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CHEMICAL ANALYSIS OF MARINE SEDIMENT FROM CHAN B'I, PAYNES CREEK SALT WORKS, BELIZE

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We report the results of soil chemistry testing at the underwater salt work of Chan b'i located in Paynes Creek National Park, Belize. Chemical soil testing such as inductively coupled plasma-mass spectroscopy has been used at other terrestrial archaeological sites to detect concentrations of chemical elements to indicate activity areas. Can soil chemistry provide insights into ancient activities not preserved in the slightly acidic marine sediment at the ancient salt work of Chan b'i, an Early Classic Maya site submerged by sea-level rise? Chan b'i is one of 105 salt works with preserved wooden architecture in a peat bog. The salt works were submerged by sea-level rise sometime after the Late Classic abandonment preserving wood, botanicals, and ceramics. Excavations at the site yielded abundant briquetage—pottery vessels used to evaporate brine over fires to produce salt. Chemical analysis was conducted on 40 sediment samples from Chan b'i. The results of this analysis indicate chemical variations throughout the site. This study extends chemical testing on terrestrial soils to submerged marine sediment at an underwater site.

Introduction

Chan b'i is one of 105 salt works discovered along the coast of Belize by the Underwater Maya project in Paynes Creek National Park related to a Classic Maya salt industry (Figure 1). Wooden buildings and ceramics are preserved underwater in a peat bog composed of red mangrove (McKillop 2005, 2009; McKillop et al. 2010a and b; Sills and McKillop 2013). Wooden buildings associated with the salt works are the only known architecturally associated preserved wood discovered in the Maya area. During the Classic period coastal peoples produced salt for the inland cities meeting the biological as well as the desired need for salt (McKillop 2002, 2005, 2009). Underwater excavations conducted in 2010 at Early Classic Chan b'i revealed an abundance of briquetage—ceramic vessels used to evaporate brine over fires to make salt indicating the function of the wooden architecture as workshop production of salt (Sills and McKillop 2013). Lacking from the cultural remains was evidence of habitation such as bones or organic refuse from fires. Inductively coupled plasma-mass spectroscopy (ICP-MS) was undertaken on 40 excavated marine samples from Chan b'i to examine anthropogenic activities as well as examining variations in the mangrove peat that spectacularly preserved the wooden architecture.

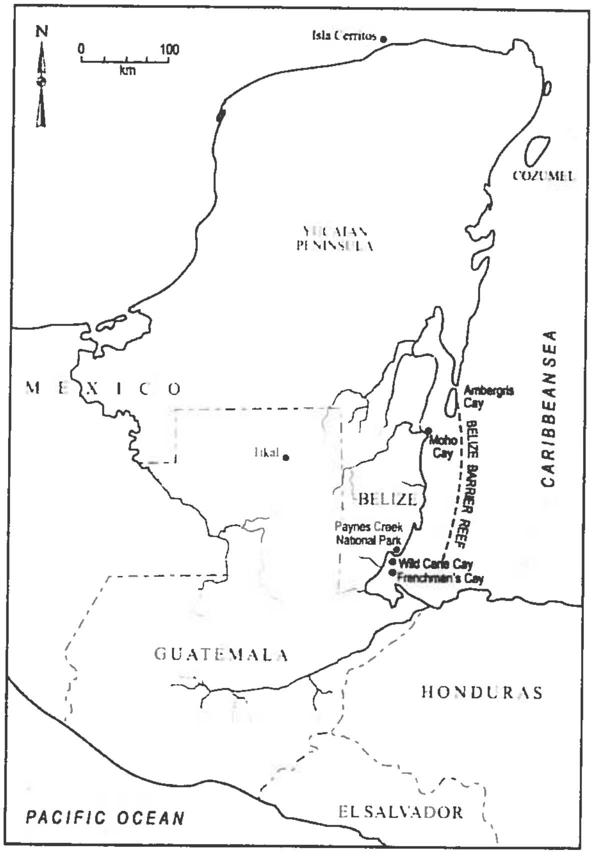

Figure 1. Map of Maya area showing Paynes Creek National Park (McKillop 2004).

