large mammals on the island. Together our results highlight the overall importance of marine resources in the region and as a critical component of early island colonization efforts. Coastal adaptation was essential for island colonization and perhaps was more widespread than previously thought, as evidenced in the mainland El Arenal-1 site in Punta Lavapié (Contreras et al. 2005).

The single-compound δ^{13} C analysis and more robust molecular evidence allowed us to reinterpret previous results indicating the use of pots for processing terrestrial animal fat (Roa et al. 2021). The exploitation of translocated ruminants was underrepresented in the El Vergel pots, contradicting the abundance of camelid remains found on Mocha Island (Roa et al. 2021). According to the chronicles of the first Europeans arriving on Mocha Island and southern Chile, camelids were important for local communities, which would have limited their availability for trading and consumption (Rosales 1877 [1674]:324–325; Van Meurs 1993; Van Noort [1600] quoted in Ijzerman 1926:57–58). Their exploitation as a source of animal protein cannot be ruled out because other culinary practices, such as roasting and drying the meat, were possibly used.

Marine products were processed in the pots alone or mixed with C_3 plants. The $\delta^{13}C$ values of these samples demonstrate that C_3 plants were exploited intensively, given that oily and lipid-rich marine products are likely to increase $\delta^{13}C$ values. Our results thus reveal that plants were the basis of the foodways of Mocha Island inhabitants. The use of leaves and stems and non-leafy plants, such as cereals and fruits, and non-leafy vegetables in the pots are concordant with the diversity of plants exploited by local Mocha Island farmers (Godoy-Aguirre 2018; Roa et al. 2015). Evidence for the epicuticular wax of leaves and stems was present in most El Vergel pots. The Mapuche people from southern Chile traditionally use the leaves and stems of some plant species found on Mocha Island for medicinal purposes. However, the culinary use of leaves with other commodities such as cereals and animal meat has also been documented in the past, including the preparation of various stews and other local dishes (Gay 2018 [1873]:197; Rosales 1877 [1674]:153–154).

Figure 4. Compound-specific δ^{13} C analysis of Mocha Island samples plotted according to their $\delta^{13}C_{16:0}$ value against $\Delta^{13}C_{(C18:0 -C16:0)}$. Blue circles indicate the four samples with a full set of aquatic biomarkers. The red circles highlight the samples with an APAA-C₁₈ E/H ratio associated with cereals, fruits, and non-leafy vegetables (Bondetti et al. 2020). Average δ^{13} C endpoints were built using modern and archaeological references from published data and this study (see Supplemental Tables 6 and 7). Mixing lines with 10% increments connecting the endpoints were calculated based on the mean relative amount of each alkanoic acid present in the products. Data were gathered from the USDA database. The dashed line indicates a -1.26‰ threshold set for the identification of ruminant carcass fat, as in Dolbunova and colleagues (2023). (Color online)



The lipid distribution of grains, seeds, and fruits is characterized by a low abundance of very longchain fatty acids and alkanes, along with a P/S ratio >1.3 (Dunne 2021; Dunne et al. 2016). Mixing these products with leaves and stems will likely produce a distribution similar to that seen for plant epicuticular wax, hence overshadowing their presence. The APAA-C₁₈ E/H ratio and δ^{13} C values revealed the exploitation of C₃ cereals, fruits, and non-leafy vegetables and their mixing with leafy plants; one may presume that the former group was overshadowed in the pots by the latter. The whole spectrum of cereals, fruits, and non-leafy vegetables may have included domestic and wild plants traditionally used in southern Chile. Chilean wineberry, Chilean strawberries, Chilean hazelnut, and *Madia sativa* seeds are wild plants used in pottery containers for roasting, preparing alcoholic beverages, and extracting oil (Godoy-Aguirre 2018; Pino Ramos et al. 2019; Schmeda-Hirschmann 1995). In the case of domestic plants, this group was dominated by beans, maize, and quinoa. However, chronicles mentioned the consumption of potatoes by Mocha Island inhabitants (Van Meurs 1993; Van Noort [1600] quoted in Ijzerman 1926:56–58), although this tuber has not yet been identified in the archaeological record of the island.

