# Geochemistry of Insular Shelves: Santa Maria Island, Azores, Portugal

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Thesis for the fulfilment of the Master of Science in Environmental Sciences, Policy & Management (MESPOM) jointly operated by Lund University – University of Manchester -University of the Aegean – Central European University

Manchester, United Kingdom, 2019



The University of Manchester

Erasmus Mundus Masters Course in Environmental Sciences, Policy and Management





This thesis is submitted in fulfilment of the Master of Science degree awarded as a result of successful completion of the Erasmus Mundus Masters course in Environmental Sciences, Policy and Management (MESPOM) jointly operated by the University of the Aegean (Greece), Central European University (Hungary), Lund University (Sweden) and the University of Manchester (United Kingdom).

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# Acknowledgements

I would like to express my gratitude to Dr. Neil Mitchell and Dr. Bart Van Dongen for the opportunity to participate in a field novel to my studies. I would also like to thank Yu-Chun Chang for his assistance in the laboratory as well as for his words of wisdom and support. Additionally, Zhongwei Zhao for providing the samples which make the backbone of this project. Last, but not least, Alastair, Paul and Sharon for humoring my inquiries and providing good company. I am fortunate enough to have had a team of advisors, peers, and technicians which helped me grow throughout this project.

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# Abstract

The insular shelf of an island is the portion of submerged land that gradually extends into the open ocean with the edge of the shelf marking the point of erosion from a previous, lower, sea-level (Quartau et al., 2014). The morphology of these features provides themselves as records for wave erosion and volcanic progradation. On a microscopic level, the distribution of shelf materials is reliant on ominous systems such as ocean currents, climate, and chemical reactions which determine their movement, form, and abundance in a given area. Ocean currents provide an energy source for the weathering of materials in its path as well as a vessel for their distribution. The climate surrounding the island also provide conditions that weather, either by precipitation or through desiccation. The outcome of these interactions depends on the chemical composition of the force as well as that of the material receiving its impact. It is by systems (climate, currents, geology) and their products (volcanic and carbonate minerals) that researchers can recreate the history of a landmass, understand its present mixing, and predict its future.

The shortage of hybrid land and off-shore studies has been a topic of researchers (i.e. Amorim et al., 2017 & Quartau et al. 2015). One theory is the lack of multidisciplinary models which bridge the gap between volcanology and oceanography (Amorim et al., 2017). Alternatively, attention has been brought to the preference of offshore studies that focus on slopes and deep ocean rather than the insular shelf (Quartau et al., 2015). In the pursuit to address this deficit the Portuguese Science Foundation (FCT) put into effect the PLATMAR (Platform Santa Maria) project. The objective of PLATMAR is to collect a globally competitive dataset of the geological and geophysical systems of Santa Maria Island of the Azores archipelago. In pursuit of these aims, PLATMAR offers opportunities for academic research projects which will contribute to their overarching goal-understanding the development of the island's slope and shelf.

In order to contribute to the overarching goal of PLATMAR, this work studied the distribution, form, and origin of volcanic and carbonate materials on the insular shelf of Santa Maria Island. Twelve sites were selected with varying depths and distances from shore and grouped based on their geographical position- Southwest (SW), Southcentral (SC), Southeast (SE) and North (N). Methods of X-ray fluorescence, X-ray diffraction, Loss on ignition, total organic carbon solid sample module and gas chromatography-mass spectrometry were used to identify elements, minerals and forms as sites transition along shelf transects.

Mineral analysis identified augite and anorthite as the volcanic materials contributing to the shelf. Concentrations of these minerals were highest in the SW and absent in the N. Carbonate minerals (calcite and aragonite) were found to be the largest contributors to the total shelf composition, nearing almost pure values in the N and SC transects.

The differences in climate and maritime conditions around the island have been identified as

determining factors of the distribution and extent of the constituent's presence. The west, facing windward, experiences more frequent precipitation which is linked with higher tidal zones, and potential energy for weathering. The east, leeward, is drier using desiccation as a mode of weathering. The northern sites, the furthest sites from the shore, were almost entirely void of terrestrial materials and largely rely on carbonates for its current composition. The southcentral transect also exhibited higher values of carbonate to volcanic ratios, however, it is suspected that this may be the result of the limitations which come from the sample size. The niche of these studies can provide essential information needed for the understanding in the geological history island volcanoes, their present state, and their future trends.

**Keywords:** Geochemistry, Santa Maria Island, Azores, Volcanic islands, Insular shelf, X-ray fluorescence, X-ray diffraction, Loss on ignition, Total Organic Carbon, Gas Chromatography-Mass Spectrometry

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# 1 Introduction

The insular shelf of an island is the portion of submerged land which gradually extends into the open ocean with the edge of the shelf marking the point of erosion from a previous, lower, sealevel (Quartau et al., 2014). The morphology of these features provides themselves as records for wave erosion and volcanic progradation. The results of these interactions differ between continental settings and islands which lead to different interpretations. Wave erosion on continents extends shelves and steadies slopes with wave attenuation. The opposite is true for islands as they widen with continuous wave action as a function of time (Ablay & Hurlimann, 2000; Quartau et al., 2014). It is with morphological observations like this that researchers can recreate the history of a landmass, understand its present, and predict its future.

Though shelf extent is believed to be an indicator of an island's age, there are events that occur in the natural world that interrupt this linear consistency. Such examples are the results of masswasting (i.e. landslides), resulting from saturation and seismic activity, accelerating the reduction of a shelf, or, alternatively, events that preserve a shelf by way of sedimentation or post erosional volcanism (Qaurtau et al., 2010). Variables which catalyze these occurrences are controlled by an island's climate, geological and geographical positioning.

On a microscopic level, the distribution of shelf materials is reliant on ominous systems such as ocean currents, climate and chemical reactions which determine their movement, form and abundance in a given area. Ocean currents provide an energy source for the weathering of materials in its path as well as a vessel for their distribution. The climate surrounding the island also provides conditions that weather, either by precipitation or through desiccation. The outcome of these interactions depends on the chemical composition of the force as well as that of the material receiving its impact. An example of this is the dissolution of inorganic carbon in the presence of acid. It is by studying both ends which researchers can gain a full understanding of not only an island's shelf but the island as a whole. Additionally, the application of these findings can benefit society when considering mitigating measures in response to natural hazards (Calado et al., 2010).

The shortage of hybrid land and off-shore studies has been a topic of many researchers (i.e. Amorim et al., 2017 & Quartau et al. 2015). One theory is the lack of multidisciplinary models which bridge the gap between volcanology and oceanography (Amorim et al., 2017). Alternatively, attention has been brought to the preference of offshore studies to focus on slopes and deep ocean rather than the insular shelf (Quartau et al., 2015). In the pursuit to address this deficit the Portuguese Science Foundation (FCT) put into effect the PLATMAR (Platform Santa Maria) project. The objective of PLATMAR is to collect a globally competitive dataset of the geological and geophysical systems of Santa Maria Island of the Azores archipelago. In pursuit of these aims, PLATMAR offers opportunities for academic research projects which will contribute to their overarching goal- understanding the development of the island's slope and shelf.

# 1.1 Aims

In order to contribute to the overarching goal of PLATMAR, this work will study the distribution, form, and origin of volcanic and carbonate materials on the insular shelf of Santa Maria island. Twelve sites were selected for the purpose of this study, each varying in depth and distance from shore and grouped based on their geographical position- Southwest (SW), Southcentral (SC), Southeast (SE) and North (N).

# 1.2 Objectives

Historically, the pursuit of political, economic and military security fueled the technological advancement associated with seafloor exploration; it is with this that the area of the North Atlantic Triple Junction is the most studied on earth (Vogt & Jung, 2018). Nevertheless, the insular shelves of the islands which the Triple Junction hosts continue to beckon exploration. In order to contribute to the knowledge of Santa Maria island's shelf, this study will collect geochemical data on sediment samples with the application of X-ray fluorescence (XRF), X-ray diffraction (XRD), Loss on ignition (LOI), Total organic carbon-solid sample module (TOC-SSM), and Gas Chromatography-Mass Spectrometry (GC-MS).

- Document qualitative characteristics with the use of a digital microscope
- Apply LOI to calculate total carbon
- Distinguish between organic and inorganic carbon with TOC-SSM
- GC-MS to determine between marine or terrestrial organic predominance
- Use XRF to quantify elemental concentrations
- XRD to identify mineral composition

## 1.3 The Azores: An Overview

It is estimated that 80 percent of volcanic activity occurs under the ocean water (Thurman & Trujillo, 2004). These events are commonly found near the seams of oceanic plates in areas of convergence or separation and hold the potential to create islands as a result of their movement.

An exception to this rule is intraplate volcanic activity- hotspot, wetspot and mantle plum. These phenomena take advantage of the weaknesses in lithospheric plates to release and deposit igneous materials. One such case where these modes of volcanism exist is the North Atlantic Triple Junction.