Chemical soil testing such as ICP-MS can detect concentrations of chemical elements to allow for the identification of activity areas and non-artifactual evidence of settlement that indicate habitation. Initial use of soil chemistry for identification of human activities focused on the concentrations of phosphates and Ph as an indication of anthropogenic organic refuse (Lippi 1998). Phosphates are a form of phosphorous that are bonded compounds fixed

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to the minerals within soils and sediments (Wells et al. 2007). The phosphate compounds are stable whereas the element phosphorous is not. Phosphate values within a soil matrix are shown to be higher in areas of anthropogenic refuse and organic remains than areas where these activities do not occur (Terry et al. 2004). At the site of Aguateca, Guatemala, high values of phosphorus helped to locate areas for food preparation, disposal, and consumption (Terry et al. 2004). Chemical sediment analysis can indicate activity areas not seen on the surface, such as refuse from meals, ash from fires, and human waste (Holliday and Gartner 2007; Hutson and Terry 2006; Lippi 1988; Middleton and Price 1996; Middleton 2004; Terry et al. 2000, 2004; Wells et al. 2000; Wells 2010). Elements such as calcium are shown to belong to areas that were enclosed spaces (Middleton and Price 1996). At the site of Palmarejo, Honduras, concentrations of aluminum, barium, iron, potassium, magnesium, manganese, sodium, phosphorus, and strontium were compared between plaza and patio areas looking for non-homogenous patterns within the samples. The results linked phosphorous, potassium, calcium, and magnesium to food preparation and consumption activities (Wells et al. 2007). We have adapted terrestrial testing using chemical analysis to the underwater Paynes Creek salt works to examine additional activity areas not apparent from the artifactual record.

Mangrove Environment at the Salt Works

The Paynes Creek salt works are located in Punta Ycacos Lagoon, an estuarine lagoon system located in Paynes Creek National Park. Today, the area is a mangrove ecosystem dominated by *Rhizophora mangle* (red mangrove) with minor amounts of *Avicennia germinans* (black mangrove) and *Laguncularia racemosa* (white mangrove) (Figure 2). At the time of occupation (A.D. 300-900), the salt works were on dry land close to the source of brackish water needed for evaporation over fire to make salt. Sea level rise inundated the sites after the Late Classic abandonment.

Punta Ycacos lagoon is supplied by fresh water from nearby Freshwater Creek that drains from the pine savannah and granite Maya mountains along with salt water from the Caribbean Sea to the east. Directly surrounding the lagoon are mangrove forests. Mangroves are classified as evergreen trees that grow along salt water coastlines or shallow water in tropical and subtropical regions between 32°N and 28°S latitude (Chapman 1975; Tomlinson 1986). Within these latitudes in the Americas they represent an area of approximately 43,161 km^2 (Mitsch and Gosselink 2000). Mangroves are not found along rocky coasts due to the lack of accretion of sediment as well as intensity of waves (Tomlinson 1986). Mangrove forests differ from other evergreens because they maintain complete fidelity to their environment, form pure stands, develop morphological adaptation to the environment such as the aerial roots of *R. mangle*, practice salt exclusion, and are isolated from terrestrial relatives (Tomlinson 1986).

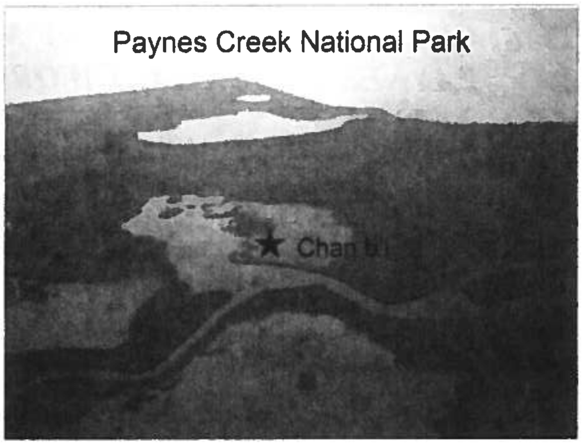

Figure 2. Aerial photograph showing the location of the underwater salt work Chan b'i, Paynes Creek National Park, Belize.

