

ABIOTIC METHANE GEOLOGIC SITES ON EARTH AND THE RELATION TO METHANE ON MARS

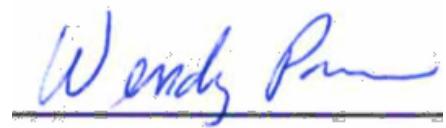
Senior Thesis

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By

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Approved by

A handwritten signature in blue ink, appearing to read "Wendy R. Panero". The signature is fluid and cursive, with "Wendy" and "Panero" being the most distinct parts.

Wendy R. Panero, Advisor
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ABSTRACT

Methane was detected on Mars in 2003 and its discovery sparked renewed interest in potential microbe existence on the red planet. This thesis examines whether the detected methane is likely to be biologically or geologically related. First, since methane is produced through the reduction of carbon molecules, the various biotic and abiotic methods that carbon is reduced are outlined. Biological methods of the production of methane include methanogenesis and metagenesis, while the geological processes involve magmatic and gas-water-rock reactions. Second, two geologic sites on Earth where abiotic methane was discovered are analyzed: Chimaera, Turkey and Orthys, Greece. Both locations have ophiolite outcrops that are conducive to serpentinization reactions. Thirdly, Mars' terrain is analyzed and compared to the geologic sites on Earth to determine similarities. It was found that regions where methane was detected on Mars are comparable to abiotic sites on Earth as they contain ferromagnesian minerals closely associated with serpentinization. Therefore, it is highly probable that the methane detected in Mars' atmosphere is from an abiotic source. However, there is not enough information known to rule out the involvement of microbes on Mars as isotopic classification of methane and noble gasses on Mars have not been determined.

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INTRODUCTION

Discovery of methane (CH_4) on Mars has intrigued the scientific community because methane could be a sign of the existence of biological processes on Mars. Earth and Mars have similar geologic formation processes and methane is rather temporary once released into the atmosphere. Although relatively low in abundance on Earth, methane is a greenhouse gas that traps heat in Earth's atmosphere. It is also the principal constituent of natural gas. Because Earth primarily runs on fossil fuel, hydrocarbons are of great importance. The alteration of organic matter by heat, temperature, pressure, and depth into oil and gas is the most significant importance of methane on Earth. On Mars, however, the presence of methane is substantial as it serves as a potential biomarker.

There are two sources of methane: abiotic and biotic. The biotic sources of methane include methanogenesis and metagenesis. Methanogenesis involves the anaerobic respiration by methanogens. Respiration from organisms account for the bulk of the methane abundance in Earth's atmosphere (Lyu et al., 2018). Metagenesis is the thermogenic degradation of organic matter in sediments and is time, pressure, and temperature dependent. Organic matter buried deep in sedimentary layers is converted into hydrocarbon molecules like methane (Etiope, 2018). The abiotic sources of methane include magmatic process and geologic reactions. Primordial gas preserved in Earth's mantle during its formation contains carbon molecules, high-temperature reactions within Earth's mantle, and the reordering of hydrogen, carbon, and oxygen fluids are magmatic processes that can produce abiotic methane (Etiope and Lollar, 2013). Near the surface, however, geologic reactions include gas-water-rock reactions involving serpentinization and the Fischer-Tropsch Type synthesis of rocks to produce abiotic methane.

Methane emissions from two geologic sites on Earth, Chimaera, Turkey and Orthys, Greece, have been studied to determine its sources of methane. Both locations have ophiolite outcrops that are conducive to serpentinization reactions. Serpentinization is the hydrolysis of ultramafic rocks. Rocks rich in iron and magnesium react with hydrogen molecules and metal minerals that serve as catalysts for the Fischer-Tropsch type reaction to produce abiotic methane (Etiope and Lollar, 2013). Isotopic composition of the gasses emitted are used to categorize the methane from the geologic sites.

The finding of methane on Mars led to theorizing the possibility of life on the red planet as thermogenic degradation of organic matter and organisms' biologic activity is the most prominent source of methane on Earth. Although Mars' atmosphere does have carbon dioxide, nitrogen and argon, the top three molecules that make up Earth's atmosphere, it lacks an ozone and liquid or vapor water. Finding the source of methane can lead to more understanding of Mars. Regions where methane was detected on Mars are comparable to abiotic sites on Earth as they contain ferromagnesian minerals closely associated with serpentinization.

PRODUCTION OF METHANE

Methane (CH_4) is produced abiotically and biologically. On Earth, the biotic formation of methane most commonly involves microbes and is known as methanogenesis. Although abiotic methane formation is not as abundant, its implications are numerous. Carbon must be reduced to produce methane. Reducing carbon requires an input of energy. For carbon to be reduced, catalysts in abiotic and biotic methane productions are used.