Tectonics in this area have spread from the west via the Mid-Atlantic Ridge (MAR), perpetuating

eastward movement of the Eurasian and Nubian plates (Sibrant et al., 2015). As a result, the diffuse plate in the center hosts anomalous characteristics such as an abnormally thick crust and intraplate archipelagos, among others, which are collectively known as the "Azores geosyndrome" (Vogt & Jung, 2018).

#### 1.3.1 The Azores Plateau

The Azores Plateau (AP) is an area of high relief found in the northern portion of the MAR. Distinguishing this feature is its ~2000m bathymetry between 33°N and 41°N which reaches 14km thick- 60% greater than its surrounding- an indication of hyper-active magma input (Kueppers & Beier, 2018; Vogt & Jung, 2018). Studies on the plateau's composition largely support the MAR as the source underlying materials with additional contributions from fissure eruptions, faults and mass wasting (Vogt & Jung, 2018; Weiss et al. 2016; Mitchell et al., 2018). Points of lithospheric weakness combined with what is largely believed to be hotspot activity provides the opportunity for seamount development. In order for these edifices to become islands they must be able to overcome weathering and mass-wasting events via higher rates of magmatic input (Quartau et al., 2015). The remanences of these efforts are observed with the use of multi-beam bathymetry and believed to be a result of the seismic activity in the area (Weiss et al., 2016).

#### 1.3.2 The Azores Archipelago

Overcoming these challenges are the Azores islands. The archipelago consists of nine islands which span between 36.8-39.9°N of the triple junction. The islands are divided into three groupsthe western group (Flores and Corvo) which lie on the North American plate, the central group (Terceira, Graciosa, Sao George, Pico and Faial) and east (Sao Miguel and Santa Maria islands). The genesis of the archipelago began ~6mya with the emergence of Santa Maria (Sibrant et al., 2015) island and its growth continues today with Pico Island (.25mya) (Metrich et al., 2014). Overall, the sediments of the Azores are of mafic and alkali basalt composition (White, Tapia & Schilling, 1979).

#### 1.3.3 Santa Maria Island

Santa Maria Island is currently found 480km east of the MAR and is the southeastern most island of the archipelago. It is bounded by the Terceira Rift to the north, the Gloria and East Azores Faults to the south, and MAR on the west (Ramalho et al., 2017).

#### 1.3.3.1 Geological History

The following historical synopsis is adapted from Ramalho et al. (2017) and elaborated on with the work of Larrea et al. (2018). The geological history of the island is one of turmoil with alternating epochs of growth and subsidence made evident by exposed marine terraces, volcanoes, and sequences. The emergence of Santa Maria occurred during the late Miocene which is marked in the northwest by the Surtseyan tuffs of the Cabrestantes formation (Larrea et al., 2018). Overlaying the

Cabrestantes is the Anjos volcanic complex with subaerial lava flow and highly weathered pyroclasts (Ramalho et al., 2017; Larrea et al., 2018). The early Pliocene brought an era of erosion as well as marine deposition (marine conglomerates and calcarenites) with occasional lahars known as the Touril complex (Larrea et al., 2018.). A second renaissance created the Pico Alto volcanic complex and is marked with submarine volcanoes, terrestrial erosion and marine sedimentation (fossiliferous and conglomerate). The late Pliocene brought both uplift (~180m (Avila et al., 2002)) and erosion which is how we find the island today (Ramalho et al., 2017). As a result of these events the island varies with topography, extent of insular shelf, and sediment composition.



Emergence and evolution of Santa Maria Island

Figure 2. (A) Geological map of Santa Maria Island after Serralheiro et al. (1987), with (B) a WNW-ESE cross section, and key for both map and section (Porto Formation is not visible at this scale). Approximate sample locations are plotted in the map. "P<sup>a</sup>" and "M<sup>to</sup>" are abbreviations for "Ponta" and "Monte," respectively. Underlying digital elevation model was generated from a 1:5000 scale digital altimetric database.

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*Figure 1. Santa Maria island hosts various formations and complexes which attest for the island's geological history (Ramalho et al., 2017).* 

#### 1.3.3.2 Sediment composition

There have been several surveys of Santa Maria Island that characterized the island's currently subaerial composition. The island's basalts are described as alkali, distinctively sodic, and enriched with trace elements (White, Tapia & Schilling, 1979; Beier et al., 2012). Among the minerals identified in the samples were basanoids, olivine, and pyroxenes with high normative nepheline content (White, Tapia & Schilling, 1979).

Unique to Santa Maria Island is its limestone stratigraphy which is exposed at two outcrops, Prainha and Lagoinhas. Prainha lies in the south of the island, 2 - 4m above sea level, and spans 800m across an area known among locals as Praia Formosa. The base of the outcrop is adjacent to the Anjos complex and contains "strongly cemented" calcareous fossiliferous basal-conglomerate (<.4m thick) that is covered by a calcareous algal mat (<0.5m thick). The uppermost layer is <1.3m thick and consists of poorly consolidated bioclastic white sands with an accumulation of loosely consolidated breccia. (Avila et al., 2002).

The Lagoinhas outcrop lies higher than Prainha at 7m above sea level and a northern exposure of ~100m (Avila et al., 2002). Lying the carbonate foundation of the Lagoinhas outcrop is the Touril sequence which is composed of ~.3m thick calcareous algal mats, covered by bioclastic sands (.7m thick), and topped with colluvium breccia (Avila et al., 2002).

The petrology of Santa Maria is among the least documented of the Azores islands (Larrea et al., 2018). Therefore, the extent of which these features influence the mixing along the insular shelf will be a point of consideration throughout the preceding analysis.

#### 1.3.3.3 Oceanography

The island is situated southeastward of the Azores current between 37°01'16"- 36°55'37" N latitude and 25°11'27"- 25°00'49" W longitude. The current originates from south of the Grand banks (~ 40°N longitude, 45°W latitude) is characterized as a narrow, jetlike, surface-current. The Azores current is in an area of transition between the Gulf Stream and North Atlantic Gyre, experiencing temporal variability linked to alterations in its width, lateral path and eddy potential energy (EPE) i.e. its narrowing and dipping further south in the summer, creating inconsistencies in eddy scales (Gyory, Mariano and Ryan, 2013; Klein & Siedler, 1989). Additionally, as the current continues towards the east, it creates eddies (Lumpkin & Pazos, 2005) of high kinetic energy (EKE) in the northern portion of Santa Maria island (35°N) (Fratantoni, 2001).

The morphology of an island's shelf is the embodiment of the interaction between ocean weathering and volcanic input (Quartau et al., 2015). In the case of Santa Maria Island, this is observed in the asymmetrical extent and shape of its insular shelf, most notable in the north. The

island's northern shelf extends 6km to 7km with a depth of -120m to -180m, while other sections only reach their extent at 1.5km and -40 to -80m in depth (Ramalho et al., 2017).

Maritime conditions alternate with season, as observed with the Azores current, therefore the study of an island's climate is essential to the interpretation of shelf composition and morphology.

#### 1.3.3.4 Climate

The role of climate in the life cycle of landmasses dictates precipitation, temperature, and vegetation which consequently act as catalysis for chemical and physical weathering as well as the transport of sediments (Rothwell & Croudace, 2015; Meirelese et al., 2013). The North Atlantic Oscillation (NAO) is a pressure system that is defined by the difference in atmospheric pressure at sea level between the Azores and Iceland (Rodwell, Rowell & Folland, 1999). Weather conditions of land masses bordering and within the NAO are linked to the positive and negative cycles of the pressure system. These phases influence temperature and precipitation patterns on the east coast of North America and across Europe. During positive phases temperatures increase in North America and Western Europe with higher precipitation in Northern Europe- the opposite is observed during negative phases. The longer the phase lasts the more extreme the temperatures, precipitation and breadth (NOAA, 2019). Rodwell et al. (1999) reported the feedback loops between the NAO and rates of sea surface evaporation, precipitation and atmospheric heating, revealing the relationship between the pressure system and climatic and oceanic conditions in the North Atlantic.

The Climate of Santa Maria is largely considered to be temperate with dry, warm, summers and annual temperatures ranging between 11.7°C- 20.3°C. Average annual precipitation on the island is 729.5mm with the most rain occurring during November to January. (Agencia Estatal de Meteorologia and Instituto de Portugal, 2011)

## 1.4 Techniques in Geochemistry

Though the Azorean islands are grouped into an archipelago, the systems that determine their morphology vary by case such as their distance from their crustal source, interactions with local currents, and the geological features of each individual island. In general, Azorean sediments are identified by their enrichment of incompatible trace elements, with the degree of enrichment increasing with distance from the MAR. The Azores current encompass the islands, however, the amount of EPE decreases with distance from the Gulf stream. Precipitation and temperatures vary not only by the island's geographical position but also with the altitude on the island itself. Sediment composition, climate, and maritime conditions vary across the Azores archipelago, emphasizing the need for island-specific studies of insular shelves.