The distribution and productivity of mangroves in antiquity as well as today are controlled by three factors: resource gradients, regulator gradients, and hydroperiod (Twilley and Rivera-Monroy 2005). Resource gradients represent aspects of the environment available for mangrove production including absorption of light, spacing of trees, and access to nutrients (phosphorus and nitrogen). Regulator gradients are conditions of the sediment such as the amount of salinity, pH, sulfides, and temperature. The final factor hydroperiod represents the frequency and duration of water submersion. A combination of these three factors determines the composition and zonation of a mangrove forest. For example, the three primary species in Paynes Creek have different tolerances to salinity. *R. mangle* is the least salt tolerant of the three but has the best morphological adaptations in the form of aerial roots to tolerate constant submersion in water (Tomlinson 1986). *A. germinans* is one of the more tolerant species withstanding saline environments up to 100 parts per thousandth (ppt.). This species is found further away from water where tides occasionally flush the roots and sediment. *L. racemosa* is more productive within intermediate saline areas (25-35 ppt.).

Coastal areas are dynamic environments that undergo constant change through tides, waves, sediment accumulation, tropical storms, and hurricanes. In addition to natural impacts, human use of coastal areas for settlement, recreation, and subsistence activities have anthropogenic impacts to the environment. The Paynes Creek salt makers utilized a coastal lagoon environment in order to produce salt. These activities left impressions in the environment. Analysis of the marine sediment macroscopically indicates that *R. mangle* dominated the edges this environment even though the area is water today. The microscopic analysis of a 1.5 meter sediment core from between Chan bi and K'ak' Naab', showed that the sediment is composed of *R. mangle*. The radiocarbon dating of the core showed a 4,000 year-record of mangrove accumulation. Loss-on ignition indicates high organic matter accounting for approximately 60% of the sediment (McKillop et al. 2010a and b). The majority of the sediment structure is composed of mangrove roots with minor amounts of leaves and wood. Elsewhere within the Belize barrier reef farther north at Pelican Cays the peat is composed of mangrove roots with the leaves and wood accounting for less than 20% of the total composition (McKee and Faulkner 2000). Relative rates of degradation of peat accumulation were measured for a year on Twin Cays. The rates of decay are higher for mangrove roots and leaves with roots contributing the most to peat accumulation (McKee and Faulkner 2000).

Evidence of a mangrove forest environment is further corroborated by species identification of the wooden posts used for the salt work architecture (Robinson and McKillop 2013, 2014). The main building material at Chan b'i has been identified as *A. germinans* from nearby forests (Robinson and McKillop 2013). Overtime the mangroves near or on the site were unable to keep pace with sea level rise inundating and preserving the salt works. This similar type of process has been documented for Glover's reef, Lighthouse reef, and Turneffe islands (Gischler 2003).

Excavations at Chan b'i

The wooden architecture at Chan b'i forms a rectangular building with one or more room divisions. The building(s) measure approximately 11 m north to south and 14.5 m east to west (Sills and McKillop 2013). There are two lines of palmetto palm posts (*Acceloracea wightii*) located to the southwest of the rectangular building. The areas inside and directly surrounding the wooden buildings are approximately 15 cm higher in elevation than the area surrounding the palmetto palm posts. The lines of palmetto palm posts found at the salt works in Paynes Creek have been interpreted as retaining walls (McKillop 2009; Sills and McKillop 2010). A radiocarbon date from one post places the site within the Chan b'i dates to the Early Classic period (A.D. 300-600) (Sills and McKillop 2013).