Biologic production of Methane

There are two ways biotic methane is produced. One is through the use of microbes, methanogens, and the other is by the organic matter degradation in sediments.

Methanogenesis

Methanogenesis is a biotic method of methane formation. This method involves methanogens which are prokaryotic microorganisms belonging to the phylum division Euryarchaeota in the domain of Archaea, also generally classified as anaerobic bacteria. Methanogens are typically located in environments with water such as freshwater and marine environments, cold sediments and hydrothermal vents (Fenchel et al., 2012). Methanogenesis produces methane as a product of anaerobic respiration of organic matter and accounts for 70% of the methane detected in the atmosphere (Lyu et al., 2018), and thermogenic degradation of organic matter and abiotic production account for the remaining methane detected.

Three methanogenic systems produce methane: hydrogenotrophic, aceticlastic, and methylotrophic. They each involve different types of methanogens. The compound that is broken down in methanogenesis is the substrate. The type of environment in which this occurs dictates the available substrate and which methanogenic pathway is taken. As seen in Figure 1, methanogenesis is a process for the successive reduction of CO_2 .

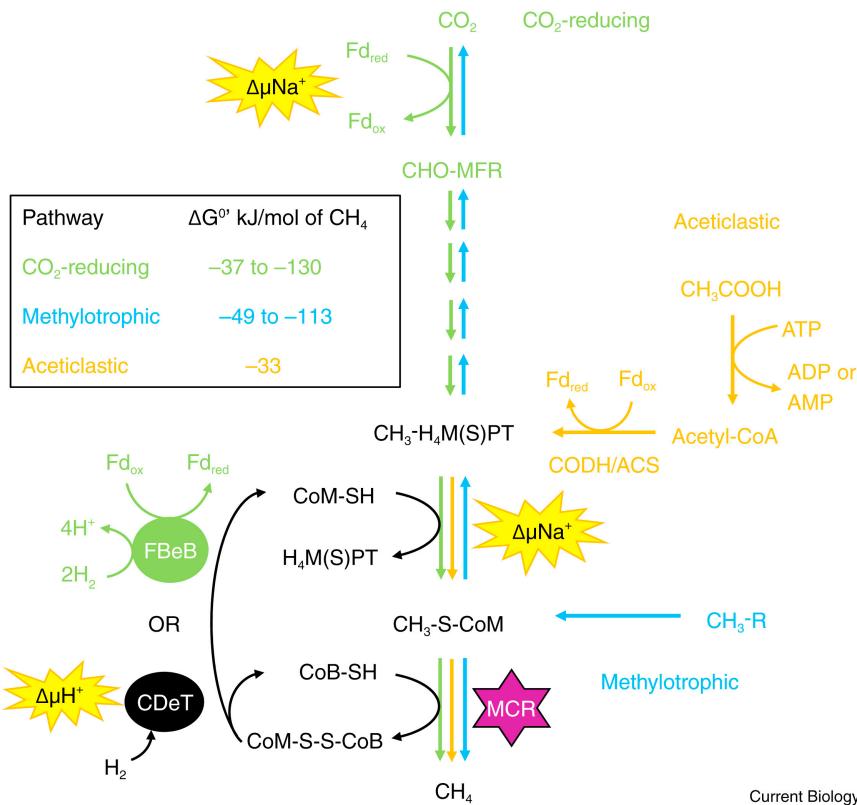


Figure 1. Three pathways of methanogenesis. Image from Lyu et al. 2018.

Hydrogen and carbon dioxide are needed for each of the three pathways. Hydrogenotrophic methanogenesis occurs in hydrogen rich environments. All methanogens consume hydrogen molecule, H_2 , and carbon dioxide, CO_2 , in a redox reaction to produce methane, CH_4 , and water, H_2O . Carbon dioxide is reduced when it loses electrons by losing its oxygen atoms and gains protons when gaining its hydrogen atoms, and the hydrogen molecule is oxidized as it gains an oxygen atom while losing a hydrogen atom in $4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ (Fenchel et al., 2012). This system is shown as the CO_2 reducing pathway in Figure 1.

CO_2 is the most oxidized form of carbon. First, the CO_2 is ligated, creating a larger molecule chain in the reducing pathway to the coenzyme methanofuran (MFR). The hydrogen molecule is responsible for generating reduced cofactors ferredoxin (Fd). The Na^+ Eha/Ehb complex transfers hydrogen molecule electrons to the ferredoxin cofactors and adds to the reduced ferredoxin. Reduced ferredoxin is used to reduce carbon dioxide and ligate it to the coenzyme methanofuran. This then generates the molecule formyl-methanofuran (CHO-MFR), which is one less oxidized state than carbon dioxide. A formyl-transferase removes the formyl group from formyl-methanofuran to add it to the coenzyme tetrahydromethanopterin (H_4MPT). Tetrahydromethanopterin is then cyclized into methenyl-tetrahydromethanopterin. That cyclized reaction is catalyzed by the enzyme tetrahydromethanopterin cyclohydrolase. Electrons are transferred to oxidized ferredoxin, and they reduce methenyl-tetrahydromethanopterin into methylene-tetrahydromethanopterin. The transferring of electrons is displayed in the flavin-based electron bifurcation (FBeB) part of Figure 1. Then the methylene group on methylene-