If it is true that climate, maritime and chemical composition are embodied in the morphology of an island's insular shelf, then its effects will be reflected in the spatial variation of an island's insular shelf's constituents. The following techniques were selected in order to detect and quantify the mineral and elemental constituents of Santa Maria Island's shelf.

### 1.4.1 X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) is a wavelength dispersive method employed in research pursuits spanning from multi- elemental soil surveys to archeological investigations (SEES, 2018). XRF induces atomic photoelectric absorption via x-ray excitation. Material to be analyzed is prepared to an anode in order to attract the high-voltage accelerated electrons. When electrons collide with the anode, the material will emit x-ray photons and characteristic radiation (Margui and Grieken, 2013). The photons from this interaction are converted into electrical pulses by a spectrometer and amplified with a multi-channel analyzer. The detection of background noise results in a gaussian- like shape which, based on the total amount of pulses, will protrude peaks indicating intensity of the energy. (Margui & Grieken, 2013). Abundance of major elements are given in weight percentages (wt.%) of the oxide form of the element. Trace elements are those which are present in less than 1000 part per million and given in ppm (Henderson, 1982).

This method is limited to the identification of elements heavier than carbon. Elements present below this range must be quantified with an alternative method prior to XRF analysis to then be integrated into the machine. The bias of the equipment is monitored by analyzing a certified reference material (CMR) (Gill, 1997).

#### 1.4.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) uses x-ray energy reflected from elemental surfaces to characterize crystalline structures of minerals and is regularly used for research in material science and mineral analysis (SEES, 2018). Samples are dried and pulverized prior to analysis.

This method is based on the idea, by René-Just Haüy, that the internal structure and atomic and molecular state is unique to each homogeneous substance. This principle is one of the foundations of XRD technology. X-ray energy is used to create incident rays which are discharged at the unknown material which diffract based on the angles of the crystal. The characteristic diffraction rays, which identify the mineral, are supported by Bragg's law (n  $\lambda = 2d \sin \Theta$ ) and can be calculated with Laue equations (Bragg, 1966). Results provide the bulk mineral composition of the powder.

The principles which this technology is based on identifies minerals based on their crystal structure, therefore, XRF is limited to materials which have crystal structures. Additionally, XRF is used in the identification of minerals and cannot provide detailed analysis on the elements within the compound.

#### 1.4.3 Loss on Ignition (LOI)

Loss on ignition (LOI) is a two-step method which selectively removes an element based on its known vaporization temperature- for the purpose of this study carbon was selected. Sample preparation requires drying and pulverizing prior to analysis.

The pulverized sample is weighed and undergoes an initial heating at 105°C in order to remove water weight from the total weight. The remaining weight represents the carbon and non-carbon materials of the sample. Secondary heating at 1000°C releases carbon from the carbonate in the form of CO2 (Heiri, Lotter & Lemcke, 2001). Pre and post heating weights are subtracted from each other, divided by the pre- weight amount, and then multiplied by 100 to get apparent LOI (Schumacher, 2002).

This method is limited in that it does not distinguish between organic and inorganic carbon. Variables affecting the outcomes during LOI are the locations of samples within the furnace, the amount of the sample, and the duration of the heating process (Heiri, Lotter & Lemcke, 2001). These vary with laboratory methods but can be monitored by comparing results with other Total Organic Carbon methods. It should be noted that this method provides a rough value as there may be other volatiles present in the sample which cannot be distinguished.

#### 1.4.4 Total Organic Carbon Solid Sample Module (TOC-SSM)

Total organic carbon (TOC) via solid sample module (SSM) is similar to the LOI method in that CO2 is released via oxidation, however, is modified in order to maximize the reaction and to distinguish between organic (OC) and inorganic carbon (IC). Samples are prepared by drying and pulverization prior to analysis.

Individual samples are weighed prior to and after each heating. The furnace is supplied with purified oxygen which is used to fuel the release of carbon dioxide. The released CO2 is carried via zero-grade air into a carbon analyzer for quantification. An aliquot of the sample is then treated with an acid (i.e. phosphoric acid) to further remove CO2 and the weight attributed to IC. The final

weight of the sample is taken for TOC calculation.

Limitations in this procedure come from the heating capacity of the furnace and the inherent nature of bicarbonate to absorb atmospheric water, and therefore altering its weight. Accuracy of this method requires that the furnace be able to reach adequate temperatures. The consequence of inadequate heating may result in portions of carbon remaining unaccounted for and the production of negative values in weight. The supply of oxygen during combustion can compensate for inadequate furnace temperatures.

#### 1.4.5 Gas Chromatography Mass Spectrometry (GC-MS)

Gas chromatography mass spectrometry (GC-MS) is the combination of two analytical methods: gas chromatography (GC) and mass spectrometry (MS). The first commercial GC-MS system came about in the 1960s as an analytical method for the quantification and identification of organic compounds in complex matrices (Sparkman, Penton & Kitson, 2011). The two instruments complement each other by fulfilling the need of the other; e.g. for MS to function the gas must be in a purified state, which GC is designed to accomplish.

Samples are injected into the GC apparatus where it is heated to the point of volatilization. The vapor is then carried by an inert gas (often helium or hydrogen), this is known as the mobile phase. The gas enters the hollow column which contains a stationary phase for the gas. The coil is incrementally heated, releasing gases based on their individual weights- the lighter gases leave first. As the gas enters the MS, it becomes ionized and then separated based on mass-to-charge (m/z) ratios, producing a mass spectrum (Sparkman, Penton & Kitson, 2011). The spectrum appears as a series of colorful peaks on a graph where the X axis is retention time and Y axis is abundance. Each peak represents an individual gas.

GC-MS is limited to organic analysis and cannot fulfill the identification of other materials. Additionally, the lengthy preparation should be monitored as the multi-step process provides the opportunity for errors (i.e. multiple vial exchanges). Errors may also be further amplified by the precision of the measurements (i.e.  $\mu$ l). Precision can be monitored by comparing the retention time of a known compound, such as an internal standard, in one chromatogram with its retention time in another.

# 2 Methods

# 2.1 Sample Acquisition

In support of PLATMAR goals, the research vessel Arquipelago surveyed the insular shelf of Santa Maria Island, successfully collecting 169 sediment samples to be used for biological and geochemical analysis. Supervision of the expedition was conducted by P.I Rui Quartau. Due to the soft nature of the sediments, the samples were retrieved via gravity grab sampler in portions of  $0.1 \text{m}^3$  and  $\sim 30$  cm deep. Once on board, samples were placed in heat-treated aluminum envelopes and stored at -4° C. Samples were transported in coolers via airplane from the Azores to the United Kingdom and stored at -20° C at the University of Manchester.

Twelve samples were separated for the purpose of the following analysis, the remainder will contribute to future works. The selected sites ranged from depths of -31m to -201m and spanned distances of 555m to 6,715m from shore (Figure 2. & Table 1.).



Figure 2. Twelve sites were selected for the purpose of collecting geochemical data and analysis of Santa Maria island's shelf. The above figure shows the location of the sites in relation to their distance from shore, depth, and associated sediment sample.

## 2.2 Laboratory Methods

The 12 sample sites represent four profiles of the insular shelf. The profiles were then studied for the spatial variation of volcanic and carbonate materials. Laboratory analysis took place in the Manchester Analytical Geochemistry Unit (MAGU) of the Williamson research center (WRC) located at the University of Manchester.

## 2.2.1 Freeze-dry

Samples were defrosted at ambient temperature (~20°C), removed from their aluminum envelopes and placed into glass jars. The tops of the jars were covered with heat-treated aluminum foil and sealed with a plastic lid. Samples were re-frozen at -20°C. Once frozen, plastic lids were removed, and the aluminum covers were punctured. Jars were placed to dry in a Mecha Tech system LyoDry Compact for 4 days at -46°C and 8.0 Torr.



Image 1. Moisture was removed from the samples using Mecha Tech system LyoDry compact. Samples were freeze-dried for four days at -46°C and 8.00 Torr.

## 2.2.2 Digital Microscope

The dried sediments were observed and photographed with a Max-See digital microscope, providing images 2-13 below. Observational estimates were made on color and size ratios as well as any distinguishing characteristics and findings. Sub-samples were selected for compositional representation and selectively for iconic findings, i.e. basalt or bioclasts.



Images 2 & 3, respectively named PM 11 & PM 12, form the northern (N) portion of the shelf.



Images 12 - 13, respectively named PM75 & PM74, form the southcentral (SC) portion of the shelf.



Images 4 - 7, respectively named PM01, PM 03, PM02, PM 04, form the southwest (SW) portion of the shelf.