At the time of excavations, the wooden architecture and ceramics at Chan b'i were 50 cm below the water surface. Transect excavations were carried out at the salt work in June, 2010, to evaluate the spatial patterning of artifacts and their relationship to wooden architecture. First, the wooden posts were relocated using a Geographic Information Systems map from the 2007 survey. Once located, pin flags placed on the north side of the posts were used to mark their location. The flags extended above the water surface. Using a compass and 30 m tape, two transects were placed across the site intersecting at right angles. The ends of each transect were marked with long PVC pipes pushed into the seafloor. Each transect was divided into one meter units. Short lengths of PVC pipes were placed into the sea floor at each meter mark (Figure 3).

Excavations proceeded along each transect using a 1 x 1 meter metal grid frame.

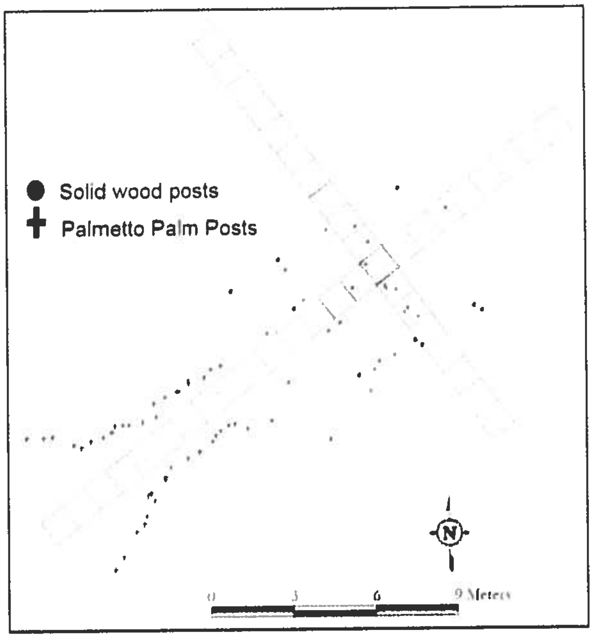

Figure 3. Transect excavation locations at Chan b'i. Sediment samples were collected from the northwest corner of each 1 X 1 m unit.

Figure 4. Photograph of acquiring the marine sediment samples at Chan b'i using a stainless steel knife and placing the sediment into Whirl-pak bags (photo by H. McKillop).

The transects were placed to extend across the site—as defined by the surface distribution of artifacts and wooden architecture—and to include inside and outside areas of the building. The results of the transect excavations are reported in the 2013 Research Reports in Belizean Archaeology (Sills and McKillop 2013).

The artifacts were studied at the field lab in Belize. After fresh water rinsing and drying, the artifacts were separated into material classes. The ceramics were sorted according to the type-variety classification for Maya pottery, which is useful for developing a site chronology. Most types fit within existing classifications for the Paynes Creek area (McKillop 2002).

The excavations revealed an abundance of briquetage located inside and directly surrounding the wooden building. Abundant charcoal mixed with the briquetage was found. Artifact density diminished between the two lines of palmetto palm posts further away from the building. At Chan b'i, briquetage comprises approximately 85% of the ceramic assemblage (Sills and McKillop 2013). Minor amounts of water jars used to store water or brine were accounted for along with a very minor amount of serving vessels.

Briquetage includes all the pottery used to evaporate brine over fires to make salt and is typical of the assemblage at the Paynes Creek salt works. Briquetage consists mainly of Punta Ycacos Unslipped jars, basins, and bowls that were placed onto clay cylinder vessel supports, inserted into clumps of clay bases and sockets placed at the top of the vessel support and connected to the pot. Clay spacers were placed between the pots to steady them over the fire to evaporate the brine and make salt cakes. Also, there are amorphous clay lumps that are the broken pieces of cylinders, sockets, spacers, and bases, as well as other salt making debris (McKillop 1995, 2002).

Methods

We report the results of 40 collected sediment samples from Chan b'i from two excavated transects (see Figure 3 and Figure 4). Sediment was excavated using a sharp stainless steel knife. A small block of sediment was cut from the sea floor at one meter intervals along the excavated transects. All samples were placed directly into whirl-pak bags. The marine sediment was exported under permit to Louisiana State University. Sub-samples were selected and sent to the Center for Geochemical Analysis at the University of South Florida.