tetrahydromethanopterin is reduced to a methyl group. Electrons from FBeB, reduced ferredoxin, and the enzyme methylene-tetrahydromethanopterin reductase reduce methylene from methylene-tetrahydromethanopterin to a methyl group creating methyl-tetrahydromethanopterin. Two processes then take place to reduce the bound methyl group. S-methyltransferase enzyme is used to transfer the methyl group to a coenzyme, labeled CoM-SH in Figure 1. As shown, a Na⁺ pump is used for the input energy in transferring the methyl group into making methyl-CoM-SH. Heterodisulfide reductase enzyme and another coenzyme is used, labeled CoB-SH in Figure 1, to separate and reduce methyl-CoM-SH. The sulfur on CoB-SH attacks the sulfur CoM-SH which separates the methyl group. The methyl group then picks up a hydrogen atom and becomes methane. Electrons from ferredoxin reduce the disulfide bridge formed shown in Figure 1 in the Cytochrome-Dependent electron Transfer (CDeT) system as CoM-S-S-CoB into free CoM-SH and free CoB-SH. The standard energy change (ΔG^0) is different for all three methanogenic pathways, but all three aceticlastic, methylotrophic, and CO₂ reducing pathways as shown in Figure 1 share three steps, including the transfer of the methyl group to coenzyme M (CoM-SH), the reduction of methyl-coenzyme M with coenzyme B (CoB-SH), and the recycling of the heterodisulfide CoM-S-S-CoB (Lyu et al., 2018).

Acetate rich environments use aceticlastic methanogens, *Methanosarcinales*, which break acetate, CH₃COOH, into carbon dioxide, CO₂, and methane, CH₄, in an anaerobic respiration; CH₃COOH → CO₂ + CH₄. The degradation of biomass in anaerobic environments such as deep hydrothermal vents and wetlands produce hydrogen molecules, carbon dioxide and acetate (Lyu et al., 2018). Acetate is activated with energy, ATP, in the aceticlastic pathway and coenzyme, Acetyl-CoA is used to break the methyl group. Tetrahydromethanopterin undergoes processes as outlined above in the CO₂ reduction pathway to generate methane.

The third methanogenic system is called methylotrophic methanogenesis, and it involves some acetoclastic Methanosarcinales and Methanomicrobials. In this system, methanol, CH₃OH, or methylamines, CH₃NH₂, act as the substrate in place of acetate to produce methane.

Metagenesis

Thermogenic degradation of organic matter in sediments is another biotic method of producing methane. The consecutive phases of diagenesis, catagenesis, and metagenesis alter the composition of organic matter in sediments (Horsfield and Rulkötter, 1994) and are displayed in Figure 2.

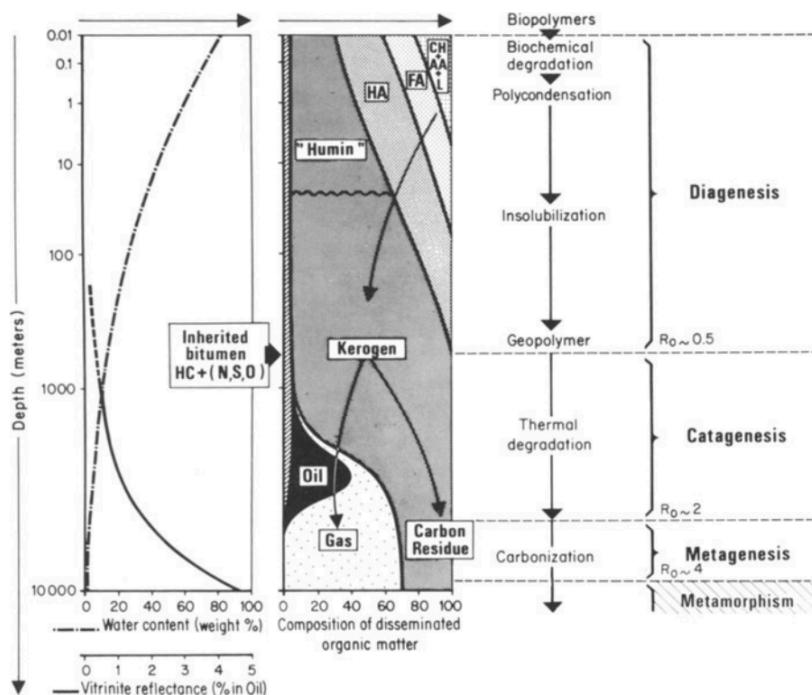


Figure 2. Thermal maturation of organic matter. Image from Tissot and Welte 1978.