Images 8 - 11, respectively named PM79, PM78, PM77, & PM76, form the southeast (SE) portion of the shelf.

## 2.2.3 Pulverization

Dried samples were removed from their jars, weighed, and then divided between two tungstencarbide mills for pulverization. The mills had been cleaned prior by pulverizing low-iron laboratory sand (silica) for 5 minutes and removed with a brush.

Each sample was pulverized in a Philips MiniMill for 15 minutes at speed 7. The powders were homogenized, any remaining pieces of solid material were removed prior to re-weighing. The powdered samples were returned to their jars, covered with aluminum foil and plastic lids to be stored at room temperature.

Mills were cleaned in between each sample by pulverizing a sacrificial portion of the preceding sample for 5minutes, removing any remaining contents from the previous sample.



Image 12. Dried sediments (left) were split into two tungsten carbide mills and pulverized with a Phillips MiniMill (center). The final product is a fine-powder (right).

## 2.2.4 XRF Pellet

Twelve grams of powdered samples and 3 grams of waxing agent were placed into an agate mill. The powder and wax were homogenized, two mills at a time, with a Fritsch pulverisette for 6 minutes at 350 rpm. Containers were cleaned with intermediate cycles of pure laboratory sand. The mixture was placed into a cylindrical pellet mold and compressed at 6 tones, producing the XRD pellet.



Image 13. The powder sample was combined with a waxing agent (left), homogenized (center), and pressed into an XRF pellet (right).

### 2.2.5 XRF

Pellets were loaded into a PANalytical Axios XRF spectrometer. Concentration of major elements were quantified with Omnian software and given in percentage. Trace elements were analyzed with Pro-Trace and quantified in part per million (ppm). LOI results were applied in order to correct for carbon content. (See appendix for full results)



Image 14. Pellets were loaded into a PANalytical Axios XRF spectrometer for elemental analysis.

## 2.2.6 XRD

Powdered samples were mixed with amyl acetate using an agate mortar and pestle and then adhered onto individual glass slides in a thin circular layer. Once dried, slides were placed into a Bruker D8 Advance diffractometer equipped with a copper source X-ray tube, producing CuK $\alpha$ 1 X-rays at a wavelength of 1.5406Å, and a Göbel Mirror a Lynxeye detector. Samples were scanned from 5-70o2 $\theta$ , with a step size of 0.02 o and a count time of 0.2s per step.

Peaks were evaluated with EVA version 5, which uses the ICDD (International Centre for

Diffraction Data) database for mineral identification. (J. Waters, Personal communication, May 1, 2019) (See appendix for full results)



Image 15. Sediments were adhered to disks and inserted into the Bruker D8 Advance diffractometer for mineral analysis.

## 2.2.7 LOI

One gram of each sample is placed into ceramic crucible- both the weights of the empty crucible and sample are recorded prior to heating. The crucible is then placed into a Genlab oven at 105°C for 1 hour, removed, cooled inside of a desiccator and re-weighed. The crucibles undergo a second heating at 1000°C for one hour in a Carbolite oven, cooled in a desiccator, and weighed. The total carbon is calculated by first subtracting the weight of the sample after 1000°C from the sample's weight after 105°C, then divided by the weight of the powdered sample, sans crucible, and multiplied by 100.

Apparent LOI (%) =  $\frac{\text{weight after 100°c-weight after 1000°C}}{\text{weight of sample}} \ge 100$ 



Image 16-19. Samples were first heated to 105°C (Image 16, top left) then set to cool in desiccators (Image 17, top right). The second heating was set to 1000°C (Image 18 & 19on the bottom left and bottom right respectively).

#### 2.2.8 TOC-SSM

Total organic carbon is calculated by subtracting inorganic carbon (IC) from total carbon (TC). In order to obtain IC and TC values, the samples underwent two treatments. Preparation of the samples required the separation of 2 portions of 50mg from each of the pulverized parent samples and placing them into ceramic boats.

The vessels were then placed into the solid sample module (SSM-5000A) for furnacing. The machine is given ~1 minute to stabilize from any disturbance prior to sample analysis. Once the sample was inserted, the carbon emissions were detected with a Shimadzu total organic carbon analyzer (TOC-VCPN). This machine uses an infrared gas detector to provide the amount of total carbon of the sample.

The second analysis used the second 50mg portion of the sample to quantify the IC from the site. The ceramic boats were positioned at the entrance of the machine, treated with 0.5ml of liquid phosphoric acid to release IC, and then inserted in to the machine for reading.

The solid sample module was calibrated using glucose for TC, and sodium carbonate for IC.

Standards (glucose and sodium carbonate) were weighed in triplicate in order to create a threepoint calibration curve: glucose (12.4mg, 25mg, 50mg) and sodium carbonate (2mg, 5mg, 10mg).

Total organic carbon (%) = Total carbon – Inorganic carbon





*Image 20 & 21 Samples were weighed in duplicate (Image 20, left) and inserted into the solid sample module (Image 21, right).* 

# 2.2.9 GC-MS

# 2.2.9.1 Ultrasonic Extraction

The pulverized samples from sites PM04 (10g), PM12 (10g), PM75 (10g) and PM79 (7g) were selected for GC-MS analysis. Each sample was placed into a centrifuge tube and individually combined with 20ml DCM/ Methanol (2:1) and 25  $\mu$ l of internal standard (tetracosane). Samples were placed in an ultrasonic bath for 15 minutes and then centrifuged for 10 minutes. Solvents were pipetted off. This process was preceded for two more rounds without the addition of tetracosane. The extracted solvent was combined in a pear-shaped flask to make the total lipid extract.



Image 22-25. Samples were placed intro centrifuge tubes (Image 22, top left) and then placed into an ultrasonic bath (Image 23, top right). Solvent and extracts were separated via centrifuge (Image

24, bottom left) allowing for solvents to be pipetted off and collected into pear-shaped flasks (Image 25, bottom right).

## 2.2.9.2 Rotary evaporation

The pear-shaped flask was attached to a vacuum rotary and partially submerged in a warm water bath. Pressure was incrementally increased until solvents completely separated (~15minutes each flask), leaving a coat of extract in the flask.



Image 26. Solvents were removed with a rotary evaporator, leaving the organic extract in the flask.

## 2.2.9.3 Elution

DCM/Methanol (2:1) was used to transfer the extract from the flasks into 3ml vials. The vials were blown down with nitrogen gas until the DCM/Methanol completely evaporated. One-hundred microliters of BF3 in Methanol (14%) was added to the extract. The vials were placed into a heating block set at 70°C for 1 hour, cooled at ambient temperature, and quenched with 1ml of water. Samples were extracted using ~3ml of DCM, passed through a sodium sulfate column and collected into a 3ml vial. Vials were blown down with nitrogen gas until the solute evaporated. Approximately 3ml of ethyl acetate was added to the extract and passed through an aluminum oxide column, collected into a 3ml vial and blown down with nitrogen gas. Thirty microliters of N, O Bis (trimethylsilyl) trifluoroacetamide (BSTFA) was added to the vials before being placed into a heating block set at 70°C for 1 hour, aliquots were separated, and solutes were evaporated with nitrogen gas. Samples were suspended in 100  $\mu$ l of hexane for GC-MS analysis.



Image 27. Samples were heated (top left), blown down with nitrogen (top right) and the final extract was collected for GC-MC (bottom).

## 2.2.9.4 GC-MS analysis

Gas chromatographic analysis injected 1  $\mu$ l of the liquid sample into an Aligent 5975C using pulsed spitless mode. The instrument was equipped with a 30m x 250  $\mu$ m x 0.25  $\mu$ m column coated with Zebron ZB-5MS. The temperature was programmed to increase from 50°C to 130°C at 20°C/min then 6°C/min until 310°C where the temperature was sustained for 15 minutes. The carrier gas used was helium. Scanning parameters were set at 50.0-650.0m/z. Gas fractions, as well as chromatograms, were analyzed with ChemStation and NIST data set.



Image 28. Extracts were injected into an Aligent 5975C for organic analysis.

# **3** Analytical Methods

#### 3.1 ChemStation and Carbon Preference Index (CPI)

Carbon preference index (CPI) is a numerical method used to identify the origin of n-alkanes found sediments and rocks based on their particular carbon number range (odd versus even) (Killops & Killops, 2005; Scalan & Smith, 1970). This calculation is widely used in determining oil maturity and in the recreation of paleoclimates (i.e. Rao et al., 2009). The principles that dictate the distribution of n-alkanes also applies to fatty-acids; both abide by the odd over even predominance. Therefore, the presence of fatty-acids can be calculated with the same formula (Fang et al., 2014).

