UNIVERSITY OF PIRAEUS

SCHOOL OF INDUSTRY AND SHIPPING

DEPARTMENT OF MARITIME STUDIES

MSc Sustainability and Quality in the Marine Industry

GEOCHEMICAL STUDIES OF MARINE SEDIMENT FROM METHNA

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Three Members of the Committee of Inquiry

"The present Dissertation work was approved unanimously by the Triple Inquiry A committee appointed by the EJT of the ICMS following the Rules of Procedure Operation of the ICMS ‘Management in Marine Science and Technology.’

The members of the Commission were:

-Professor Fani Sakellariadou supervisor

-Emeritus Professor Vasilios Tselentis member

-Assistant Professor Anastasia Christodoulou member

The approval of the Dissertation by the Department of Maritime Studies University of Piraeus does not imply acceptance of the author's opinions.

INTRODUCTION

The process of completing this dissertation spanned over four months and involved several key phases. One of the most intensive parts was gathering data. Combined with this, I dedicated significant time to extensive research, reviewing numerous references, and conducting experiments to ensure a solid foundation for my work. Additionally, I invested considerable effort in analyzing data for the maps and diagrams that are in this dissertation. I want to express my gratitude to all those who assisted me in finishing this dissertation.

Above all, I am very thankful to my supervisor, Professor Ms. Fani Sakellariadou. I relied on her guidance and support for my research. She showed me how to operate the instruments, gave me samples and resources, and encouraged me consistently. I am grateful for her support in enabling the completion of this dissertation and for consistently having faith in me.

I would also like to express my gratitude to the members of my committee, and I highly appreciate their time and contributions.

My friends and family deserve a huge thank you. Their support and faith in me motivated me to persevere on this journey. Their support was essential for me to accomplish it.

Finally, I would like to express my gratitude to all the professors and staff members of this graduate program. Their instruction has proven to be extremely helpful, not only in my academic pursuits but also in the guidance it offers for navigating life. I am extremely grateful for their support during this whole experience.

ABSTRACT

This thesis examines the geochemical composition of marine sediment samples collected from the Methana Peninsula, an important location within the South Aegean Volcanic Arc in Greece. The research uses FTIR Spectroscopy to analyze the properties of these sediments, specifically looking at identifying both organic and inorganic compounds and how they are linked to the volcanic activity in the area. The FTIR examination identified notable peaks associated with different functional groups, suggesting the existence of compounds like aliphatic hydrocarbons, aromatic substances, and alcohols or esters. The variety in the sediment composition was potentially influenced by local volcanic processes and environmental conditions and is indicated by differences in spectral peaks among samples.

Keywords: FTIR, South Aegean Volcanic Arc, Spectroscopy, IR, Geochemical Analysis

ΠΕΡΙΛΗΨΗ

Η παρούσα διατριβή εξετάζει τη γεωχημική σύνθεση δειγμάτων θαλάσσιων ιζημάτων που συλλέχθηκαν από τη Χερσόνησο των Μεθάνων, μια σημαντική τοποθεσία εντός του Ηφαιστειακού Τόξου του Νοτίου Αιγαίου στην Ελλάδα. Η έρευνα χρησιμοποιεί Φασματοσκοπία FTIR για να αναλύσει τη σύσταση και τις ιδιότητες αυτών των ιζημάτων, εστιάζοντας ειδικά στον εντοπισμό τόσο οργανικών όσο και ανόργανων ενώσεων και πώς αυτές συνδέονται με τη ηφαιστειακή δραστηριότητα στην περιοχή. Η ανάλυση FTIR εντόπισε αξιοσημείωτες κορυφές που συνδέονται με διαφορετικές λειτουργικές ομάδες, υποδεικνύοντας την ύπαρξη ενώσεων όπως αλειφατικοί υδρογονάνθρακες, αρωματικές ουσίες και αλκοόλες ή εστέρες. Οι διαφορές στις φασματικές κορυφές μεταξύ των δειγμάτων υποδηλώνουν τη μεταβλητότητα στη σύνθεση των ιζημάτων, η οποία ενδέχεται να επηρεάζεται από τοπικές ηφαιστειακές διεργασίες και περιβαλλοντικές συνθήκες.

Λέξεις κλειδιά: FTIR, Ηφαιστειακό τόξο Νοτίου Αιγαίου, Φασματοσκοπία, IR, Γεωχημική ανάλυση

Contents

1. Aim and Methodology

The aim of the dissertation is to analyze the mineral and organic components of marine sediments from the Methana Peninsula, part of the South Aegean Volcanic Arc, using the Fourier Transform Infrared Spectroscopy (FTIR) method. The study seeks to identify the organic and inorganic compounds present in the sediments, examine their relationship with the region's volcanic activity, and establish a link between volcanic processes and sediment composition. The process included gathering sediment samples and using FTIR to analyze and detect their functional groups. The spectra were analyzed against reference data to identify the organic and inorganic compounds. These substances were subsequently connected to volcanic eruptions by utilizing both the reference information and the discoveries from this research. This procedure assisted in identifying the impact of volcanic eruptions on the makeup of the sediment.

2. Introduction

The Methana Peninsula is a section of the South Aegean Volcanic Arc, which is characterized by tectonic activity which is situated in the northeastern Peloponnese of Greece. Due to the region's volcanic past, multiple geothermal springs and volcanic formations can be found here, which have shaped the surrounding marine environment and the landscape.

Throughout the ages, the region's marine sediment composition has been significantly impacted by volcanic activity (Cassidy et al., 2014). In addition to providing insight into the effects of volcanic emissions and other environmental factors on nearby ecosystems, these sediments are important records of geological and natural processes. Rock weathering, and organic material deposition are just a few of the factors that can affect marine sediments (Husson and Peters, 2018). We can learn more about the mechanisms of sculpting the environment by examining these sediments. Exploring the connection between sediment composition and volcanic activity is made possible by the Methana Peninsula's distinctive volcanic features (Tzanis et al., 2020). Methana's unique contributions to local geochemical cycles are still largely unknown, despite earlier research on other regions of the South Aegean Volcanic Arc being the focus of previous works (Dotsika et al., 2008).

Fourier-transform infrared spectroscopy (FTIR) is a vital analytical tool used in this study to examine the marine sediments around Methana. FTIR measures the absorption of infrared light by materials to identify a wide range of organic and inorganic compounds.

3. South Aegean Volcanic Arc

The South Aegean Volcanic Arc (Figure 1) is an important chain of volcanoes situated in the Aegean Sea, which is a part of the complex tectonic environment of the Eastern Mediterranean. The continuous collision of the African and Eurasian plates along the Hellenic Arc causes this phenomenon. This procedure results in the mantle above the subducting plate undergoing partial melting, resulting in the creation of magma that ascends to create volcanic formations. The continual movement of these tectonic plates causes this area to have a high level of geological activity (Vougioukalakis, et.al, 2019)

The Arc started developing during the late Miocene period and has remained active till now, with volcanic activity changing over millions of years. There were numerous volcanic landforms, such as stratovolcanoes[1], calderas[2], lava domes, and underwater volcanoes that can be found in the area (Vougioukalakis et al, 2019).

[1] A volcano with a cone shape formed by multiple layers of solidified lava and volcanic ash.
[2] Caldera: A big, bowl-shaped hollow that is created when a volcano erupts and then caves in.

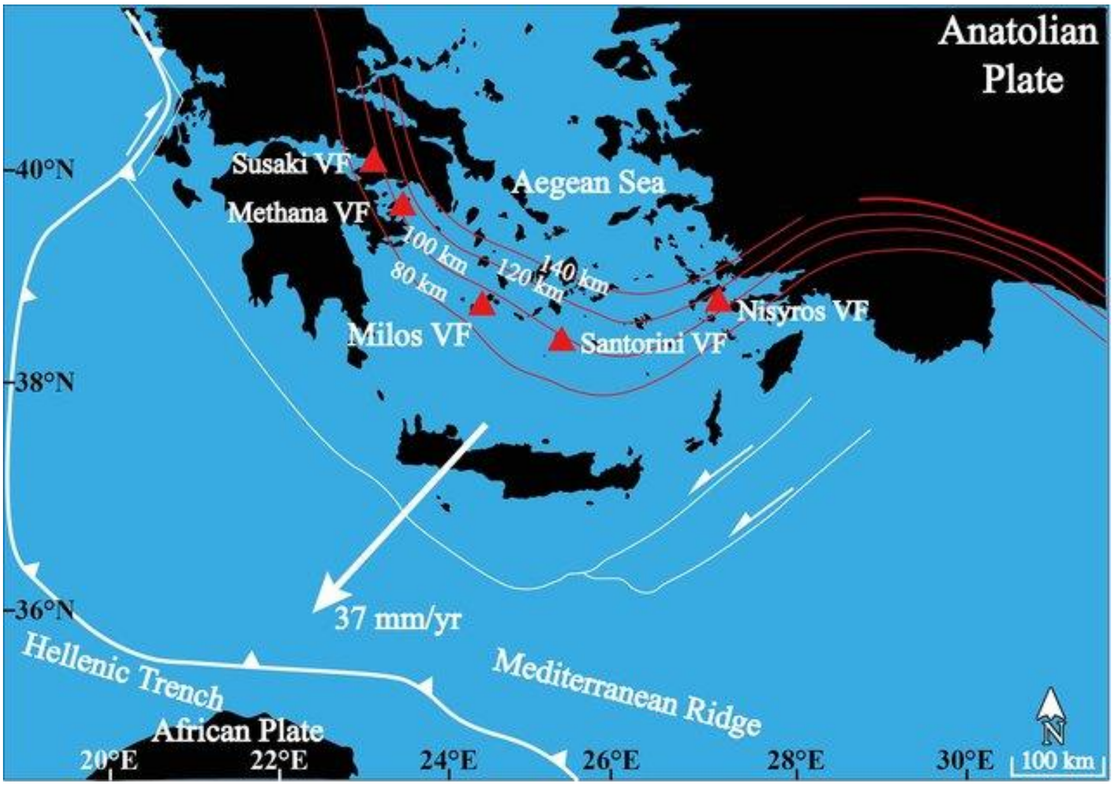

Figure 1(Map of the South Aegean Volcanic Arc (SAVA). Red triangles indicate volcanic fields Zhou, X., Kuiper, K., and Wijbrans, J.R. et.al 2021)

These diverse volcanic formations provide opportunities for scientists, mostly geologists and oceanographers, to investigate various volcanic processes and their effects on the environment, and the coastal areas (van Hinsbergen et al., 2004).