The metagenesis phase in the continuum of thermal maturation of hydrocarbons is where natural gas is primarily produced. Methane can make up to almost 90% of natural gas (Etiope, 2018). Metagenesis is time, pressure and temperature dependent. Organic matter buried deep in sedimentary layers is converted into hydrocarbon molecules. Over time, burial depth increases and the organic matter preserved in sediments undergo high temperature and pressure changes. Diagenesis occurs in relatively shallow subsurface. This phase involves the degradation of organic matter, producing water, carbon dioxide and kerogen, a complex hydrocarbon. Catagenesis occurs deeper at increased temperature and pressure. Oil and some gas are formed during this phase. Metagenesis occurs at even higher temperatures and pressures and is where methane is formed.

Abiotic Production of Methane

There are two distinct processes for the abiotic production of methane. One is the magmatic process which includes primordial gas as a source of abiotic methane, high-temperature reactions in the mantle, and the reordering of hydrogen, carbon, and oxygen fluids. The second method of abiotic methane production involves geologic reactions between gas, water, and rock.

Magmatic Process

Primordial gas is thought to have been brought by chondritic, non-metallic, meteorites and preserved in Earth's mantle during its formation, “either the carbon was supplied in comparatively high concentration as hydrocarbon compounds, as in the carbonaceous chondrites...or the carbon was supplied in the form of carbonates, carbides and elemental carbon, as present in many meteorites” (Gold, 1979). Though it is possible primordial gas is a

source of abiotic methane, the amount of primordial methane is most likely negligible (Etiope and Lollar, 2013).

High-temperature reactions within the mantle is another magmatic process of abiotic methane production. One reaction that occurs at high temperatures in the mantle to produce abiotic methane involves the hydrolysis of metal carbides, compounds composed of carbon and metal. An example is the hydrolysis of aluminum carbide reaction: $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 3\text{CH}_4 + 4\text{Al(OH)}_3$ (Etiope and Lollar, 2013). Another reaction occurring at about 1000°C producing abiotic methane is the synthesis reaction of water, iron(II) oxide and calcite to produce methane and byproducts: $8\text{FeO} + \text{CaCO}_3 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}_2\text{O}_3 + \text{CH}_4 + \text{CaO}$ (Etiope and Lollar, 2013).

The last magmatic process of abiotic methane production is the reformation of carbon-oxygen-hydrogen fluids into methane. This process occurs at about 500°C to 600°C and is named late magmatic (Etiope, 2013, p.279). For example, carbon dioxide and water atoms reorder to equilibrate magmatic carbon dioxide: $\text{CO}_2 + 2\text{H}_2\text{O} = \text{CH}_4 + 2\text{O}_2$ (Randall, 1928). This reaction is only possible “for extreme melt compositions that have large crystallization temperature ranges” (Potter and Konnerup-Madsen, 2003).

Geologic Gas-Water-Rock-Reactions

Abiotic methane is also produced as a result of geological reactions of which include: post magmatic high temperature reactions, the metamorphism of carbonate-graphite rocks, the decomposition of iron-carbonate, the methanation of carbonate, the reduction of uncatalyzed aqueous carbon dioxide, and the Fischer-Tropsch Type synthesis (Etiope and Lollar, 2013).

Figure 3 illustrates abiotic and biotic methane presence in geologic environments.

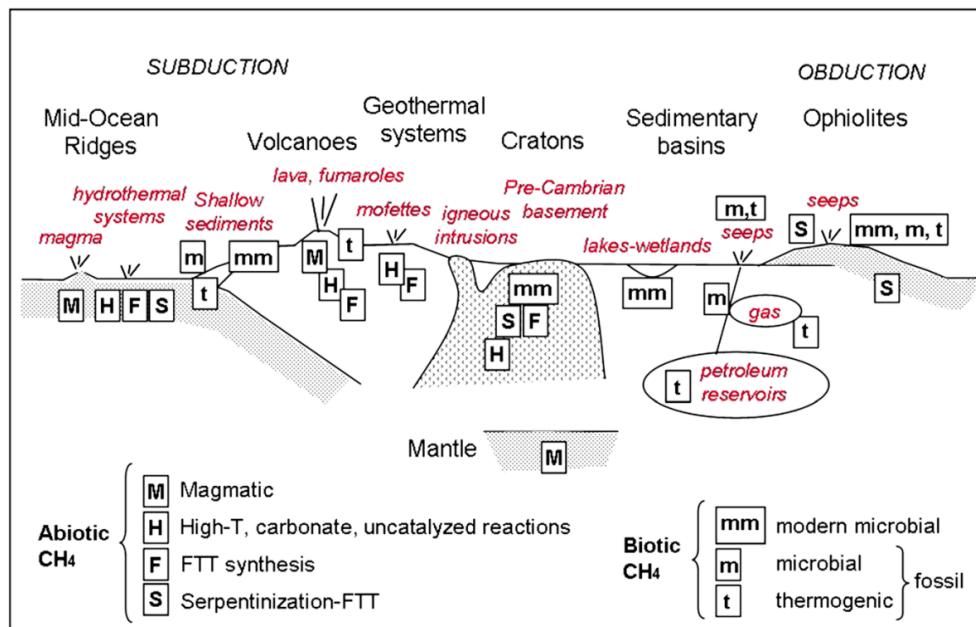
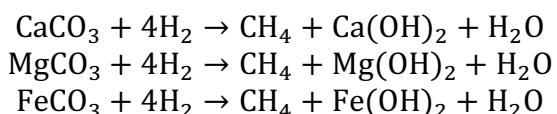