Results

Forty sediment samples were chemically characterized from Chan b'i. The samples were analyzed in an inductively coupled plasma-mass spectrometer for the calibrated concentrations of 20 elements: barium (Ba), copper (Cu), lead

Table 1. Summary statistics for the primary elements.

	Minimum	Maximum	Range	Mean	Median	Standard Deviation	Coefficient of Variation
Ba	0.010	0.130	0.120	0.036	0.034	0.022	0.000
Cu	0.280	0.500	0.220	0.359	0.357	0.047	0.002
Pb	0.040	0.350	0.310	0.141	0.137	0.065	0.004
Hg	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ni	0.170	0.900	0.730	0.466	0.282	0.289	0.083
P	0.490	6.330	5.840	2.025	1.739	1.169	1.367
Sr	1.330	11.400	10.070	3.867	3.787	1.964	3.857
Zn	0.770	1.950	1.180	1.248	1.228	0.207	0.043
Ti	0.340	4.890	4.550	1.444	1.205	1.044	1.089
Cr	0.030	0.290	0.260	0.118	0.062	0.084	0.007
Co	0.010	0.080	0.070	0.041	0.038	0.018	0.000
Y	0.050	0.250	0.210	0.116	0.113	0.047	0.002
U	0.050	0.920	0.870	0.314	0.223	0.244	0.060
Na	665.620	3844.360	3178.740	1893.423	1764.105	815.271	664666.914
Mg	15.800	89.660	73.860	45.232	44.618	19.437	377.784
Al	-0.520	687.040	687.560	146.493	108.372	146.136	21355.656
K	67.570	209.010	141.440	135.252	132.747	40.789	1663.777
Ca	138.360	2393.180	2254.820	400.494	341.486	368.229	135592.777
Mn	0.210	3.460	3.260	1.322	1.135	0.897	0.804
Fe	37.750	297.140	259.390	136.864	117.925	62.108	3857.342

(Pb), mercury (Hg), nickel (Ni), phosphorus (P), strontium (Sr), zinc (Zn), titanium (Ti), chromium (Cr), cobalt (Co), yttrium (Y), uranium (U), sodium (Na), magnesium (Mg), aluminum (Al), potassium (K), calcium (Ca), manganese (Mn), and iron (Fe). The results are reported in parts per million (ppm). Summary statistics including the minimum, maximum, range, mean, median, standard deviation, and coefficient of variation for each of the 20 elements are presented in Table 1. Eleven elements exhibit little or no variation. These are Ba, Cu, Pb, Hg, Ni, Zn, Ti, Cr, Co, Y, and U. These elements, which have very low concentrations in the sediment, represent heavy metals and rare earth elements (Figure 5). Due to their low concentrations these elements are difficult to assess in relation to human activities such as salt production activity areas. A side-by-side boxplot of these elements show that the majority are represented by less than 2 ppm except for Ti which has concentrations less than 5 ppm. The remaining nine elements show variation from one to two standard deviations that warrant further discussion: These are P, Sr, Na, Mg, Al, K, Ca, Mn, and Fe.

Sodium and calcium are directly associated with calcareous sediments from brackish and saline contexts. A side-by-side boxplot of the two elements shows the range of chemical concentrations (Figure 6). Sodium is expected within a salt water lagoon. However, the sediment samples contain much lower concentrations than those found in open sea water which is typically around 36,000 ppm.

The sodium values range from 665 ppm to 3,844 ppm. Sodium and potassium can be associated with the production of ash from fires (Middleton