Islands of the South Aegean Volcanic Arc:

The South Aegean Arc includes volcanoes, like Methana, Kos, Milos, Santorini, Nisyros, and Egina. Each has its volcanic history and features, which contribute to the history of the South Aegean Volcanic Arc.

Egina: The island of Egina (Figure 2) is primarily volcanic, with volcanic activity dating back to the Lower Pliocene era. 4.7 and 4.3 million years ago, different volcanic substances were laid down in a shallow underwater environment. The main volcanic activity occurred between 3.9 and 3.0 Ma.[3], forming the central and southern areas of the island with lava domes and flows. Volcanic activity likely declined from 3.0 to 2.1

[3] Ma =Megaannum it is a unit of time equal to 1,000,000 years

million years ago, with the last eruptions happening between 2.1 and 2.0 million years ago. Tectonic lines impact the volcanic characteristics of the island, which contain a hot spring and geothermal reservoirs. The volcanic rocks come in a variety of compositions and geochemical properties, ranging from basaltic andesites to dacites. (Francalanci, L. et.al, 2005)

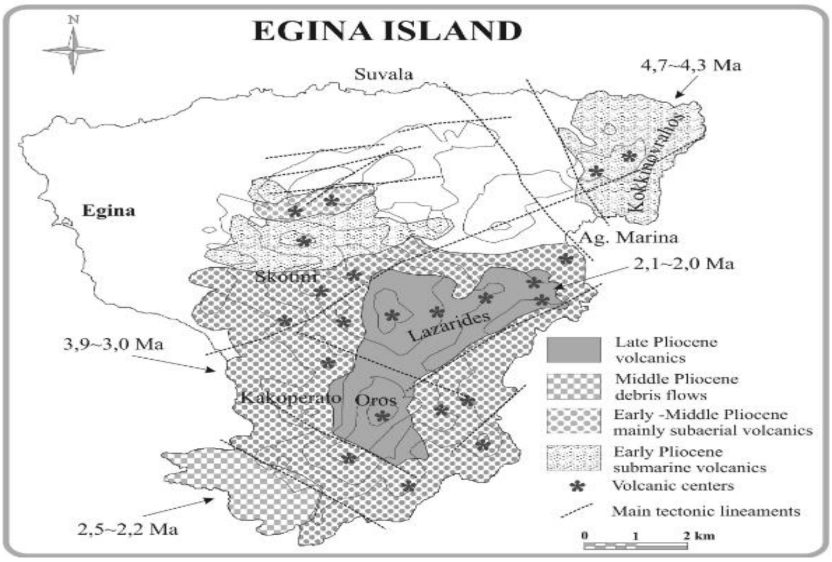

Figure 2 (Egina Island geological sketch map, Francalanci, L., Vougioukalakis, et.al 2005)

Milos: Known for its unique landscapes (Figure 3), sulfur mines, and geothermal fields, it is the westernmost volcanic island in the Arc. The Milos Island Group does not have a main volcano, but Antimilos stands out as a composite volcano with lava domes and flows. Milos, Kimolos, and Polyegos are composite volcanoes with lava domes and layers of volcanic material. The most ancient rocks found on Milos are approximately 3.5 million years old. Between 3.5 and 1.6 million years ago, the islands were formed due to volcanic activity, including notable rhyolitic eruptions during the Quaternary period (Francalanci et al., 2005)

The region experiences frequent geothermal activity and earthquakes, resulting in hydrothermal explosions and debris flows. The majority of the rocks are andesites and dacites, each with different potassium and Strontium isotope ratios (Francalanci et al., 2005)

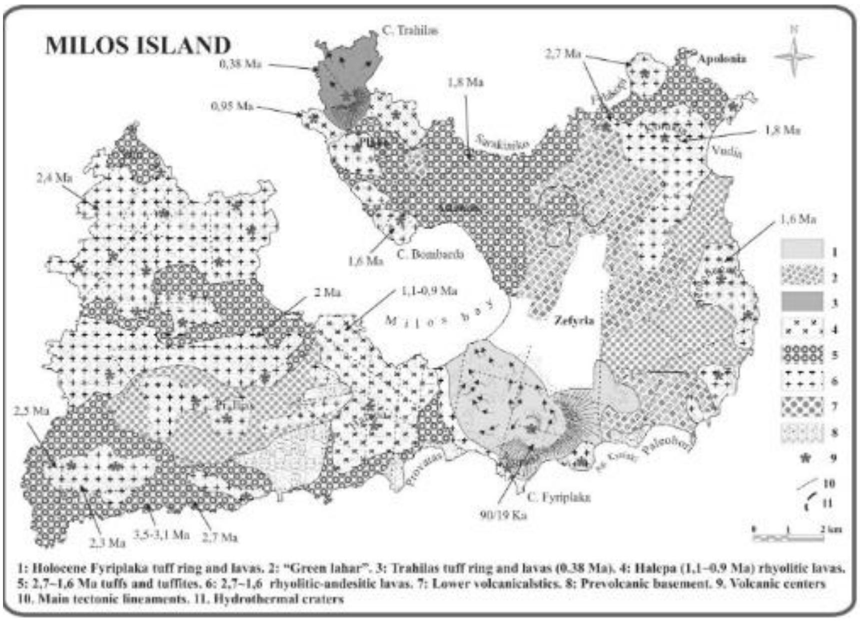

Figure 3(Milos Island geological sketch, Francalanci, L., Vougioukalakis et.al 2005)

Santorini (Thera): The most famous and active volcano of the Arc, the Santorini volcanic field (Figure 4) is located at the center of SAVA (South Aegean Volcanic Arc). It includes Santorini Island, the Christiana islets, and the Kolumbo underwater volcano. Santorini has experienced multiple explosive eruptions, and caldera collapses throughout its volcanic history, with the most recent significant event being the Minoan eruption around 3,600 years ago.

The volcanic process includes various phases and produces a variety of volcanic materials, from basalt to rhyolite (Francalanci et al.,2005). This varied volcanic record

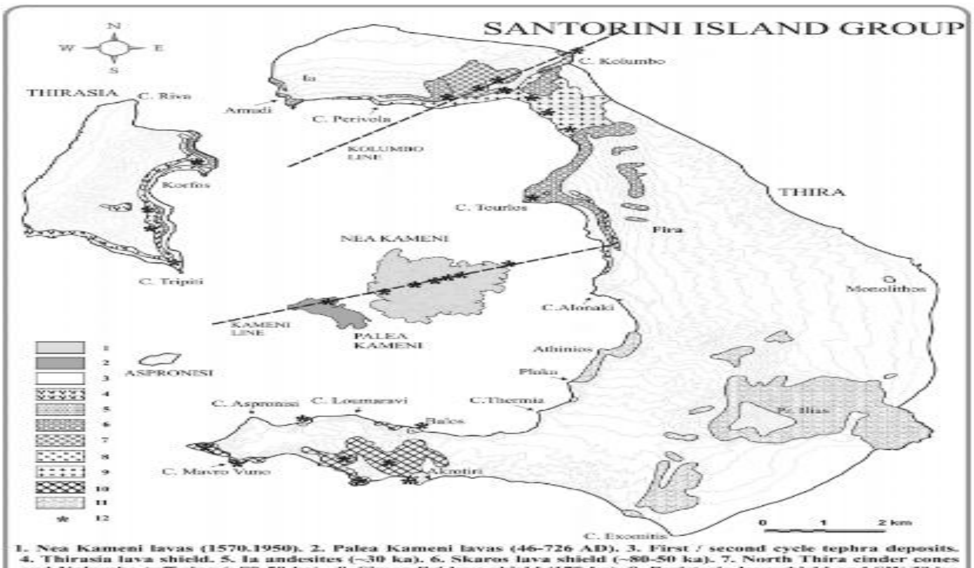

Figure 4 (Santorini Island group geological sketch map, Francalanci, L., Vougioukalakis et.al 2005)

demonstrates the dynamic and intricate characteristics of the Santorini volcanic field.

Nisyros: Nisyros Island (Figure 5), a small (42 km²) young composite volcano, features a central caldera and a condensed cone shape. Located in the eastern part of the Arc, this island has a large caldera formed by explosive eruptions. Radiometric dating suggests Nisyros emerged in the last 160,000 years, though some age estimates remain inconsistent.

Recent activity includes hydrothermal explosions and a high-enthalpy geothermal field, with ongoing seismic activity influencing the island's faults. The island's volcanic rocks range from basaltic andesites to rhyolites. Chemical analyses show a range of TiO_2[4] contents and trace elements, with distinct trends in post-caldera domes (Francalanci et al., 2005)

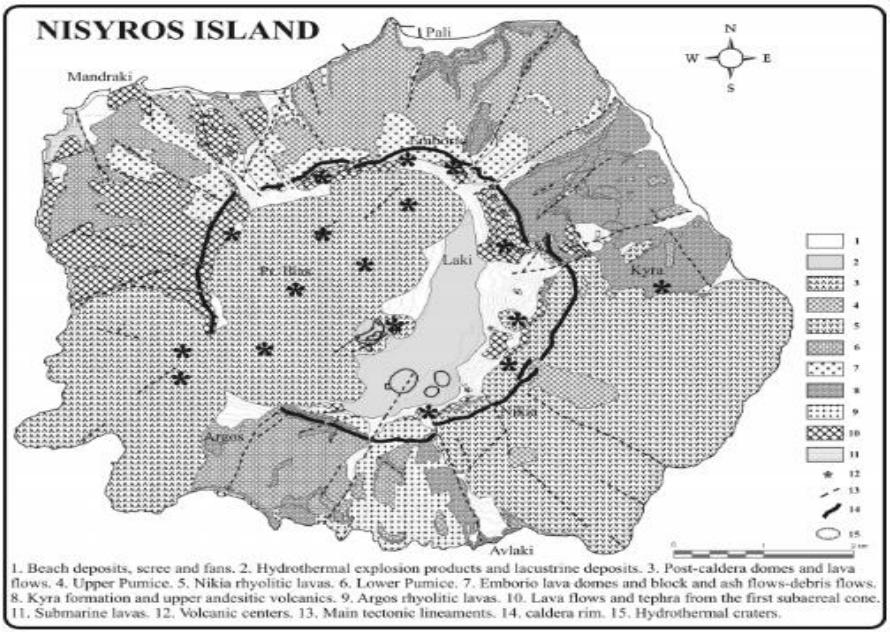

Figure 5(Nisyros island geological sketch map, Francalanci, L., Vougioukalakis et.al 2005)

Methana: Situated at the western end of the Arc, (Figure 6) it is characterized by its numerous volcanic domes, geothermal springs, and an important volcanic history. In addition, it serves a crucial role in geological studies, sampling, exploring, and learning about its geothermal springs. The reason is that the geothermal systems of the

[4] Titanium dioxide, or titania, is an inorganic compound made from titanium.

area are important to understanding the geothermal activity linked to the area's volcanic eruptions. They provide important data on geochemical compositions, helping scientists in understanding the connection between the magmatic system and the surrounding environment, such as groundwater and hydrothermal systems. Furthermore, it has the youngest volcanic products in the Saronikos Gulf area, with the oldest dated at 0.9 million years old (Francalanci et al., 2005).