The index uses either the weight or the mole percentages of a carbon-number to create ratios; the changes in ratios being reflections of the abundance of the source (Scalan & Smith, 1970). Chromatograms derived from the gas chromatography (GC) were analyzed through ChemStation software equipped with a NIST dataset. Ion selection (m/z) was set to 74 in order to distinguish peaks associated with fatty acid compounds. In the chromatogram, the height of the peak (y-axis) reflects the abundance of the compound and the x-axis documents the retention time which is a result of the compound's weight. The carbon-number of the compound can be identified through NIST search engine. The area of the peaks, calculated through manual integration, are grouped by odd and even carbon-numbers to represent marine and terrestrial presence. There have been several revisions and critiques to the accuracy (i.e. Marzi, Torkelson, Olson, 1993) (Killops & Killops,2005) (Scalan & Smith, 1970) of representation however the following equation will be used for the purposes of this study:

$$CPI = 0.5x \left( \frac{\Sigma C_n + C_{n+2} + C_{n+4} + C_{n+6} \dots}{\Sigma C_{n+1} + C_{n+3} + C_{n+5} \dots} \right) + 0.5 x \left( \frac{\Sigma C_n + C_{n+2} + C_{n+4} + C_{n+6} \dots}{\Sigma C_{n-1} + C_{n+3} + C_{n+5} \dots} \right)$$

Limitations of this method come from the creation of a single number which is intended to reflect a series of values which inherently undergo temporal variations and therefor compromising the truth of the ratio (Scalan and Smith, 1969). Additionally, laboratory methods may be reflected in sample values i.e. the amount of sample used during ultrasonicate extraction. Precision can be monitored by comparing the retention time of a known compound.

#### 3.2 GeoMapApp and Proxy Elements

When studying the movement of a material researchers can use an element or mineral from the whole as a proxy for recreating the movement and life cycle of the material (Rothwell & Croudace, 2015). The chosen element depends on the study; however, the choice should consider the element's susceptibility to alterations and points of origin. For example, the selection between iron (Fe) and titanium (Ti) as a proxy element representing the movement of terrestrial material would favor Ti due to its resilience to redox reactions (Peterson et al., 2000).

For the purpose of this study silicon (Si) and aluminum (Al) will be used as proxies for the dilution of volcanic material along the Santa Maria Island's insular shelf. In order to pair the submarine materials with its terrestrial origin, terrestrial values of Al and Si were derived from a land study by Beier et al. (2013) and entered into GeoMapApp with their geographical points; these are the element's "original value". Similarly, the submarine values of Al: Si were entered with their geographical points into the program. The ratio values at both the land and marine sites produce a color indicative of the abundance of the elements Al and Si. Marine sites were then matched with the nearest terrestrial site with the same color to identify points or origin and termination.

In order to create a single numerical representation, the Si values from adjacent sites were averaged to make an "original" concentration- the number of sites in the average corresponded to the number of sites within the adjacent grouping (See images 29-32 below.). Dilution of volcanic elements were then calculated by multiplying the amount of the element detected in the marine location (V2) by 100 and then divided by the terrestrial values (V1).

Dilution = 
$$\frac{V2 \times 100}{V1}$$

This method is limited in that, aside from redox reactions, elements can have various points of introduction and removal. Magnesium, for example, would not serve for the purpose of this study as its presence is found in both volcanic (anorthite) and calcite (carbonate) rendering its origin inconclusive. The selection of Al and Si is based on their known presence in igneous rocks (Walther, 2005) and its terrestrial identification by Beier et al. (2013) and White, Tapia & Schilling (1979).



Image 29. Transect SW and the similar terrestrial sites.



Image 30. Transect SC and the similar terrestrial sites .



Image 31. Transect SE and the similar terrestrial sites



Image 32. Transect N showed no similarity to the composition of the adjacent land in regard to Al:Si content, however two sites were selected for dilution calculations.

Coordinates and values provided by Beier et al. (2013) were plotted with GeoMapApp. The sites selected for Si dilution were chosen based on their similarity of Al:Si values, indicated by the similarity in color (Images 29-32). Four sites were averaged for the dilution calculations of the SE

and SW and two were used for N and SC. The distinct color difference between the points of N and the adjacent shore are indicators of the extreme difference in composition.

# 4 Results and Discussion

The twelve marine sediment samples were grouped based on their geographical position on the insular shelf of the island (Table 1.). Methods of XRF, XRD, LOI, TOC-SSM and GC-MS were used to analyze the elemental, mineral and carbon composition of the samples. Datasets from these methods have been interpreted with the aims of identifying the ratios of dominating minerals, origins of the material and trends in their presence within the shelf.

Site	Group	Distance (m)	Depth (m)	Gradient
PM-01-SW	South West	707	45	0.06
PM-03-SW	South West	996	63	0.06
PM-02-SW	South West	1020	65	0.07
PM-04-SW	South West	1575	151	0.16
PM-11-N	North	6044	98	0.02
PM-12-N	North	6715	119	0.03
PM-74-SC	South Central	10145	31	0.03
PM-75-SC	South Central	1232	42	0.05
PM-79-SE	South East	556	84	0.15
PM-78-SE	South East	677	116	0.26
PM-77-SE	South East	822	148	0.22
PM-76-SE	South East	103	201	0.24

*Table 1. Twelve sites were selected from varying depths and distances from shore. They were then grouped based on their geographical location.* 

# 4.1 Volcanic material and analysis

The presence and absence of volcanic materials most notably differs based on the geographical location on the shelf. This is made evident by the complete absence of volcanic minerals in the northern transect and their presence, albeit highly variable, in the south. The minerals detected with XRD were anorthite and augite. The chemical composition of these minerals both include Si and support its use as a proxy for the movement of volcanic materials. The element is present in the

northern transect despite the lack of associated minerals, indicating an alternative input as well as providing a numerical value for background Si. The strongest correlation between volcanic minerals and Si dilution is found in the southwestern transect with ratios of volcanic to Si resulting in .9, 1.2, 1.1 and 1 with increasing distance from shore.

#### 4.1.1 XRD

XRD analysis identified anorthite and augite among the minerals present in the samples (Graphs 1-3 below\*) supporting the mafic classification of the island's basalts. Volcanic minerals did not have a consistent presence in the sites as they were most prevalent in the SW samples and absent in the N. The presence of augite is the more frequent mineral among the sediments which contained volcanic minerals and appears with higher concentrations than anorthite. Augite was the sole volcanic representative in the SC group. Both minerals were detected in the SE transect, however, anorthite was intermittent. Of the groups, the SW transect contained the highest total weightpercent of volcanic minerals.



Graph 1. Augite held higher concentrations throughout the transect.



Graph 2. Anorthite was absent in the SC group, however, augite was detected.



*Graph 3.* Augite was detected throughout the transect with anorthite appearing in two sites.

\*The northern transect was not graphed for volcanic minerals as none were identified at those sites.

### 4.1.2 Dilution: Si

Terrestrial Si data collected by Beier et al. (2017) was used to represent "original" values for Si. Dilution was calculated by multiplying the amount of Si found on the shelf by 100 and dividing by the value at the origin. The distribution of volcanic minerals varied by depth, distance and geographical location on the island. The most extreme decrease in silica content occurs at groups N (97%) and SC (94%). Dilution in SE varied with sites and ranged between 79-90%. Silica was most conserved in the SW transect with dilution values ranging between 69-85%, lacking a linear trend. These values are visualized in Graphs 4-7 below with relation to depth and distance.



Graphs 4 (left) & 5 (right). Location of the north (orange) and south central (yellow) study sites in relation to depth and distance from shore with anorthite and augite values. The minerals were not detected (N.D) at sites PM-11-N and PM-12-N. Volcanic minerals only appear as augite in the SC sites, anorthite was not detected. The dilution of volcanice minerals is highest in these two groupings.



Graphs 6 (left) & 7 (right). Dilution of Si from its point of origin to the sites on the insular shelf yielded higher percentages in the sites which also contained volcanic minerals. Silica values at N and SC maintain their values while values fluctuate throughout transects SE and SW. N.D indicates minerals which were not detected

#### 4.1.3 Discussion

During a terrestrial survey of the island, White, Tapia and Schilling (1979) identified olivine among the volcanic minerals on Santa Maria, the presence of which was not detected on the insular shelf. Instead, XRD detected augite which is a pyroxene mineral associated with olivine. Augite is considered to be frequently occurring and essential component of mafic basalts (Anthony, 2001) and therefore the more likely of the two minerals to appear. Additionally, Le Bas et al. (1986) listed basanites as one of the most abundant rocks on the island- a common constituent of which is augite. Analysis can conclude that augite is more likely to be found on the shelf based on its naturally occurring frequency, essential presence in mafic basalts and its association with olivine and basanite. Future studies can investigate what dictates the mineral's movement and why its deposition is favored at its neighboring sites.