Quinoa seeds were the most abundant plant remains found at every Mocha Island site (Roa et al. 2021), and quinoa likely comprises a major part of the C_3 plant residues found in the pots. Its use in southern Chile was reported since the Early Ceramic period (1550–950 cal BP) from wild-type quinoa managed by hunter-gatherer groups (Adán and Mera 2011; Campbell and Quiroz 2015; Roa et al. 2018). Its ability to adapt to different environments without much maintenance investment may have facilitated its early management and incorporation into local foodways (Planella 2019).

The recent arrival of maize on Mocha Island and southern Chile (around 950 BP) would have required a period of experimentation and adaptation to the local temperate conditions. This might have influenced the degree to which the El Vergel farmers exploited maize; it was possibly restricted to the production of fermented beverages. The two pots used for processing maize likely also included C_3 plants. The different $\Delta^{13}C$ offsets between the two samples possibly indicate the mixing of maize with C_3 plants with varying proportions of $C_{16:0}$ and $C_{18:0}$ alkanoic acids. Incorporating other starchy plants into the pot may have enhanced the fermentation process for producing maize-based beverages (Arriaza et al. 2016). From the residue data, we can argue that maize was not consumed as a staple food by Mocha island farmers; otherwise, we would expect more samples showing high $\delta^{13}C$ values, possibly with a negative $\Delta^{13}C$ offset due to the mixing of C_3 and C_4 plants, as indicated by our simple linear model. Therefore, we suggest that the high $\delta^{13}C$ and relatively low $\delta^{15}N$ values for human bone collagen described in previous studies might not necessarily represent a preferential consumption of maize over aquatic resources. Low trophic-level marine organisms such as mollusks might also have been preferentially consumed, an interpretation supported by the faunal evidence from the island.

Conclusion

The permanent settlement of Mocha Island by the El Vergel farmers required the translocation of domestic crops and tamed animals. Previous studies referred to the exploitation of marine resources as only a secondary activity and stressed the continuity of farming to support the dense populations on the island. Our organic residue analysis revealed that the El Vergel pottery of Mocha Island was mainly used for exploiting plant commodities and marine products. Plant commodities were the basis of the local diet; however, maize was not a staple and might have been mainly destined for the production of fermented beverages. Plant products were mixed with aquatic resources, although different types of plants were also simultaneously exploited. Marine commodities were a source of animal protein and may have compensated for the limited availability of terrestrial animal products during certain seasons and complemented the exploitation of translocated ruminants.

The use of pottery indicates that local and translocated resources were an important part of the foodways of the El Vergel coastal farmers from Mocha Island. Local marine resources complemented translocated domestic plant commodities such as maize and quinoa, sustaining a mixed economy where farming, coastal foraging, hunting, and fishing were practiced. Perhaps it was only when this mixed economy developed that the dense populations could be supported on Mocha Island following its settlement by the El Vergel farmers. More studies focusing on mainland sites are needed to characterize better the foodways and socioeconomic strategies of the El Vergel farmers inhabiting coastal and inland areas.

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Data Availability Statement. Potsherds are stored at the Escuela de Antropología, Pontificia Universidad Católica de Chile. For future analyses, permission should be requested from the Consejo de Monumentos Nacionales, Chile. The generated isotopic and molecular data are stored by the corresponding author and at the BioArch database. Access to this database is restricted to the Department of Archaeology, University of York.

Competing Interests. The authors declare none.

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Supplemental Text 1. Cooking experiments and archaeological maize for δ^{13} C references.

- Supplemental Table 1. Mocha Island Potsherds.
- Supplemental Table 2. List of Products.
- Supplemental Table 3. Summary of the Molecular and Isotopic Data.
- Supplemental Table 4. Phytanic acid SRR-Isomer References.

Supplemental Table 5. Modern References for the APAA-C18 E/H Ratio.

Supplemental Table 6. Archaeological Maize from the Iluga Túmulos Site.

Supplemental Table 7. δ^{13} C References.

Supplemental Figure 1. Boxplot for APAA C20/C18 ratio of samples P25-1.13, P25-1.10, P23-2.2, and P5-1.13 (references from Bondetti et al. 2020).

Supplemental Figure 2. Partial chromatogram of Sample P25-1.10 showing APAAs C18, C20, and C22. APAA-C18 isomers are labeled A-I.

Supplemental Figure 3. Partial ion chromatogram (m/z 75) of the total lipid extract (solvent extract) of sample P25-1.5 showing a distribution of fatty alcohols and fatty acids.

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