The latest significant event was the formation of the Kameno Vuno dome around 230 BC. The volcanic features include lava domes, flows, and debris flows. The activity appears to have been continuous but at a low rate (Francalanci et al., 2005). The submarine volcanics nearby are about one million years old. The rocks are mainly andesites and dacites with low potassium content (D'Alessandro et al., 2008)

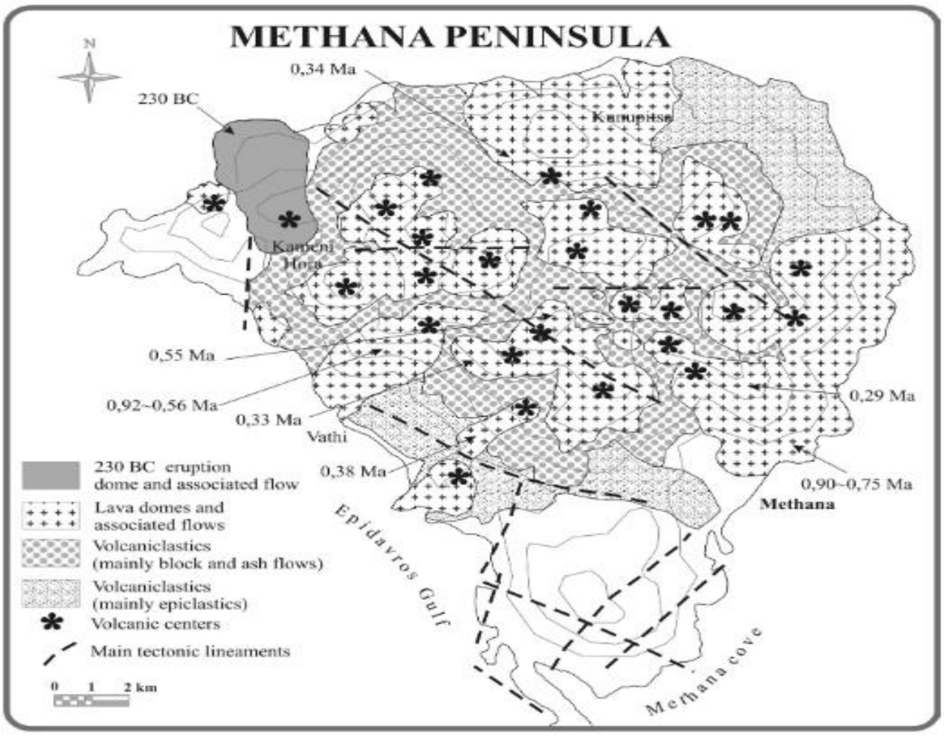

Figure 6(Methana island geological sketch map, Francalanci, L., Vougioukalakis et.al 2005.)

Kos: The island of Kos (Figure 7) is 2/3 covered by volcanic pyroclastic deposits and domes that have resulted from two periods of intense volcanic activity. In both periods the volcanic centers are in the south of the island. The springs are no longer below the sea surface and are covered by marine sediments (Francalanci et al., 2005).

Volcanic activity from the Pliocene (3.4 to 1.6 Ma) in the South Kos area formed dacitic and rhyolitic domes, such as those found on Pyrgussa and Pahia islets, which are now buried under the Kos Plateau Tuff. The largest eruption happened approximately 161 thousand years ago, creating the Kos Plateau Tuff, which covered an area of five thousand square kilometers. Discussions continue regarding the specific location of the vent and the structure of the caldera for this event. The volcanic rocks on Kos vary from rhyolites to K dacites[5] (Francalanci et al., 2005).

The volcanic activity that influenced the geomorphology of Kos and the surrounding islands includes periods of volcanic eruptions where lava, volcanic particles, and pyroclastic materials flooded the areas around active points. Such activities (lava flows, pyroclastic flows, volcanic eruptions) occurred during the formation of the volcanic arc in the region.

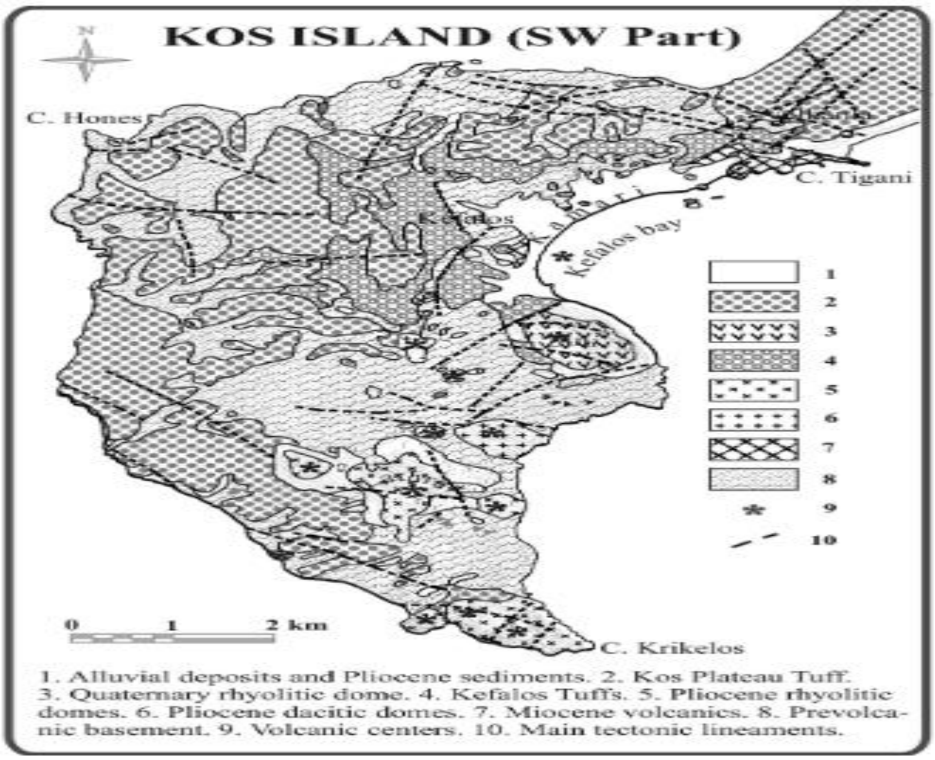

Figure 7 [South Kos geological sketch map, llanci, L., Vougioukalakis et.al 2007)

Tectonic movements in the region have created the curved structure of the volcanic Arc, while active or past volcanic activity has added volcanic rocks to the geological background. These movements continue to affect the distribution of volcanic materials

[5] *High potassium* (K) *Dacites (https://geologybase.com/dacite/)*

and the appearance of the geological landscape. Economic development in the islands has led to environmental problems like erosion, coastal degradation, and water management challenges (Tserkezis et al, 2016 ; Andriotis, 2004).

There are some projects that are being implemented to enhance sustainable tourism (https://www.originaltravel.co.uk/travel-guide/greece/sustainability) and safeguard fragile ecosystems (Hasiotis and Monioudi, 2017). Conservation efforts also aim to protect the islands' natural beauty, such as coastal dunes, wetlands, geothermal springs, and unique plant and animal species.

The four-gulfs and their geodynamic position in the Hellenic Arc:

These four gulfs are four subparallel neotectonic basins with the same NW-SE trend as the Hellenic arc in the segment studied, but each belongs to a different geodynamic area of the Arc. Saronikos Gulf (Figure 9) lies on the volcanic arc within the Pliocene volcanics of Aegina and the Pleistocene volcanics of Methana and Sousaki and allows them to study the plates movement and their impacts over time (Francalanci et al., 2005).

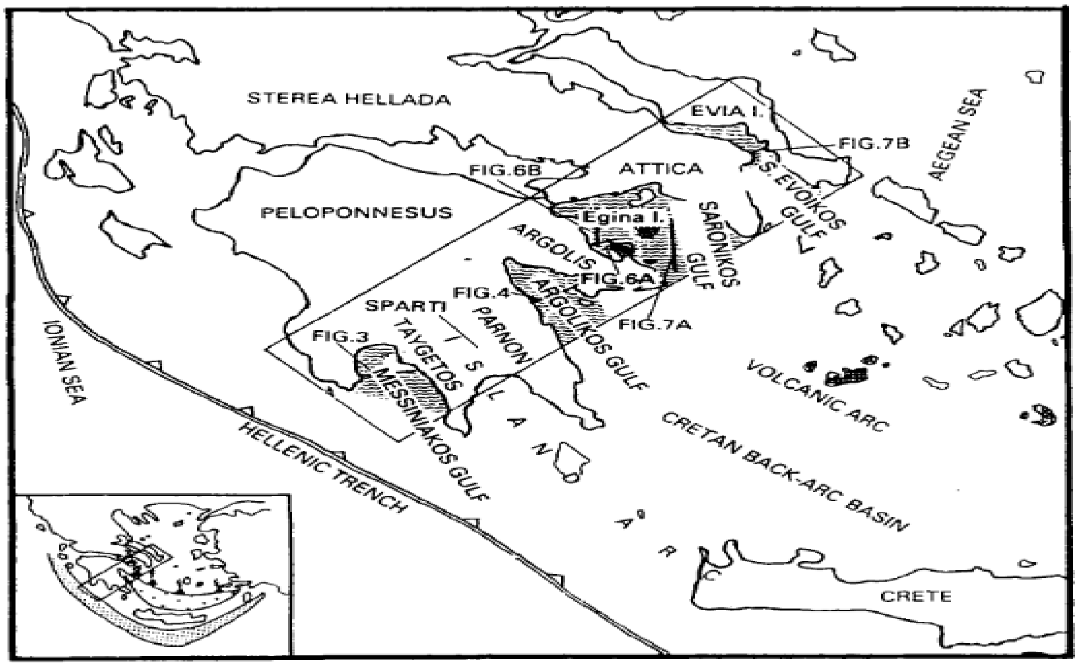

Figure 2(Location of the four studied gulfs and their geodynamic position in the Hellenic arc, Papanikolaou, D., Lykousis, V., et.al 1988)

The western part of the South Aegean Volcanic Arc, including Sousaki, Aegina–Poros–Methana, and Milos, mostly has smaller, single-eruption volcanoes. The central (Santorini) and eastern (Kos–Nisyros) parts of the arc have larger, complex volcanoes with calderas craters[6]. This difference in volcanic morphology indicates varying magma supply and storage conditions along the arc.