Figure 3. Map of abiotic and biotic methane presence in geologic environments. Image from Etiope and Lollar 2013.

Specific geological environments allow for gas-water-rock chemical reactions to occur and produce methane without the involvement of organic matter (Etiope and Lollar, 2013). These chemical reactions occur in geothermal systems and hydrothermal vents where gas, rock, and water can easily react with each other under a wide range of temperatures. For instance, gas-water-rock chemical reactions occur in environments rich in ultramafic rocks such as in the ophiolites region and where there are igneous intrusions as shown in Figure 3.

Post-magmatic, high-temperature reactions occur at temperatures around 200°C to 500°C and involve carbon dioxide, water, and metal oxides (Etiope and Lollar, 2013). These reactions are the same as the aforementioned high temperature magmatic reactions, but occur after the magma has solidified and after the igneous rocks have formed. Another geologic gas-water-rock reaction that produces abiotic methane is the metamorphism of a talc and carbonates reacting with carbon and water , $Mg_3Si_4O_{10}(OH)_2 + 3CaCO_3 + 6C + 2H_2O \rightarrow 3CaMg(CO_3)_2 + 4SiO_2 + CH_4$ (Etiope and Lollar, 2013). This metamorphic reaction occurs at temperatures below 400°C. Retrograde metamorphism is the recrystallization of a parent rock under cooler conditions.

Carbonate-gas reactions can occur between 250°C to 800°C. In hydrogen molecule-rich environments, carbonates are able to decompose at lower temperatures and the decomposition of carbonates can occur at about 300°C in a reduction reaction to produce abiotic methane (Etiope and Lollar, 2013). The methanation of carbonates such as calcite, magnesite, and siderite react with hydrogen molecules to produce methane and by products.



Serpentinization

Serpentinization and the Fischer-Tropsch type synthesis are the most common methods by which abiotic methane is formed. Serpentinization is the hydrolysis of ultramafic rocks, rocks rich in iron and magnesium, to form serpentine, hydrogen molecules and metal minerals that serve as catalysts for the Fischer-Tropsch type reaction. The hydrolysis of ferromagnesian minerals produces hydrogen molecules and secondary minerals. The molecular hydrogen produced from the serpentinization of minerals like olivine ($(\text{Mg},\text{Fe})_2\text{SiO}_4$) and pyroxenes ($(\text{Mg},\text{Fe})\text{SiO}_3$) is then used to reduce carbon molecules to form methane (Oze, 2012). The Fischer-Tropsch type synthesis requires a catalyst which is typically a product of serpentinization like iron and nickel to reduce carbon molecules to form methane. The serpentinization process occurs in hydrothermal vents and geologic locations where mafic rocks are located like mid-ocean ridges and subduction zones.

Figure 4 is from a water-rock interaction laboratory serpentinization experiment from Oze (2012). It shows that the presence of chromite increased methane production. Chromite (FeCr_2O_4) is a common mineral in serpentinization systems. Chromite and magnetite are minerals used as catalysts in the Fischer-Tropsch synthesis to reduce carbon molecules into methane.