Anorthite, or anorthosite, is a calcium-rich plagioclase feldspar (Spudis, 2000). The mineral is formed by slow cooling, indicative of an intrusive genesis. Its presence, per the limitation of this study, is exclusive to the southern portion of the island with its highest concentration being in the SW. The shelf of the SW is relatively narrow (<1.5km) which Quartau et al. (2010;2015) identify as a morphological feature resulting from volcanic progradation. The climate on the west of the island is windward, experiencing the brunt of the prevailing winds and enhanced precipitation (NOAA, 2019b.)- forces which are associated with enhanced erosion. The geology adjacent from this grouping is the Anjos complex, a sequence of subaerial lava flows which have a sea-level marker of 11m (Ramalho et al., 2017) indicating that the feature is in the range of the island's semidiurnal tide (1.8m to 0.2m in the Azores), which are magnified in times of high winds (Gomes & Pinto, N.D). Therefore, this study concludes volcanic contributions to the shelf in the SW result from the erosion of terrestrial driven by precipitation, wind, and tidal zones from the Anjos complex.

Both volcanic minerals were present in the SE shelf. The transect faces the Pico Alto complex which is a series of submarine magma overlain by subaerial volcanic materials. The altitude of the subaerial magma is well above sea level and away from the forces of marine weathering. In addition to the temperate climate, the island frequently experiences intense storm events which create downwelling currents in the southeast and. These storm-induced currents transport nearshore sediments to deeper portions of the shelf (Meierelese et al., 2013). Alternatively, Ramalho et al. (2017) categorizes the eastern portion of the island as leeward, or warm and dry (NOAA, 2019b.). With this, analysis identifies climate weathering via desiccation and downwelling as the mode of distribution.

An interesting point of conversation is the SC transect which, despite the detected values of its neighbors, contains 5-2% of volcanic material which is exclusively represented by augite. The geology of the land near the group includes portions of the Anjos (subaerial basalt) and Touril (marine sedimentation) complexes as well as the Prainha outcrop. According to Meirelese et al. (2013), storm events drive cross-shelf deposition, though this is not reflected in the SC transect. The lack of volcanic contributions can provide an example of the limitations of this study and need for more study sites horizontally in the SC area. The surface sediments of these sites are a snapshot of the conditions at the specific location at a specific time. Future studies should extend individual transects in order to enhance representation of the shelf's constituents. Additionally, it would be interesting to monitor compositional changes before and after storm events.

## 4.2 Carbonate material and analysis

#### 4.2.1 LOI

The primary application for LOI during this study is for the correction of carbon detection during XRF analysis, however, these values can also be considered as rough estimates of carbon content in each sample (Luczak, Janquin &Kuoka, 1997). LOI analysis found that sediment samples from the island's shelf range from 67%-100% carbon composition (Graph 8 & 9 below). The site with the most carbon content is found in the northern transect with PM-12-N containing 100%, however, SC contains the highest average with 96%. Carbon increases with depth and distance from shore in transects N and SC. The lowest average LOI is found in the SW (73%) which also hosts the site with least amount of carbon PM-03-SW. Sediments from SE range from 80-94% LOI. Values in transects SW and SE fluctuate with no distinct trend. The maximum theoretical yield for pure CaCO3 is 44%, LOI values were calculated to represent their percent of the theoretical maximum.



*Graph 8. Carbonate content increased with depth and distance in the N (blue) and SC (red) groupings. Both groups show an increase of LOI (y-axis) with increased distance from shore (x-axis).* 



*Graph 9. Carbonate materials were consistently present in the SW (blue) and SE (orange) groupings. LOI fluctuates individually within each grouping but are overall linear.* 



Graphs 10 (left) & 11 (right). Dilution of carbonate with distance shoreward. PM-12-N from the northern grouping (red) held the highest value with an LOI of 100%. The SC grouping (yellow) consistently held LOI of >90%. Both groupings increased in LOI with distance from shore.



*Graph 12 (left) & 13 (right). Sediments from the N and SC sites increase with distance and depth while the values fluctuate in the SE (green) and SW (blue) transects.* 

## 4.2.2 Total organic carbon-solid sample module (TOC-SSM)

The analysis for the total organic carbon (TOC) of the samples found that inorganic carbon (IC) dominated over organic carbon (OC) in all sample sites (Graph 14-17 below). A noteworthy anomaly is the ratio of OC to IC found at site PM-75-SC (0.43) compared to its partner PM-74-SC (0.01). Inorganic carbon in the SE group increased from 87-99% with depth. TOC values of several sites resulted in negative values; this occurs from insufficient heating during analysis. Discrepancies of less than 3% are considered acceptable (A. Bewsher, Personal communication, May 1, 2019)



Graph 14 (left) & 15 (right). Though inorganic carbon was the dominant form of carbon in all samples, the ratio values of IC to OC at the SC (yellow) site PM-75-SC is an outlier and beckons further investigation.



Graph 16 (left) & 17(right). IC and OC percentages were calculated as a proportion of the TC detected at each site. Negative values (i.e. site PM-78-SE in green) reflect errors from laboratory equipment, likely from insufficient heating, however, errors of less than 3% are considered acceptable (A. Bewsher, Personal communication, May 1, 2019)

### 4.2.3 XRD: Carbonates

Two carbonate minerals were identified by XRD analysis: calcite and aragonite. The ratio of aragonite to calcite decreases from 1.5 to 0.5 in the SW group (Graph 20.), demonstrating the shift of carbonate mineral from aragonite to calcite with distance. The groupings SE (Graph 21.) and SC (Graph 19.) are dominated by the calcite form of carbonate, with the aragonite to calcite ratio decreasing with distance: 0.8 to 0.5 for SC and 0.5 to 0.3 for SE. The dominance of calcite in the N (Graph 18.) transect is less variable with a ratio of 0.2.



Graph 18. (left) shows the dominance of calcite over aragonite in the N group. Graph 19. (right) visualizes a narrower ratio between the two minerals in the SC group compared to the N group as well as a preferential shift toward calcite with increased distance and depth.



Graph 20. The shift from aragonite-dominant to calcite-dominant is seen in the SW transect (left) with increasing depth and distance from shore. Conversely, calcite remains dominant despite depth and distance in the SE transect (Graph 21, right).

## 4.2.4 GC-MS

The x-axis of the chromatogram identifies the retention time, or the moment when the compound is detected, and the y-axis is the relative abundance of the material. Each compound has its associated moment of release; however, overlap can occur when composition is similar and augment an abundance peak. Alternatively, if there is too little sample used during the preparation the peak may not be represented at all. The use of an internal standard serves as a point of reference for its known composition and controlled presence. The area of the internal standard can therefore be compared to the area of the detected compound to calculate the amount of the unknown.

Interestingly, the peaks for the internal standard, tetracosane, as well as some of the targeted carbon-numbers (C19 - C30) were not visible in the chromatograms. Due to the lack of peak identification, a fair CPI could not be calculated. It is suspected that the reason for the lack of these

key points is the result of an insufficient amount of the starting sample used during the ultrasonic extraction phase. Future studies should take this into consideration when preparing samples for GC-MS analysis. This is not to say that visual observation cannot be made by the chromatograms as there are distinct differences in peaks and retention times and it still holds true that lighter carbon compounds, i.e. of marine origin, release during early retention times. Please see Chromatograms 1-4 for visual observations of retention times and abundance.

The following descriptions are in regard to ion 74 as the focus and carbon-numbers between C20 and C30. Carbon chain-lengths of  $\geq$ C20, the identified threshold for fatty-acid ratios, are found at and after the retention time 22.34 minutes; C20 is present in all samples. The maximum carbon-number (C30) is found at sites PM-75-SC and PM-79-SE at retention time 33.94, its presence is absent in PM-04-SW and PM-12-N. Carbon chains greater than C27 were not identifiable at PM-12-N and after C28 for PM-04-SW.

The incomplete list of values prevented the use of CPI as a statistical index in the identification of marine to terrestrial organic carbon. It can be observed, however, that PM-04-SW and PM-12-N show more activity in earlier retention times than PM-75-SC and PM-79-SE. Activity for the sites noticeably decreases in abundance after 30 minutes, indicating that lighter carbons are the most abundant and therefore that these sites largely accumulate carbon from marine sources.



Chromatogram 1. The full chromatogram for site PM-04-SW. The intensity of the peaks after C20 indicate more complex, long-chain-carbon. This suggests, then, that the sample site is located at a point where it accumulates terrestrial carbon as well as marine.



Chromatogram 2. The full chromatogram for site P-12-N. The intensity of the peaks after C20 indicate more complex, long-chain-carbon. This suggests, then, that the sample site is located at a point where it accumulates terrestrial carbon as well as marine.



Chromatogram 3. The full chromatogram for site PM-75-SC. Early retention time activity indicates that the sample is more abundant in short carbon chain material and therefore suggests that the sample site is at a location which accumulates marine carbon versus terrestrial.