Volcanic activity along the arc is linked to fault lines[7]. The volcanic zones run roughly steep to the arc: east-west at Sousaki, east-northeast to west-southwest at Milos, northeast to southwest at Christiana–Santorini–Kolumbo, and northwest to southeast at Kos–Nisyros–Yali. These fault lines play a crucial role in controlling the ascent of magma and the resulting volcanic activity (Vougioukalakis, 2019).

The volcanic rocks of the arc typically consist of andesite, dacite, and rhyolite, with a calc-alkaline composition typical of subduction zone volcanoes (Piper and Piper, 2005). This composition results from the melting of the mantle segment, which is enriched with volatiles (H_2O, CO_2, and sulfur compounds SO_2) and elements such as Potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), are involved in the composition of andesite, dacite, and rhyolite. In addition, the presence of barium (Ba), strontium (Sr), and lead (Pb) reveals how complex the evolution of the Aegean Arc is.

Methana, Milos, and Nisyros are known for their high-temperature geothermal fields (Francalanci et al., 2005). Research has focused on developing these areas for geothermal energy, which is a promising alternative energy source in Greece. The exploration of these geothermal fields could significantly contribute to sustainable energy production (Andritsos et al., 2010)

Figure 3 shows the volcanic arc position at the Aegean plate and the boundaries of the Aegean plate.

[6] A crater is a bowl-shaped depression that emerges on top of a volcano, usually near the central opening from which volcanic substances like lava, ash, and gases are expelled during an eruption.
[7] Faults are the names given to the boundaries between tectonic plates. Phenomena like earthquakes, volcanic eruptions, and the formation of mountains take place along fault lines.

Figure 3(Location map of the Aegean Sea and the surrounding lands. The dashed line indicates the boundaries of the Aegean plate, and the arrows indicate the motion of the plates relative to Eurasia. Kiratzi, A.A., Louvari, E. 2003)

Figure 4 shows all the islands that are part of the South Aegean volcanic arc and its locations on the Greek map.

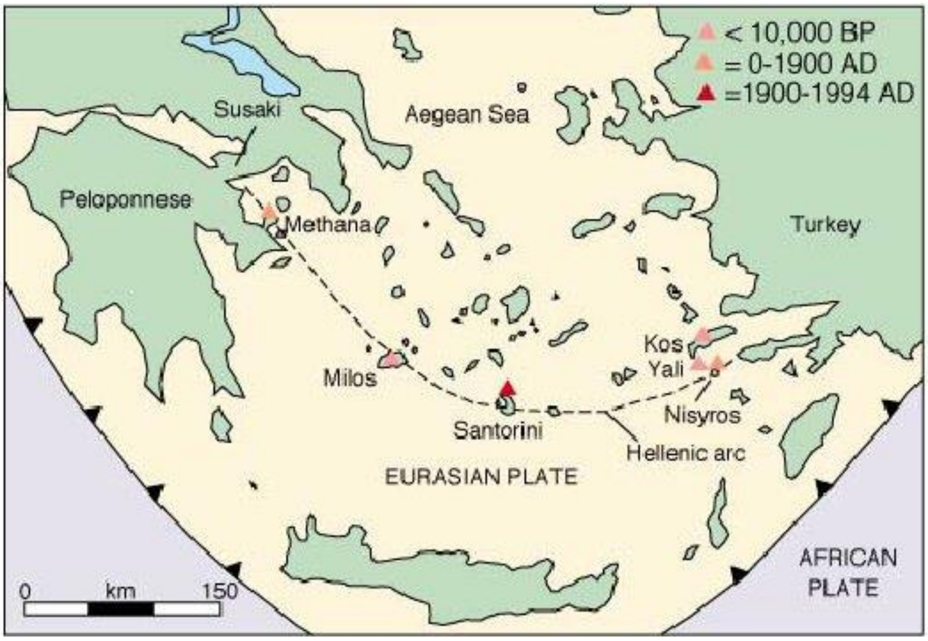

Figure 4(Volcanic centers of the Hellenic Volcanic Arc. Papageorgiou, E., Lagios, , et.al, 2006)

The SAVA[8] in Greece comprises numerous volcanic islands, all highlighting distinct volcanic characteristics influenced by tectonic processes. The volcanic activity on Aegina, Milos, Santorini, Nisyros, Methana, and Kos highlights their dynamic role in the South Aegean Volcanic Arc with geothermal areas, high-temperature fields, caldera

[8] SAVA: South Aegean Volcanic *Arc*

collapses, continuous activity, volcanic domes, and pyroclastic deposits. These islands are important locations for exploring geothermal energy and studying volcanoes due to tectonic forces, subduction processes, and magmatic evolution shaping their arc.

Prioritizing sustainable tourism and ecosystem preservation has become important, ensuring a balance between development and conservation. The South Aegean Volcanic Arc presents significant geothermal potential and dynamic tectonic activity. It also offers insights into subduction zone volcanoes and opportunities for renewable energy, underlining the significance of environmental protection and scientific research in the area.

4. The study:

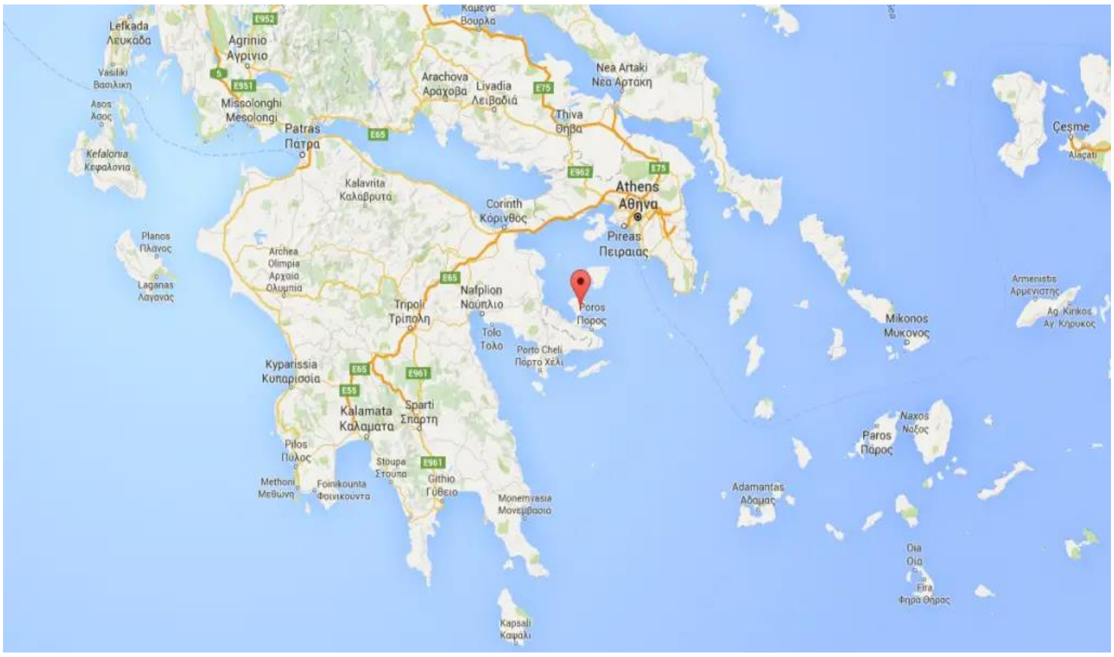

Figure 5(Methana location in Peloponnese penisnsula, https://www.google.gr/maps)

Methana’s additional information:

Known for its volcanic movement and thermal springs, Methana (Figure 5) highlights around thirty volcanic domes, with the most later forming in Kameni Chora within the 3rd century BC. The peninsula is part of the South Aegean Volcanic Arc, which includes other significant volcanic sites like Milos, Santorini, and Nisyros.

Despite its geothermal potential, Methana remains underexplored. The Methana volcano, reaching up to 380 meters, is characterized by basaltic landforms and classified as a magma arch. The volcanic rocks are primarily andesite, basaltic andesite, and dacite. Figure 6 show one of Methana's lava dome.

Figure 6(https://decade.earthchem.org/d/212020)

Methana's peaks, terrain and eruptions

The highest peak on the peninsula reaches 740 meters, surrounded by other peaks of similar height. The Methana Peninsula is characterized by a steep and rugged landscape that is typical of its volcanic origins, with its highest peak reaching 740 meters. The region's active geological past within the South Aegean Volcanic Arc is reflected in this terrain, which has been shaped by intricate tectonic processes.

Methana's terrain and eruptions

The mountainous terrain of the peninsula has been sculpted over millions of years by volcanic eruptions, lava flows, and tectonic shifts, resulting in the creation of numerous volcanic domes and steep slopes. These craggy volcanic landforms that we see today are the result of magmatic activity that pushed molten rock to the surface, creating lava domes, and then cooled. The genesis of these peaks is intimately associated with Methana's location in the SAVA, where ongoing geological activity has resulted from the subduction of the African Plate beneath the Eurasian Plate (Pe-Piper, 2013).