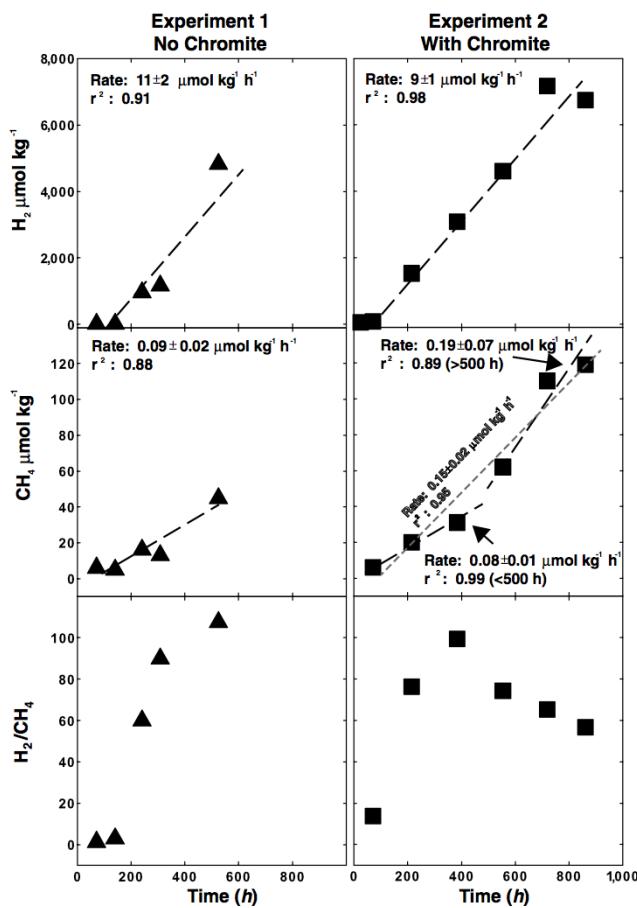


Figure 4. The abundance of H_2 and CH_4 and the H_2/CH_4 ratio in relation to time and presence of chromite. Figure from Oze et al. (2012).

Figure 4 shows that chromite increased the rate of abiotic methane production and the total amount of methane produced. The presence of chromite did not affect hydrogen production as that is due only to serpentinization, not the Fischer-Tropsch synthesis.

Distinguishing Abiotic from Biotic Methane

Methane gas found in most geologic environments is generated from multiple sources and is, therefore, typically a mixture of abiotic and biotic methane. The source of methane is important to many disciplines including petroleum exploration, interpretation of the geochemistry of rocks and the presence or indication of life (Etiope and Lollar, 2013). Isotopic data are used to differentiate between abiotic and biotic methane.

Etiope and Lollar (2013) added noble gas composition to the original Schoell diagram to help distinguish the origin of methane (Figure 5). Schoell's plots of isotopic diagram of carbon-deuterium shows the genetic zoning of methane. Etiope and Lollar's $\delta^{13}\text{C}$ vs $\delta^2\text{H}$ diagram builds on Schoell's original plot by adding isotopic composition of noble gasses. Helium is a primary noble gas used to differentiate between abiotic and biotic methane. The three typical sources of helium are atmospheric, radiogenic-crustal and mantle (Etiope and Lollar, 2013). Regions were categorized based on the correlation of their isotopic compositions associated with the noble gasses (Figure 5).

Methane with higher ^{13}C and ^2H isotopes indicate the methane to be abiotically produced. Since serpentinization systems are found in mafic and ultramafic rocks, mantle sourced helium is present with methane that have high amounts of ^{13}C and ^2H isotopes. The isotope fractionation of the abiotic synthesis of methane produces carbon and hydrogen isotopic values enriched in ^{13}C and ^2H , whereas the biotic synthesis of methane produces methane depleted in ^{13}C and ^2H isotopes as shown later in Figure 6.