Chromatogram 4. The full chromatogram for site PM-79-SE. Early retention time activity indicates that the sample is more abundant in short carbon chain material and therefore suggests that the sample site is at a location which accumulates marine carbon versus terrestrial.

#### 4.2.5 Discussion

When considering depth as a variable, the deepest site, PM-76-SE (20m), resulted in an LOI of 79% compared to an LOI of 94% at the shallowest site, PM-74-SC (31m), demonstrating the effects of the lysocline. Pressure increases with depth which in turn discourages the precipitation of carbonate and shifts to dissolution (Killops & Killops 2005). Though not demonstrated with the depths of this study, if the sampling were to continue researchers would find the carbon compensation depth (CCD)- the point where carbonate supply and dissolution are equal resulting in the absence of carbonate all together. This point varies based on temperature, chemical composition of the water and the form of the mineral itself (Killops & Killops 2005). Future studies may consider the continuation of transects SE and SC for the determination local CCD. Additionally, LOI for groups N and SC were found to have the highest carbon composition as individual sites and groupings. Both sites lie adjacent to the limestone outcrops Prainha and Lagoinhas, however, are situated on different hemispheres of the island. The LOI values of the N and SC transects increase with distance suggesting a marine source, however, more data points will be needed to determine any definitive trends. The LOI method is limited in that it is considered a rough method as well as it does not elaborate on the carbonate materials measured. For further analysis of carbonate characteristics, the study will interpret results from TOC-SSM. The majority of carbon in the ocean is in the form of dissolved inorganic carbon (Killops & Killops, 2005). Inorganic carbon has been linked to the presence of high net primary production

and chlorophyll-a concentration in the Azores area (Amorim et al., 2017) which is reflected in the results of the marine dominated organics detected by GC-MS. Additionally, the distribution of carbon is determined by the pH of seawater in a sequence of equilibria (Figure 1.) (Killops & Killops, 2005).



CO2+H2O <-> H2CO <->HCO3- +H<sup>+</sup> <-> CO3<sup>2-</sup> +2H

Figure 1. The inorganic form of carbon is a result of pH. The minerals identified with XRD identified calcite and aragonite which both carbonates, indicating pH higher than average seawater.

Inorganic carbon is the more common form found in seawaters and specifically so in dissolved form. There are three forms of inorganic carbon in the ocean- carbonic acid, bicarbonate and carbonate- the mass fraction of which is determined by the pH of the water. This study identifies carbonate minerals as the dominating form of inorganic carbon. Carbonates have a preference of pH higher than the average seawater, therefore its presence, compared to other forms, is an indication of a high pH (Figure 1.). If this is true, then the ratios of volcanic to carbonates in the SW (Figure 2.) are the result of a localized change of pH. This statement is supported with the presence of halite, a bicarbonate inorganic carbon mineral which prefers comparatively lower pH.



*Figure 2. XRD mineral analysis identified halite in the SW transect. The above spectrum pertains to PM-01-SW. Additional spectrums can be found in the appendix.* 

For GC-MS analysis, it is interesting that the necessary peaks were not present after C27 at PM-12-N and after C28 for PM-04-SW. This is the result of the amount of sample used during the extraction process. Future studies should increase sample amount to >7g. Despite this limitation, visual observations note that lighter fatty-acids dominate the samples and do so more distinctly at site PM-12-N and after C28 for site PM-04-SW, the furthest of the four sites from shore, 6715m and 1575m respectively.

It is worth noting the annual algal bloom which occurs in the North Atlantic. Visser et al. (2011) found that this phenomenon begins to the south of the island in a northern migration (Figure 3.). The peak of chlorophyll *a* is detected between March and April. This analysis then suggests that the amount of marine-derived organic carbon has a distinct temporal variation and would reach its highest abundance on the shelf shortly after the peak of primary production in April.



Figure 3. Satellite observations for chlorophyll a were used by Visser et al. (2011) in order to monitor the migration of the North Atlantic's annual algal bloom. Primary production begins to increase in December and January, peaking in March and April and ending by the summer months of July and August. (Figure from Visser et al., 2011)

# 5 Conclusion

In the study of 12 sediment samples all were found to be largely composed of inorganic carbonate minerals. Sediments with the highest carbonate to volcanic ratio are found in the northern sites of the island followed by the sites in the southcentral transect. The groupings N and SC are also the furthest sites and exhibit an increase in carbon content with increasing distance from the shore. Their locations being adjacent to limestone outcrops can be speculated as the potential sources for their carbonate or, alternatively, signals of favorable conditions for carbonate precipitation. The increase in LOI with distance indicates a marine-driven carbonate supply, though, more study sites are needed in order to make an adequate trend. Distinguishing the two groups is the aragonite to calcite (a:c) ratios; sites from the north which maintained a 0.2 a:c and SC decreased from 0.8 to 0.5 a:c. The prevalence of aragonite over calcite, under modern ocean conditions, is found to be an indicator of warm, shallow, marine environments and temperatures in the south-central and southwest. Graphs 22-25 below summarize volcanic to carbonate ratios found in the sediment samples from each site.



Graph 22 (left) & 23 (right), show the volcanic to carbonate minerals against the insular shelf profile. Analysis of sites from the N group (red) did not detect volcanic minerals and averaged 5% for sites in SC (yellow). The highest percentage of carbonates from this study were found in N group. These groups contrast against the sites in groups SE and SW, advocating for further study sites in the N and SC.



Graph 23 (left) & 24 (right), show the volcanic to carbonate minerals against the insular shelf profile. These groups contrast against the carbonate- dominant groups N and SC, and demonstrate horizontal mixing on the shelf of the island.

Carbonate minerals are the dominating materials of island's insular shelf. These are created within the earth as well as on its surface. The parent formula is CaCO3 which is then altered as a reflection of depth, temperature and surrounding elements of compatible ions. At earth's surface, carbonate minerals are created via biotic and abiotic systems, the determination of which mineral is produced is at the bay of the faunal community, temperature, and pH of the area. In their biogenic form, the mineral is used for the construction of the hard parts of marine organisms, such as their skeleton or shell (Nichols, 2009). Alternatively, the mineral can precipitate from waters saturated with the compound but is restricted or encouraged based on the local pH.

The most common mineralization of carbonate is calcite and aragonite. Both minerals have the same formula CaCO3 but can be distinguished by their crystal structure (Nichols, 2009). Calcite is the most common and stable of the two. Its abiotic formation occurs under conditions of high heat and, relative to aragonite, low pressure. The crystal arrangement allows for Ca to be exchanged with elements of similar ions; i.e. Mg replacing Ca to 11-19% to create "high- mg calcite" (Nichols, 2009). Echinoderms and barnacles are examples of marine organisms which are capable of conducting this elemental exchange.

The creation of islands has long since been an interest of explorers and scientists. It is with the curiosity of biologists that began to hypothesize their creation. Afterall, how could the colonization of a species come to be on such distant landmasses? One such early hypothesis was that islands were the result of foundered, or sunken, continents (Menard, 1986). The arena for conversation was opened with the discovery by Charles Darwin of red clays and globerina ooze, materials which do not form on continents, on the ocean floor and hence proposing that continents and oceans were distinct (Menard, 1986). This pivotal moment emphasized the importance of understanding and characterizing the ocean floor in order to create a sound judgment of what lays on top.

The gap in knowledge of the insular shelves of islands has been noted by many researchers. Hypothesis have identified the lack of multidisciplinary specialists and specific focus on deep ocean rather than the shelf. Though, these obstacles have been overcome in the past with the goal of national security and economic interest pushing exploration to further, deeper, and more remote regions of the North Atlantic. I would like to present, then, that the lag in insular shelf exploration can be resolved with the emphasis on incentives such as hazard mitigation and sustainable planning. Objectives that can accelerate the progress of these studies should enhance communication between individual studies and relate the findings to societal problems.

Language barriers were often found during this study- with many documents left unread due to their publishing in alternative languages (i.e. Portuguese) and therefore limiting its impact in the field. Consequences of this can lead to the exhaustion of resources with the duplication of studies or withholding information that holds the potential to make future studies more efficient.

National and economical security has been drivers for the ocean's study in the past and can still perpetuate adjacent endeavors today. Santa Maria island is known for its sandy white beaches have been found to be composed of carbonate minerals. The current state, and future trend, of ocean conditions is one which suggests warmer temperatures and higher acidity. This phenomenon is known as ocean acidification. Findings of this study provide a case study of the effects that pH and temperature have on the composition of an island's shelf (the SW transect). More over how much they can vary within one island.