The region's frequent volcanic eruptions not only raised the peaks of Methana but also left behind layers of volcanic rock that now dominate the geology of the peninsula, mostly andesite and dacite. The terrain's durability and steepness are largely due to the erosion-resistant volcanic rock, and the continuous tectonic movements that have created fractures and elevated different parts of the peninsula have further sculpted the landscape.

The coastline is steep, and there is no significant hydrological network, as rainwater tends to seep into cracks in the volcanic soil (https://www.vathi-methana.gr/mobile/en_geografia.html).

Methana is characterized by a semi-arid climate, with mild winters and long dry periods from early May to mid-September. This climate affects both the vegetation and human activities in the area, contributing to its semi-arid environment (Lantzas, 2012)

Methana's Meteorological data:

Temperature:

Because of its proximity to the Aegean Sea, Methana enjoys a semi-arid Mediterranean climate with hot, dry summers and warm, rainy winters. Because of the sea's moderating impact, the temperatures (Figure 7) in winter (December to February) often range from 10°C to 15°C (50°F to 59°F). Frost is rare in this area. As for the summer (June to August), with low humidity, highs can reach 28°C to 34°C (82°F to 93°F). Nights can get cooler, especially when sea breezes and wind come from the south (www.meteoblue.com)

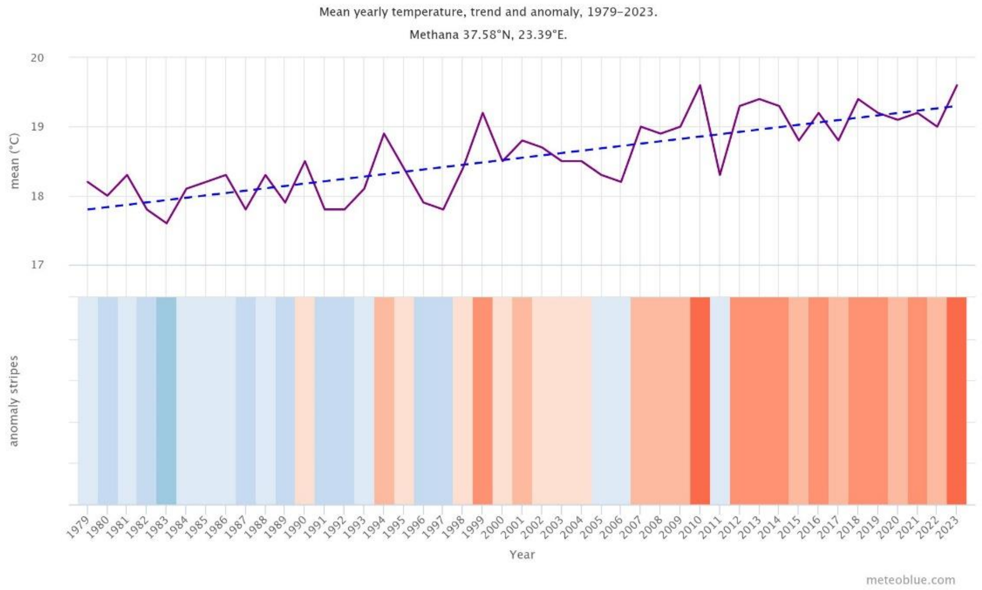

Figure 7(Mean yearly temperature from 1979-2023 for Methana Peninsula, https://www.meteoblue.com/en/climate-change/methana_greece_257126)

Precipitation:

The winter months receive the majority of the year's rainfall, which averages between 400 and 500 mm, though the precise amounts can differ from year to year. Usually, summers are dry, with little to no rain falling between June and August (Figure 8).

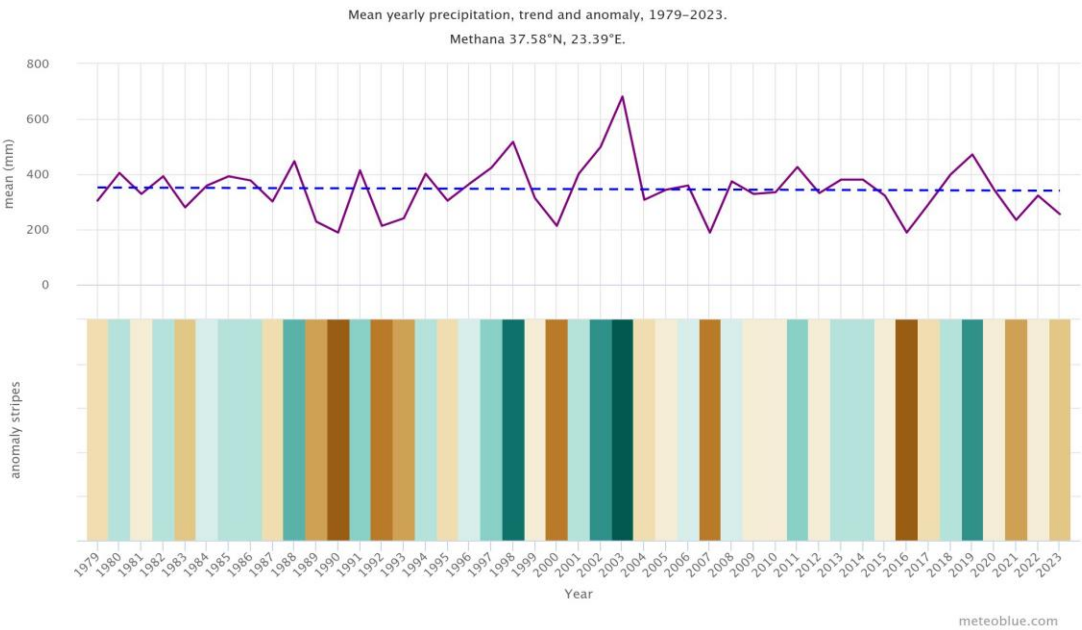

Figure 8(Mean precipitation from 1979-2023 for Methana, https://www.meteoblue.com/en/climate-change/methana_greece_257126)

Wind:

The area is well known for its northern winds, especially the seasonal Meltemi wind, which blows over the Aegean Sea in summer to lower the temperature and bring in colder air.

Figure 9 shows the monthly wind speed for the Methana area. All through each month, the wind speed ordinarily ranges from 10 to 20 km/h, with occasional gusts reaching up to 30 km/h. On less than five days per month, wind speeds surpass 30 km/h or drop below 10 km/h. When combined with the wind direction shown within the following figure, the north and northeast shorelines of Methana are particularly vulnerable to potential climate change impacts.

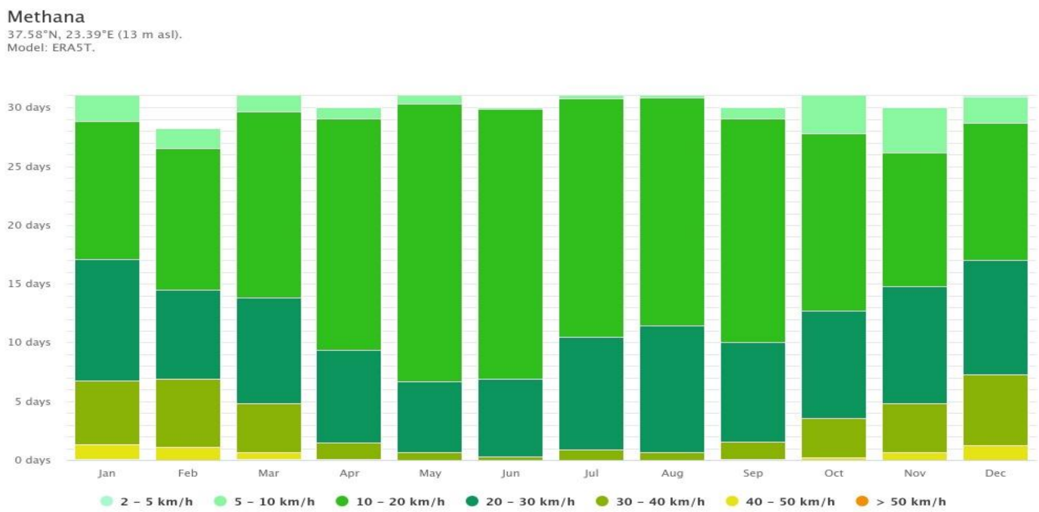

Figure 9(monthly wind speed for Methana, https://www.meteoblue.com/)

Sunny and cloudy days:

In terms of sunny or cloudy days (Figure 10), Methana has a high level of sunshine all year round, with summer days reaching up to 12 or 14 hours. Besides summer period, it is an area that is partly cloudy.

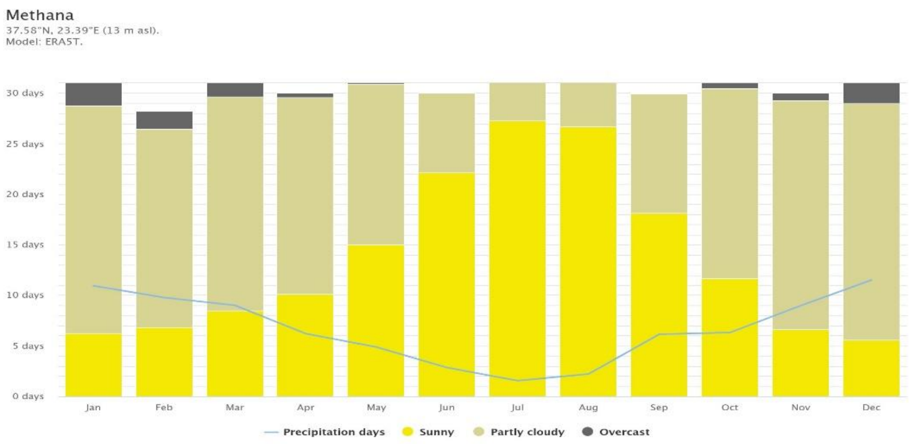

Figure 10(Methana monthly (2023) precipitation, sunny, cloudy days, https://www.meteoblue.com/en/weather/historyclimate/climatemodelled/methana_greece_257126)

Vegetation and Biodiversity:

Low plants, herbs, and shrubs that are typical of the Mediterranean region cover the Methana Peninsula. Olive trees and pine woods are also widely distributed, particularly in remote or less developed places. The varieties of plants and agricultural activities are influenced by the rich in minerals volcanic soil (https://www.topoguide.gr/mountains/peloponnese/advs_methana/methana_vegetation_en.php). However, there is less vegetation in some places because of the arid climate. Methana's volcanic nature is a contributing factor to its geothermal characteristics, which include fumaroles[9] and hot springs.