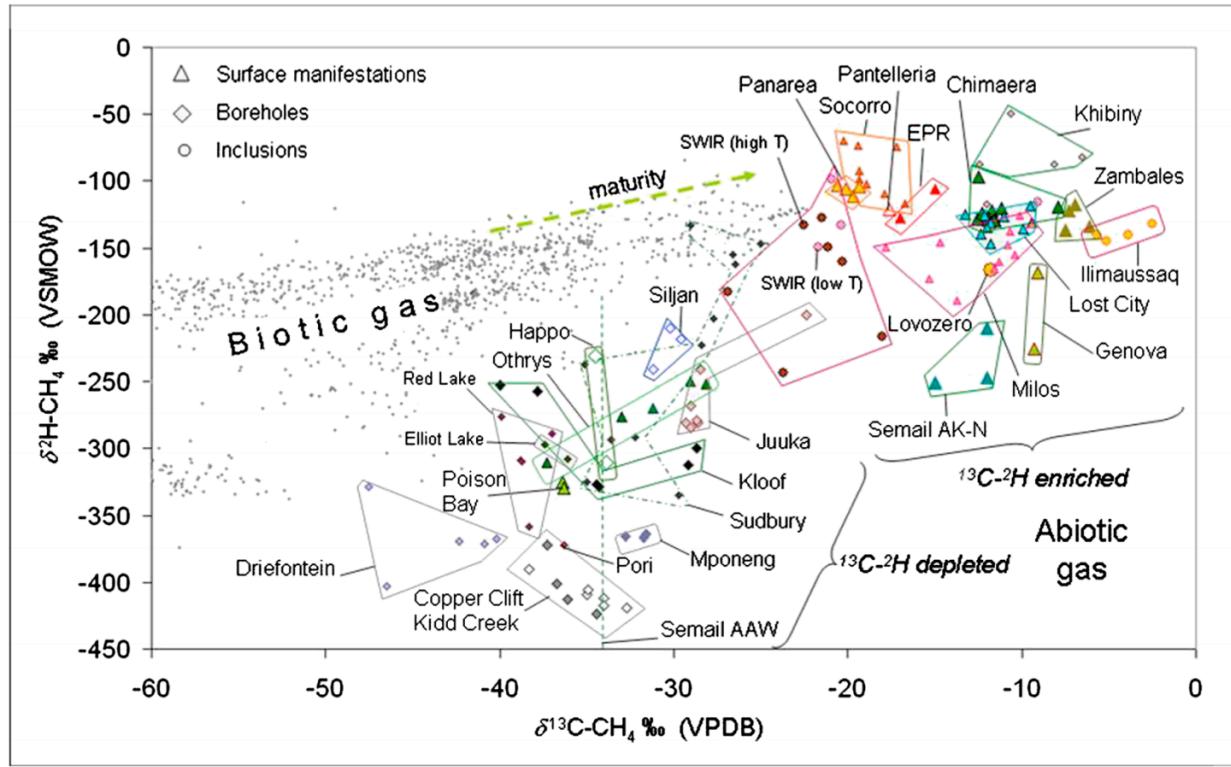


Figure 5. Etiope and Lollar's (2013) $\delta^2\text{H}$ vs $\delta^{13}\text{C}$ diagram showing a relationship between the hydrogen to methane ratio and carbon to methane ratio.

Figure 5 is a plot of where abiotic and biotic gas sites are located on $\delta^2\text{H}$ abundance to $\delta^{13}\text{C}$ graph. Abiotic methane gas is produced in locations with ultramafic rock like Chimaera, Turkey; Genovea, Italy; with hydrothermal fields like the Lost City; and igneous rock like Lovozero, Greenland. On the other hand, locations that are primarily sedimentary are where biotic methane is produced (Etiope and Lollar, 2013). This is expected as serpentinization is more likely to occur in sites with ultramafic rock, whereas sedimentary basins typically have methane produced by the thermogenic degradation of organic matter in sediments or methanogens.

Figure 6 is another $\delta^2\text{H}$ vs $\delta^{13}\text{C}$ diagram showing which type of methane is associated with the ratio of on abundance $\delta^2\text{H}$ to $\delta^{13}\text{C}$.

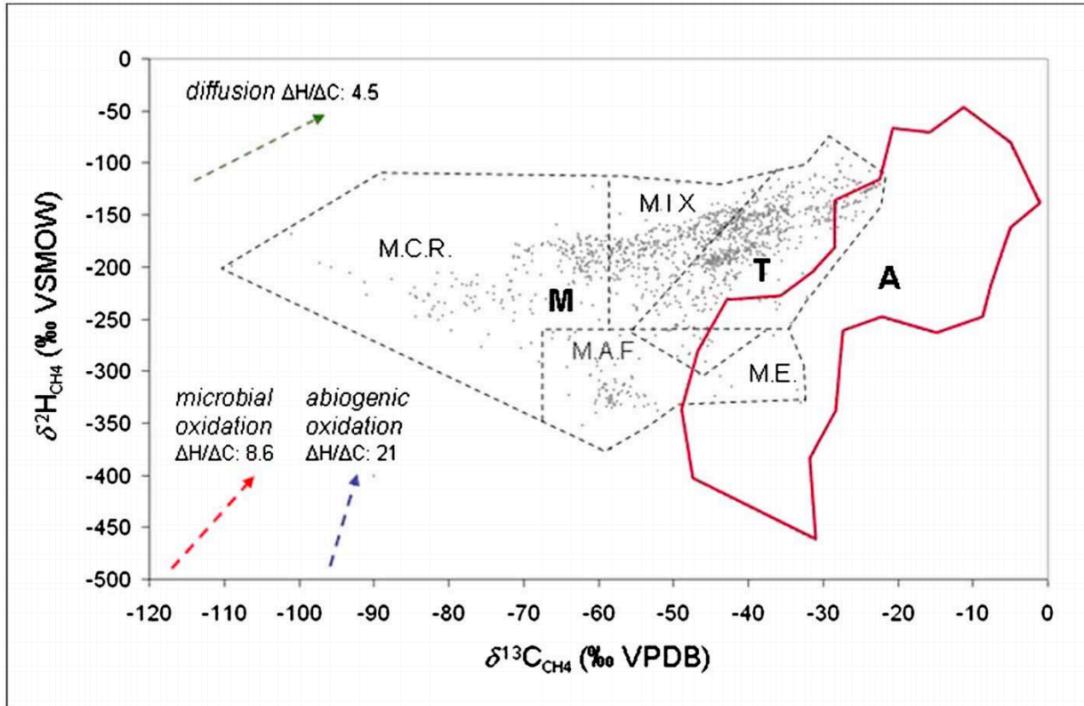


Figure 6. Etiope and Lollar's (2013) diagram of $\delta^2\text{H}$ vs $\delta^{13}\text{C}$ showing a relationship between the hydrogen to methane ratio and carbon to methane ratio. Thermogenic, T, microbial, M, microbial carbonate reduction, M.C.R., microbial acetate fermentation, M.A.F., microbial evaporitic, M.E., and abiotic, A, are segmented on the graph (Etiope and Lollar, 2013).