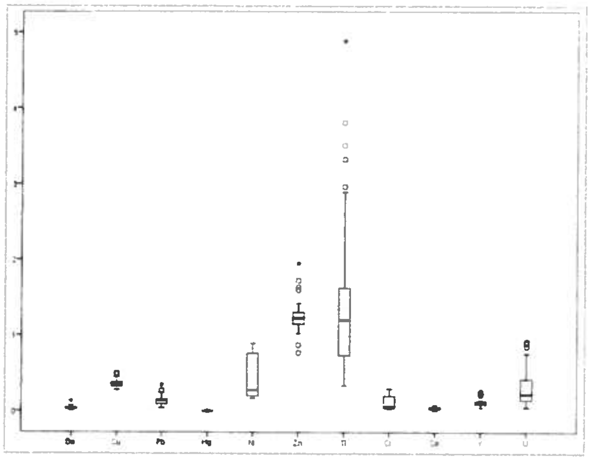

Figure 5. Side-by-side boxplot of the minor and trace elements exhibiting little or no variation (ppm, n =40). These elements are Barium (Ba), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni), Zinc (Zn), Titanium (Ti), Chromium (Cr), Cobalt (Co), Yttrium (Y), and Uranium (U). The open circles represent 1.5 spread of the interquartile range and the asterisks represent 3.0 spread of the interquartile range.

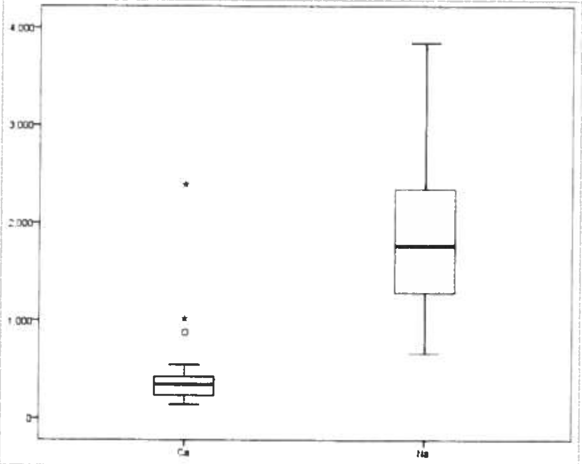

Figure 6. Side-by-side boxplot of Sodium (Na) and Calcium (Ca) (ppm, n=40). The open circles represent 1.5 spread of the interquartile range and the asterisks represent 3.0 spread of the interquartile range.

and Price 1996). Salt making at the site would require wood for fuel. The large amounts of charcoal recovered from excavations support the interpretation that variation in sodium values represent areas where salt was evaporated or areas where the remains of fires were swept. Calcium concentrations are not uniform among the samples. Instead, calcium has a fairly wide range extending from a minimum of 138 ppm to 2,393 ppm. Variations of calcium can be associated with limestone sediments drained from the mainland or washed in from coral. Calcium can be deposited from mangrove oysters that typically grow on the prop roots of *R. mangle*, or calcium could be associated with the erosion of limestone tempered pottery.

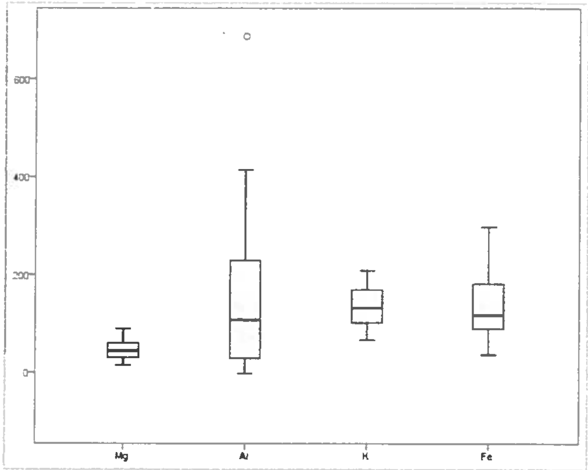

Figure 7. Side-by-side boxplot of Magnesium (mg), Aluminum (Al), Potassium (K), and Iron (Fe) (ppm, n=40). The open circles represent 1.5 spread of the interquartile range and the asterisks represent 3.0 spread of the interquartile range.