Water Resources:

Methana lacks a significant network of rivers or streams. Rainwater mostly infiltrates through the cracks in the volcanic rocks, limiting water retention and leading to challenges in agriculture and vegetation growth, as crops and plants struggle with drought conditions. This limited water availability has forced local farmers to rely on alternative water sources, such as rainwater harvesting or groundwater extraction, to sustain agriculture (Dotsika, et al, 2010).

[9] Fumaroles are openings in the ground where hot gases, mostly steam and volcanic gases, escape from beneath the Earth's surface, usually in volcanic areas.

Soil and Land Use:

Volcanic activity has resulted in fertile but rocky soils on Methana, rich in minerals that support the growth of certain crops. The main agricultural practices are olive growing, viticulture, and small-scale farming, as the nutrient-rich soil enhances the quality of olives and grapes, which thrive in these conditions despite the rocky terrain. However, the rugged landscape and limited water retention present challenges for expanding agriculture beyond these resilient crops (https://www.topoguide.gr/mountains/peloponnese/advs_methana/methana_geography_en.php).

Volcanic Activity, seismicity and geological map

The crust in the Methana region is approximately 20 kilometers thick due to extension and magma intrusion, making it a key site for studying the effects of plate tectonics and magma formation (Tzanis et al., 2020). Volcanic activity here, which began in the transition from the Pliocene to Pleistocene, predominantly features volcanic domes composed of andesitic and dacitic lavas. The most recent eruption, forming the Kameno Vouno dome, occurred in the 3rd century BC. Seismic activity in the Saronic Gulf is largely influenced by tectonic structures rather than volcanic movements (Makris et al., 2004).

Geological map of Methana:

The geological map of Methana (Figure 11) and its surrounding areas reveals a diverse range of formations, including volcanic rocks, limestones, carbonates, and faults. These features have been shaped by volcanic eruptions and tectonic activity over millions of years. This diversity makes Methana an ideal natural laboratory for studying various aspects of volcanism and tectonics (Volti, T.K., 1999).

Submarine volcanic activity has also been identified a few kilometers NW offshore of the Kameno Vuno center (Papanikolaou, et.al 1988). The volcanic arrangements are estimated to be around 1.0 million years old, a conclusion based on measuring the thickness of the sedimentary layers that have accumulated on top of them. (Pe-Piper, and Piper, 2005).

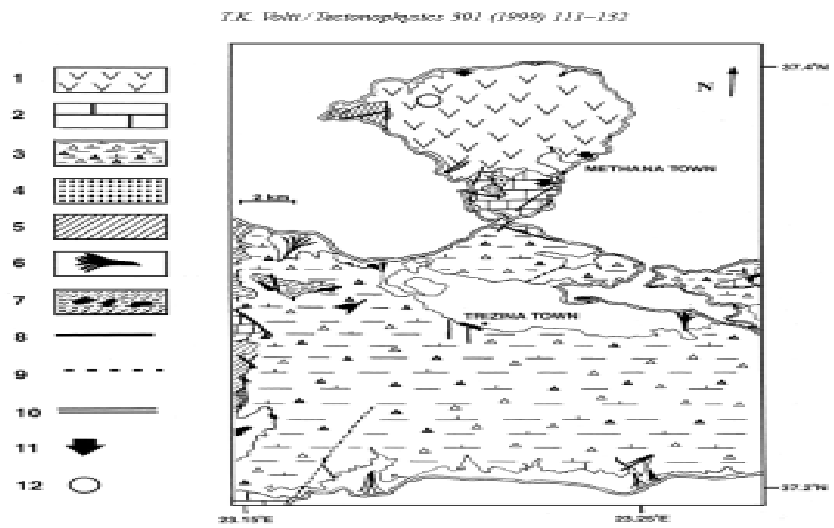

Figure 11 Geological map of Methana and surrounding regions: 1 = volcanics of Quaternary age; 2 = limestones of Cretaceous age; 3 = flysch of Mesozoic–Tertiary age; 4 = conglomerates of Cretaceous age; 5 = carbonates (Pantokrator limestones) of Triassic age; 6 = Quaternary alluvia; 7 D serpentines and ophiolites of Jurassic age within the Mesozoic carbonates and the flysch; 8 = fault; 9 = fault inferred or covered; 10 = coastline; 11 = thermal springs; 12 = location of the most recent eruption , Magnetotelluric measurements on the Methana Peninsula (Greece): Modelling and interpretation, (Volti, T.K. 1999

Hydrothermal Activity:

Methana's volcanic activity has resulted in geothermal springs in three locations on the peninsula. The first, called Loutra Methanon, is situated south of the main settlement. Water rich in hydrogen sulfide emerges from cracks in the white limestone into a small lake connected to the sea. The water temperature varies throughout the year (volcano trails, volcanic hot springs) These springs have been a focal point for both therapeutic and scientific interest, given their unique mineral content and heat source.

Figure 12 shows where we can detect thermal and cold water, volcanic products, sedimentary deposits as well as faults[10] and villages.

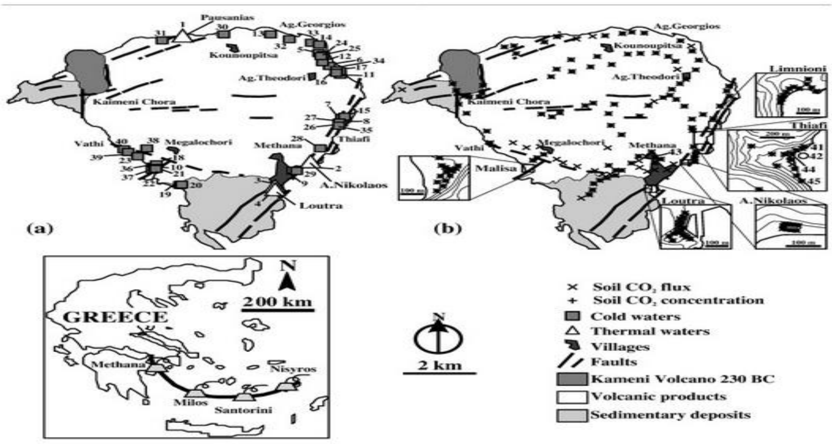

Figure 11 (Geographical location and simplified geological map of Methana, D'AlesMichas, G., et.al,2008)

Figure 13 shows most of the area is covered with volcanic sediments. The eastern and southern parts of Methana include pelagic zone deposits, including limestones and dolomites. In the northern part, meta-sedimentary and late sedimentary rocks are present.

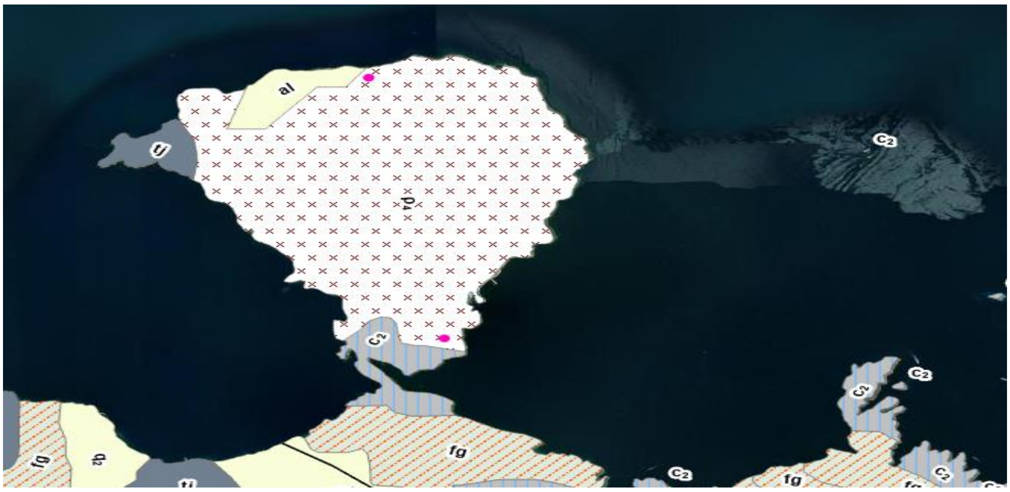

Figure 12(Geological Map by IGME https://gaia.igme.gr/portal/apps/webappviewer/index.html?id=61dc7b67790944a198d4dbdc876d1a3c)

[10] Faults are fractures in the Earth's crust where rocks on opposite sides have shifted relative to each other.

Methana, being the westernmost section of the volcanic arc, is significant for studying volcanic activities within the region. This incorporates analyzing the formation of volcanic rocks, the composition of magma, and the geodynamic conditions of the arc (D'Alessandro et al., 2008). The geothermal areas in Methana, as well as in Milos, Santorini, and Nisyros, are some of the most notable in Greece.

SOM in SAVA and Methana:

Sedimentary Organic Matter (SOM) refers to organic material in sediments that originates from decomposed marine life, terrestrial plants, volcanic ash, and microbial activity (Pedrosa Pàmies et al., 2015). SOM is abundant in coastal and offshore sedimentary layers, such as those in the South Aegean Volcanic Arc and Methana (Karageorgis et al., 2020). It plays a crucial role in understanding the carbon cycle, sediment processes, and hydrocarbon potential (Nierop et al., 2007). In volcanic areas, ash and lava deposition can rapidly preserve SOM by limiting oxidation (Bisson et al., 2023). Additionally, SOM enhances soil quality, aiding plant growth and reestablishment after volcanic eruptions (Paul, Veldkamp, & Flessa, 2008).

5. Fourier-transform Infrared Spectroscopy (FTIR):

Fourier-transformed infrared (FTIR[11]) is the preferred method for mid-IR spectroscopy as it provides quantitative information rapidly and accurately (Ferreira et al., 2022). It is a technique used to identify organic, polymeric, and in some cases, inorganic materials by detecting molecular vibrations and identifying functional groups in samples. This spectrometer obtains an infrared spectrum by collecting the interferogram of a sample signal, which has the infrared frequencies, applies the Fourier transform to the digitalized signal, and outputs the spectrum (Griffiths et al, 2007).