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# 7 Appendix

# 7.1 MAX-SEE images of samples

# 7.1.1 Northern transect (N)





7.1.2 Southcentral transect (SC)



# 7.1.3 Southwest transect (SW)



# 7.1.4 Southeast transect (SE)



# 7.2 Loss on ignition (LOI)

Group	SW	SW	SW	SW	Ν	Ν
Sample site	PM-01- SW	PM-03- SW	PM-02- SW	PM-04- SW	PM-11- N	PM-12- N
Weight of empty crucible (g)	14.82	14.74	11.38	14.76	16.54	14.80
Weight of crucible and sample (g)	16.00	15.75	13.13	15.97	17.40	15.57
Sample weight (g)	1.18	1.02	1.75	1.21	0.85	0.78
Weight of crucible and sample after heating at $105^{\circ}$ C (g)	16.00	15.75	13.12	15.96	17.39	15.57
Water loss (g)	0.01	0.01	0.01	0.01	0.01	0.01
%H2O loss	0.72	0.76	0.61	0.81	0.64	0.64
Weight of crucible & sample after heating at 1005°C (g)	15.63	15.44	12.48	15.56	17.08	15.23
Weight loss between 110 and 1000 (g)	0.37	0.30	0.64	0.39	0.31	0.34
Apparent LOI%	31.12	29.68	36.57	32.56	36.54	43.88

Group	SC	SC	SE	SE	SE	SE
Sample site	PM-74- SC	PM-75- SC	PM-79- SE	PM-78- SE	PM-77- SE	PM-76- SE
Weight of empty crucible (g)	16.80	16.61	19.26	18.15	18.65	16.64
Weight of crucible and sample (g)	17.96	17.50	20.09	18.94	19.99	17.51
Sample weight (g)	1.16	0.90	0.84	0.78	1.35	0.87
Weight of crucible and sample after heating at $105^{\circ}$ C (g)	17.95	17.50	20.09	18.93	19.98	17.50
Water loss (g)	0.01	0.01	0.01	0.01	0.02	0.02
%H2O loss	0.82	0.92	0.85	0.94	1.36	1.72
Weight of crucible & sample after heating at 1005°C (g)	17.47	17.11	19.76	18.60	19.50	17.19
Weight loss between 110 and 1000 (g)	0.48	0.39	0.33	0.32	0.47	0.31
Apparent LOI%	41.64	43.00	38.77	41.32	35.06	35.07

Site	SSM-TOC (TC-IC) as (%)	SSM-TC (%)	SSM-IC (%)
PM-01-SW	0.536	7.986 (Avg.8.14 + 7.832)	7.45 (Avg.7.404 + 7.496)
PM-03-SW	-0.108	7.224	7.332
PM-02-SW	1.182	10.016	8.834
PM-04-SW	-0.09	7.55	7.64
PM-11-N	0.562	10.918	10.356
PM-12-N	0.262	10.846	10.584
PM-74-SC	0.114	10.024	9.91
PM-75-SC	3.084	10.274	7.19
PM-79-SE	1.368	10.32	8.952
PM-78-SE	-0.274	9.336	9.61
PM-77-SE	0.294	8.094 (Avg. 8.218 + 7.97)	7.800 (mean of 7.874 + 7.724)
PM-76-SE	0.062	8.142	8.08
Glucose			
TRIAL 5mg		5.303	
END 10mg		10.31	
END 20mg		21.85	
Sodium Carbonate			
END 2mg			1.904
END 5mg			4.503
END 10mg			9.837

# 7.3 Total organic carbon- solid sample module (TOC-SSM)

\*Negative values are the result of machine error. This occurs if carbon does not completely oxidize during furnacing.



# 7.4 Gas chromatography-mass spectrometry (GC-MS) Chromatograms 7.4.1 PM-04-SW



## 7.4.3 PM-75-SC

	Na	Mg	Al	Si	P2	S	Cl	К	Ca	Ti
PM-01-SW	1.41	5.37	4.24	13.46	0.25	0.39	0.36	0.54	36.12	1.20
PM-03-SW	1.69	7.54	3.50	11.76	0.24	0.57	0.71	0.38	37.94	1.05
PM-02-SW	1.32	5.74	2.17	6.55	0.17	0.56	0.57	0.24	42.20	0.63
PM-04-SW	2.29	7.01	3.53	10.02	0.25	0.82	1.22	0.39	36.30	0.92
PM-11-N	1.27	6.38	0.59	1.17	0.11	0.89	0.77	0.07	50.68	0.08
PM-12-N	1.13	6.43	0.82	1.16	0.10	0.83	0.69	0.06	43.48	0.08
PM-74-SC	1.99	5.78	0.87	2.71	0.11	0.77	1.26	0.13	42.38	0.22
PM-75-SC	2.08	5.79	0.94	2.58	0.14	0.81	1.35	0.13	40.72	0.19
PM-79-SE	1.91	7.25	2.16	5.15	0.21	0.80	1.15	0.17	38.27	0.45
PM-78-SE	2.24	5.60	1.85	4.29	0.14	0.85	1.39	0.16	39.01	0.28
PM-77-SE	2.59	5.95	3.44	8.28	0.18	0.92	1.74	0.36	35.67	0.66
PM-76-SE	2.78	6.24	3.81	9.19	0.20	0.88	1.69	0.39	33.69	0.63

# 7.5 X-Ray Fluorescence (XRD): Major element concentrations (%)

	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Br	Sr
PM-01-SW	0.02	0.14	4.43	0.01	0.01	0.01	0.00	0.01	0.00	0.21
PM-03-SW	0.04	0.05	3.85	0.01	0.01	0.00	0.00	N. D	0.00	0.22
PM-02-SW	0.02	0.04	2.35	N. D	0.01	0.00	0.00	N. D	N. D	0.25
PM-04-SW	0.01	0.08	3.45	0.01	0.01	0.00	0.00	0.01	0.00	0.21
PM-11-N	N. D	0.02	0.54	N. D	0.00	0.00	N. D	N. D	0.00	0.25
PM-12-N	N. D	0.01	0.47	N. D	0.00	0.00	N. D	0.01	0.00	0.20
PM-74-SC	0.01	0.02	0.97	0.00	0.00	0.03	N. D	0.00	0.01	0.29
PM-75-SC	0.01	0.01	1.02	0.01	0.01	0.00	N. D	0.02	0.01	0.27
PM-79-SE	0.02	0.04	2.56	0.01	0.01	0.00	0.00	0.01	0.01	0.22
PM-78-SE	0.02	0.03	1.63	0.01	0.01	0.00	0.00	0.01	0.01	0.22
PM-77-SE	0.02	0.05	3.47	0.00	0.01	0.00	0.00	N. D	0.01	0.21
PM-76-SE	0.02	0.05	3.39	0.01	0.02	0.00	0.00	0.02	0.01	0.19

\*N.D = none detected

# 7.6 X-Ray Diffraction (XRD)

Sample	Phase Name	Weight %	Sample	Phase Name	Weight %
PM-11-N	Aragonite	18 43	PM-12-N	Aragonite	16.46
	Calcite magnesian	79.61		Calcite magnesian	81.52
	Halite	1.15		Halite	N.D
	Hydrotalcite	0.82		Hydrocalcite	2.02
PM-74-SC	Aragonite	41.00	PM-75-SC	Aragonite	31.84
	Calcite magnesian	52.04		Calcite magnesian	63.95
	Halite	1.55		Halite	1.85
	Augite	5.42		Augite	2.36
PM-01-SW	Anorthite	12.56	PM-03-SW	Anorthite	10.02
	Aragonite	42.71		Aragonite	29.04

	Calcite magnesian	28.21		Calcite magnesian	36.15
	Halite	0.50		Halite	0.64
	Augite	14.81		Hydrotalcite	0.99
	Hydrotalcite	1.21		Augite	23.16
PM-02-SW	Anorthite	6.28	PM-04-SW	Anorthite	11.12
	Aragonite	35.75		Aragonite	24.37
	Calcite magnesian	46.37		Calcite magnesian	48.86
	Halite	0.66		Halite	1.61
	Hydrotalcite	0.68		Augite	10.98
	Augite	10.27		Hydrotalcite	3.07
PM-79-SE	Anorthite	5.80	PM-78-SE	Anorthite	N.D
	Aragonite	28.30		Aragonite	27.71
	Calcite magnesian	56.71		Calcite magnesian	64.57
	Halite	1.49		Halite	1.76
	Augite Px	4.58		Augite	4.86
	Hydrotalcite	3.12		Hydrocalcite	1.11
PM-77-SE	Anorthite	4.48	PM-76-SE	Anorthite	N.D
	Aragonite	15.66		Aragonite	16.33
	Calcite magnesian	67.65		Calcite magnesian	63.90
	Halite	1.95		Halite	2.67
	Hydrotalcite	1.51		Hydrocalcite	2.86
	Augite	8.75		Augite	12.93
				Quartz	1.31

\*N.D = none detected







#### 7.6.5 PM-01-SW





#### 7.6.7 PM-02-SW



#### 7.6.9 PM-76-SE





### 7.6.11 PM-78-SE