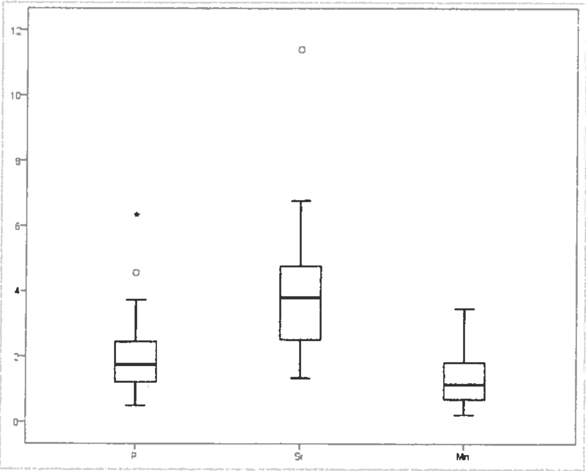

Figure 8. Side-by-side boxplot of Phosphorus (P), Strontium (Sr), and Manganese (Mn) (ppm, n=40). The open circles represent 1.5 spread of the interquartile range and the asterisks represent 3.0 spread of the interquartile range.

Magnesium, aluminum, potassium, and iron are also represented in the sediment chemistry. Side-by-side box plots show variations in the range of these concentrations that may provide insights into environmental reconstructions as well as human activities (Figure 7). Magnesium derives from limestone, aluminum from clays and sands, potassium from water, and iron from gleyed soils. However, the differences in the concentrations of these samples can be the result of human activities. The briquetage found at Chan b'i consists of a sand temper that mixed with the sediment can account for variations especially for the elements of aluminum and iron (McKillop 2002). Magnesium and potassium have been linked to food preparation and consumption activities (Wells et al. 2007). However, due to the context of Chan b'i as a salt work, magnesium and potassium could represent the ash from fires.

Phosphorus, strontium, and manganese can be linked to human activities. These elements are relatively low concentrations (less than 400 ppm) but do exhibit variation (Figure 8). Phosphorus can be associated with the deposition of organic matter. In the context of a mangrove peat sea floor these concentrations are most likely associated with the organic remains of *R. mangle* found microscopically from column samples (McKillop et al. 2010a and b).

Conclusions

Chemical characterization of marine sediment at the Chan b'i salt work extends testing from terrestrial soils to inundated archaeological sites. This study follows successful soil analysis at other Maya sites, including Aguateca, Cerén, Chunchucmil, and Coyote (Hutson and Terry 2006; Parnell et al. 2002; Terry et al. 2004; Wells 2004). Human activities are represented within the variations of chemical concentrations at Chan b'i relating to a Classic Maya salt industry. The salt work is associated with wooden architecture allowing for an opportunity to evaluate the location of activities within a salt workshop (Sills and McKillop 2013). Variations in sodium, magnesium, aluminum, potassium, and phosphorus designate the remains of fires from the evaporation of salty water over fires supporting the interpretation that these sites were salt workshops.

The results of sediment chemistry from the underwater site of Chan b'i are comparable to results from inland sites (Huston and Terry 2006; Parnell et al. 2002; Terry et al. 2004; Wells 2004; Wells et al. 2007). Human activities leave behind chemical signatures that exhibit high and low variations. These variations can be compared within an archaeological site to find activities not represented within the artifactual record. The importance of sediment chemistry is not necessarily comparing two separate sites since each soil environment is different. Instead, the significance is within datasets that show large ranges of an element with high standard deviations (Wells et al. 2007). However, these differences do form patterns or non-homogeneous areas that can be tied through ground truth to a specific activity. For example, heavy metals including copper, iron, mercury, manganese, lead, and zinc were associated with pigment production activities at Cerén (Parnell et al. 2002), painted urban houses at Piedras Negras in Guatemala (Wells et al. 2000).

Mangrove peat, an anaerobic sediment, has preserved wooden architecture as well as botanicals at the Paynes Creek salt works. The variations in chemical signatures from Chan b'i indicate the peat preserved elements associated with human activity. Heavy and rare earth metals show low concentrations at Chan b'i specifying these as the base chemical levels of the *R. mangle* peat substrate. The fibrous *R. mangle* roots that form the sea floor bonded elements indicative of human activity such as sodium, magnesium, aluminum, potassium, and phosphorus to the roots. The non-homogenous character of the elements in the sediment samples has successfully extended the use of sediment chemistry to a marine environment.

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