Mid-Infrared Region in FTIR:

Although FTIR analysis may not be suitable for every molecule, most inorganic and organic compounds found in the environment can be detected using infrared

[11] Fourier-transform infrared spectroscopy is a method utilized to acquire an infrared spectrum of absorption or emission from a solid, liquid, or gas.

spectroscopy. The majority of FTIR research in soils and environmental sciences is concentrated on the mid-infrared (MIR) region of light, which spans from around 4000 to 400 cm−1 (Parikh et.al, 2014)

FTIR is widely used to measure absorption in the mid-IR range because many organic and inorganic molecules absorb infrared light within this range. The mid-IR spectrum is the most widely used in the sample analysis, but IR spectra can also contribute to providing information about the samples analyzed. [Nandiyanto, et.al (2019)]

The mid-IR spectrum is divided into four regions (Figure 14):

(i) the single bond region (2500-4000 cm^{-1}),

(ii) the triple bond region (2000-2500 cm^{-1}),

(iii) the double bond region (1500-2000 cm^{-1}), and

(iv) the fingerprint region (400-1500 cm^{-1}).

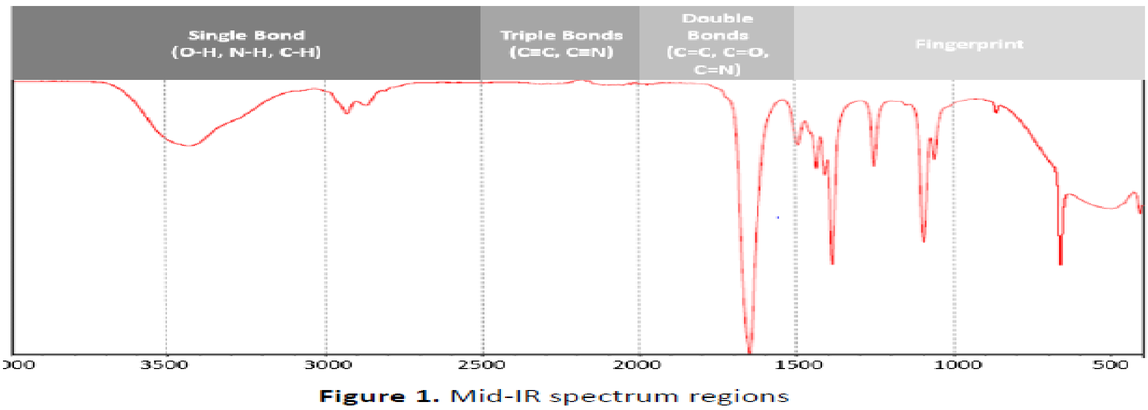

Figure 13(Mid-IR spectrum regions, Nandiyanto, et.al (2019))

Fourier-transformed infrared (FTIR) is the preferred method for mid-IR spectroscopy as it provides quantitative information rapidly and accurately (Ferreira et al., 2022). It is a technique used to identify organic, polymeric, and in some cases, inorganic materials by detecting molecular vibrations and identifying functional groups in samples.

FTIR Mechanism:

The spectrometer obtains an infrared spectrum by collecting the interferogram of a sample signal, which contains the infrared frequencies, applies the Fourier transform to the digitalized signal, and outputs the spectrum (Griffiths et al, 2007). This process allows FTIR to analyze a wide variety of samples.

Applicability of FTIR:

Although FTIR analysis may not be suitable for every molecule, most inorganic and organic compounds found in the environment can be detected using infrared spectroscopy. The majority of FTIR research in soils and environmental sciences is concentrated on the mid-infrared (MIR) region of light, which spans from around 4000 to 400 cm−1 (Parikh et.al, 2014).

Spectral Range and Quality:

FTIR can measure spectra in the range of 4000 to 400 cm^{-1}, with a resolution of approximately 4 cm^{-1}. Some FTIR instruments can also be optimized for other spectral ranges such as near-infrared or far-infrared (Griffiths et al, 2007). FTIR spectra are known for their high quality (Valavanidis, 2006).

Functional Group Detection:

FTIR is effective due to its ability to detect functional groups that change dipole moments and absorb infrared radiation (Maynard & Johnson, 2018). Functional groups such as carbohydrates, lignins, cellulose, fats, and lipids—containing elements like oxygen (O), nitrogen (N), and sulfur (S)—demonstrate high chemical reactivity, such as metal sorption (Maynard & Johnson, 2018). FTIR's ability to detect these functional groups contributes to its widespread use in environmental science and materials analysis.

Positive and negative aspects of FTIR:

There are several benefits to using FTIR. FTIR analysis can find compounds as small as 10 to 20 microns. In many cases, the analysis does not damage or limit the sample. This technique measures absorbance bands across the mid-infrared spectrum simultaneously, allowing a large amount of analytical information to be gathered quickly. The analysis itself can be completed rapidly. Furthermore, FTIR is useful for analyzing a wide variety of organic substances and some inorganic ones. Additionally, wavelength measurements in FTIR are precise, which allows for quick and highly accurate analytical techniques such as spectral subtraction (https://www.innovatechlabs.com/newsroom/672/stuff-works-ftir-analysis/)

Some negative aspects of FTIR are first that the analysis exposes the sample to all mid-infrared frequencies at once and any noise occurring in one part of the infrared source radiation can spread across the spectrum. Changes in atmospheric conditions can affect FTIR results, making it challenging to use extremely sensitive samples or those needing long-term study. Also, it is primarily a bulk analysis method, making it effective for identifying broad categories of substances within a compound but less capable of detecting trace amounts of materials mixed with others (https://www.innovatechlabs.com/newsroom/672/stuff-works-ftir-analysis/).

Applications for FTIR:

Because of its range of applications in examining and characterizing materials at the level of molecules, FTIR is widely used in numerous diverse areas. When combined with meteorological data, FTIR can be used in atmospheric chemistry and environmental studies to provide details about the state of the environment. Its employment too incorporates geography, which is helpful within the examination of rocks, minerals, and silt. FTIR is fundamental for characterizing natural matter, deciding the mineralogy and composition of marine sediments, researching biogeochemical cycles, and surveying the chemistry of marine silt in coastal and marine situations. In expansion, overwhelming metal and poison examinations, as well as the assessment of the impacts of volcanic movement on marine sediments, are performed with it (Ghebleh G. et al., 2021)

Regions, stretch types and elements of FTIR table:

Figure 15 shows the regions (fingerprint and analytical), the stretch types (hydrogen, triple bond, double bond, and single bond stretches), and the elements (C, H, N, O, etc.).

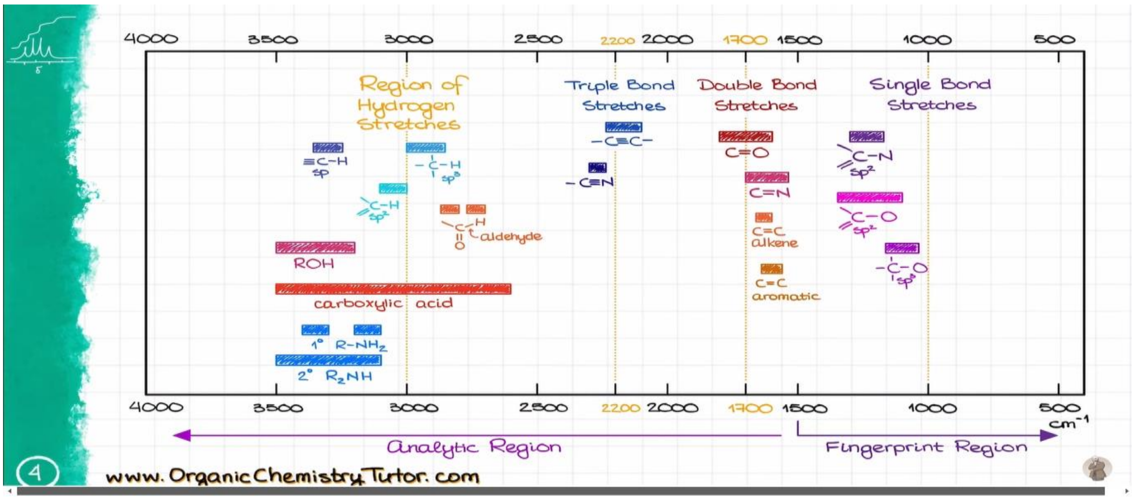

Figure 14(FTIR Table, www.organicChemistrytutor.com)

FTIR Instrument:

The one that will be used is the Perkin Elmer Spectrum Two Fourier Transform Infrared (FTIR) Spectrophotometer (Figure 16). The accessory comes with a flat ZnSe crystal top plate, making it easy to sample powder solids (Sakellariadou et al, 2018).

Figure 15(Perkin Elmer Spectrum Two Fourier Transform Infrared (FTIR) spectrophotometer)

Analysis process on FTIR:

The sample analysis process on FTIR is the following as its being described from Figure 17. The FTIR analysis process involves several steps: first, infrared energy is emitted from a black-body source and passes through an aperture. The beam then enters the interferometer for spectral encoding, producing an interferogram. Next, the beam interacts with the sample, where specific frequencies are absorbed based on its characteristics. The resulting signal is measured by a specialized detector before being digitized and sent to a computer for Fourier transformation, ultimately producing the infrared spectrum for interpretation.

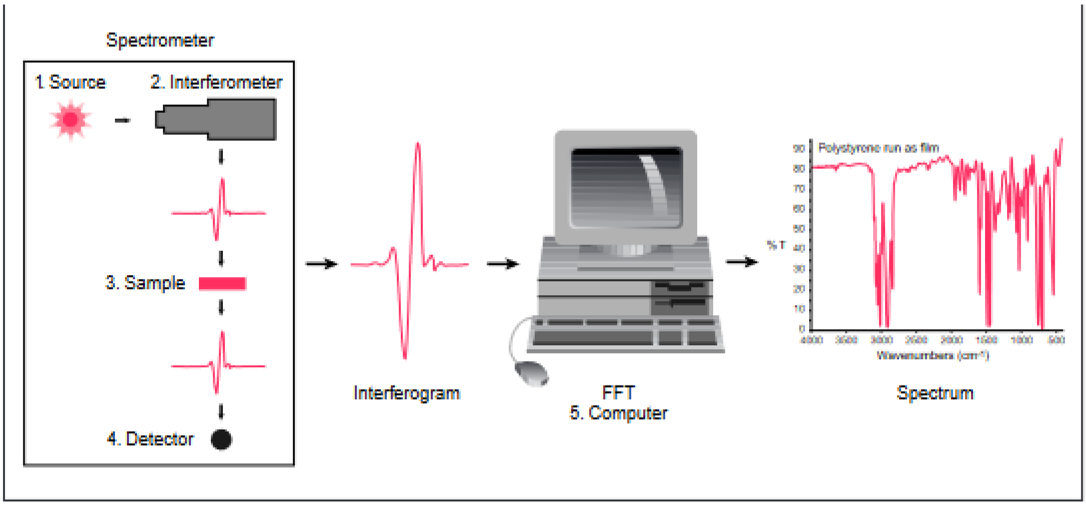

Figure 16(FTIR Sample analysis process, https://www.chem.uci.edu/~dmitryf/manuals/Fundamentals/FTIR%20principles.pdf)

6. Methods

Process:

Marine sediment samples were collected from Methana, specifically samples M1 and M2 (Figure 18). Initially, each sample was weighed using an analytical balance to ensure accurate measurements. Following this, the samples were dried to remove moisture, which could interfere with infrared analysis. The dried samples were then finely ground using a mortar and pestle, turning them into powder. This preparation was crucial for ensuring consistent FTIR (Fourier Transform Infrared) analysis, as it minimizes moisture and large particles that can affect IR light transmission. Finally, the FTIR spectrometer detected the IR spectra, providing peaks and results for each sample.

METHANA	**SAMPLE M1**	**SAMPLE M2**
WET	16812 +- 0,001 gr	16331 +- 0,001 gr
DRY	11273 +- 0,001 gr	10357+- 0,001 gr

Figure 17(Samples weight before and after)

FTIR Spectra Collection:

M1 spectra:

In the figure 19 we have the spectra of M1. The forge gauge was 87 and the observed peaks are 574 cm⁻¹ (98.8% T) a sharp signal with weak intensity, 785 cm⁻¹ (98.7% T) a sharp signal with medium intensity and 1010 cm⁻¹ (92.8% T) a broad signal (U shape) with strong intensity.

All peaks belong at the fingerprint region (1450 - 500 cm⁻¹).

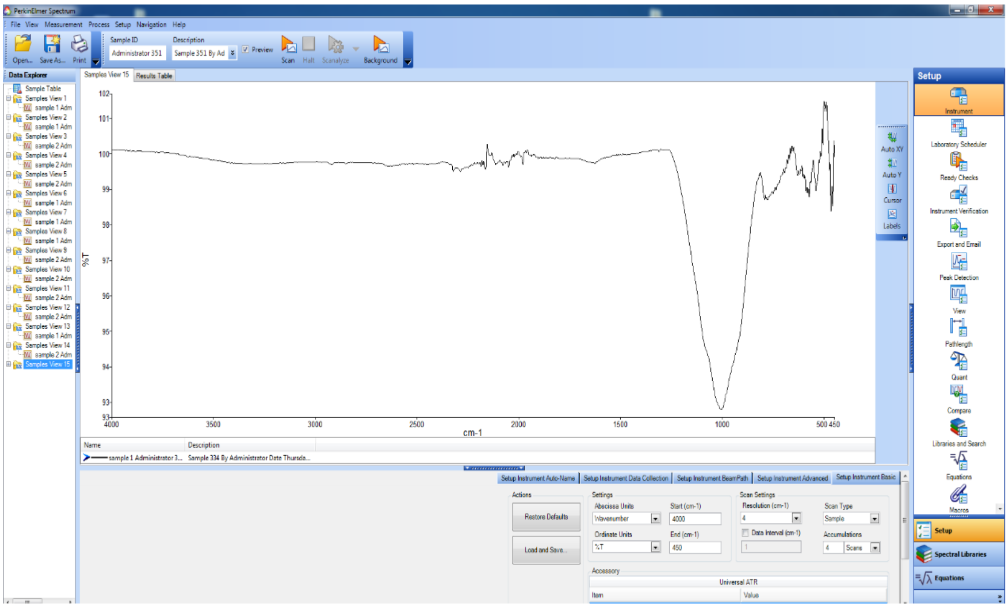

Figure 18(M1 spectra in FTIR)

M2 spectra:

Figure 20 shows the spectra of M2. The forge gauge was 86 and the observed peaks are 576 cm⁻¹ (98.7% T) a sharp signal with weak intensity, 792 cm⁻¹ (97.8% T) a broad signal with medium intensity, 870 cm⁻¹ (91.4% T) a sharp signal with strong intensity, 1020 cm⁻¹ (89.3% T) a broad signal with strong intensity and 1415 cm⁻¹ (91.4% T) a sharp signal with strong intensity. All peaks are also within the fingerprint region (1450 - 500 cm⁻¹). The transmittance values indicate that a small percentage of the photons are absorbed by the sample at each frequency.

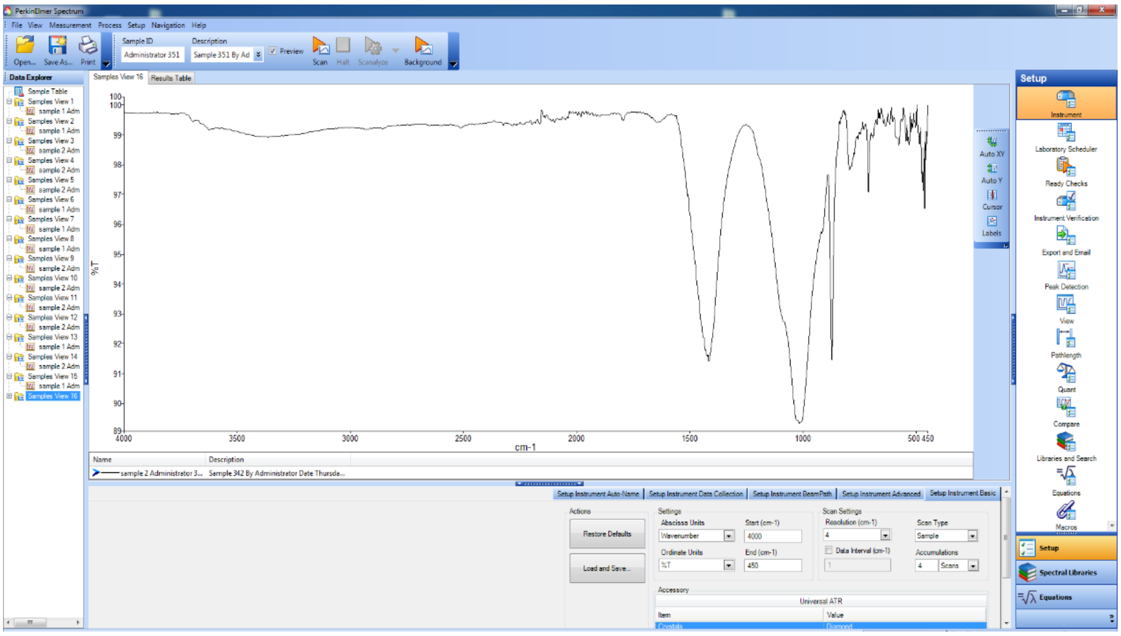

Figure 19(M2 spectra in FTIR)

7. Results and Interpretation of Spectra:

Sample M1 (Figure 25) reveals three notable peaks, indicating key chemical bonds. The strong and narrow peak at 574 cm^{-1} (98.8% T) suggests the presence of C-Br linkages (Bellamy, 1975; Nandiyanto et al., 2019). A moderate peak at 785 cm^{-1} (98.7% T) is associated with aromatic C-H out-of-plane bending (Coates, 2000; Bellamy, 1975), pointing to the presence of aromatic structures. Additionally, the broad peak at 1010 cm^{-1} (92.8% T) corresponds to C-O bonds found in alcohols or carbohydrates (Bellamy, 1975; Coates, 2000). These peaks highlight the presence of halogenated, aromatic, and oxygen-containing compounds in sample M1.

Sample M2 (Figure 26) displays five distinct peaks, indicating various chemical bonds. The strong peak at 576 cm^{-1} (98.7% T) suggests the presence of C-Br bonds (Bellamy, 1975). A peak at 792 cm^{-1} (97.8% T) correlates with C-H out-of-plane bending in benzene rings (Bellamy, 1975; Nandiyanto et al., 2019), while the distinct peak at 870 cm^{-1} (91.4% T) is linked to aromatic C–H bending vibrations (Bellamy, 1975; Coates, 2000). The wide peak at 1020 cm^{-1} (89.3% T) is associated with C-O stretching vibrations commonly found in alcohols and phenols (Bellamy, 1975). Finally, the sharp peak at 1415 cm^{-1} (91.4% T) indicates C-H bending vibrations in alkanes, specifically from methyl (CH_3) or methylene (CH_2) groups (Bellamy, 1975; Stevenson & Goh, 1971). These peaks suggest a complex chemical structure in sample M2, including halogenated, aromatic, and oxygen-containing compounds.

8. Conclusions:

The variation in peak intensities and shapes between the two samples suggests differences in their molecular composition, with M2 showing a richer array of peaks due to its higher moisture content. Both samples exhibit similarities in bromine, aromatic, and oxygenated structures, but M2 has more complex aromatic and aliphatic features.

Connection between Methana's volcanic activities and the samples:

The presence of C-Br bonds in both samples (with peaks at around 574-576 cm^{-1}) indicates the presence of halogenated substances, likely introduced by volcanic gases and the erosion of volcanic rocks (Aiuppa et al, 2008 ; Bellamy, 1975).

The peaks at 785 cm^{-1} in M1 and 792 cm^{-1} in M2 point to the presence of aromatic hydrocarbons, which are typically associated with volcanic emissions and the breakdown of organic materials influenced by volcanic activity (Guiñez et al., 2020 ; Nandiyanto et al., 2019).

Furthermore, the C-O bonds detected at 1010 cm^{-1} in M1 and 1020 cm^{-1} in M2 correspond to C-O stretching vibrations, commonly found in alcohols, esters, and carbohydrates, potentially originating from organic material altered by volcanic processes (Von Aulock et al., 2014 ; Coates, 2000). These observations highlight the influence of volcanic activity on the chemical makeup of the sediment samples. These findings suggest a strong connection between Methana's volcanic activities and the composition of its marine sediments.

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