Figure 6 shows at what percentage carbon and hydrogen methane production processes occur. It was found that less than 40% of the $\delta^{13}\text{C}$ isotope is present in abiotic methane.

Another method to differentiate abiotic methane from biotic methane is from the hydrogen to carbon present ratio. Rates of hydrogen and methane production were modeled to show a relationship between the H_2/CH_4 ratio and the type of methane production. Low H_2/CH_4 ratio suggest that the type of methane production was biotic and high H_2/CH_4 ratios suggest methane was produced through processes of serpentinization (Oze et al., 2012). Because serpentinization results in the production of H_2 , a higher amount of hydrogen molecules is expected to be present where abiotic methane is found, whereas, in the biotic production of methane, microbes through a process of methanogenesis convert molecules such as acetate and methanol into methane without producing hydrogen molecules. Therefore, a higher H_2/CH_4 ratio suggests serpentinization as the source of methane.

GEOLOGIC SITES OF ABIOTIC METHANE ON EARTH

There are very few locations of abiotic methane emissions on Earth. Abiotic methane is more likely to be present at locations conducive to serpentinization. As reviewed in the abiotic methane section, hydrogen molecules are products of serpentinization. The H₂ molecules are then able to react with carbon dioxide in the Fischer-Tropsch type synthesis to form complex hydrocarbons. Serpentinization occurs in ophiolitic rocks.

Ophiolites directly translated is snake stone in Greek. Ophiolite rocks are mafic and ultramafic rocks from the oceanic crust that have been thrust onto continental rocks. Ophiolites are found at orogenic belts. The Hellenic Orogeny took place in the late Mesozoic Era, Jurassic period, and it transformed present Greece and Turkey's geology. Ophiolites are found on the central-west coast of Turkey and central-east coast Greece. Basalt, gabbro, and peridotite primarily make up ophiolites, and they are serpentinized to produce abiotic methane in water-gas-rock reactions.

The oxidation of Fe²⁺ in magnesium-rich and forsteritic produces magnetite and hydrogen molecules. The diatomic hydrogen is then used in a Fischer-Tropsh type synthesis to react with carbon dioxide to produce methane, and the magnetite is used as a catalyst. The Fischer-Tropsh type synthesis usually occurs at high pressures and temperatures; however, with the use of catalysts, the reaction can occur at low temperatures even below room temperature.

Chimaera, Turkey

The Chimaera seep, also known as Yanartaş, “flaming rock” is located by Çıralı, a village near Olimpos, Turkey. It is notable for the burning fires on the rocky mountainside. Figure 7 shows an image of flames erupting due to the gas seepage. The temple of the Greek god of fire, Hephaestus, is located by the site and the name of the region, Chimaera, is a reference to a hybrid beast who breathed fire in Greek mythology. Flames in Chimaera have been documented “back to at least two millennia” (Etiope et al., 2011).



Figure 7. Flames in Chimaera, Turkey. Image from Independent 2019.

Within the ophiolitic outcrop, “gas is emitted from at least 50 main vents from fractures” (Etiope et al., 2011). The continuously gas emitted produces the famous burning flames like the one in Figure 7.

The Chimaera seep is located in a large ophiolite outcrop in Çirali, Turkey. Abiotic methane is emitted annually from the Chimaera seep. The Fischer-Tropsch type synthesis reaction occurs at the Chimaera seep to produce the gas seepage. Tekirova ophiolites are rich in chromite. Chromite is also a source of catalyst for the Fischer-Tropsch type synthesis. As displayed earlier, Figure 4 shows the rate at which chromite increases methane production.

The map below shows the lithology of the Antalya complex. It was formed from the Mesozoic Beydağları Carbonate Platform during the Late Cretaceous (Parlak, 2016). The Tekirova ophiolites are thought to be formed due to the tectonic forearc stresses (Bağcı and Parlak, 2009). The Antalya complex is primarily made of sedimentary rock, sandstone, conglomerates and limestone, and igneous rock, ophiolites and basaltic pillow lavas. Chimaera seep lies on the fault marked in Figure 8 and is adjacent to the Tekirova ophiolite outcrop and Tekedağ limestones.

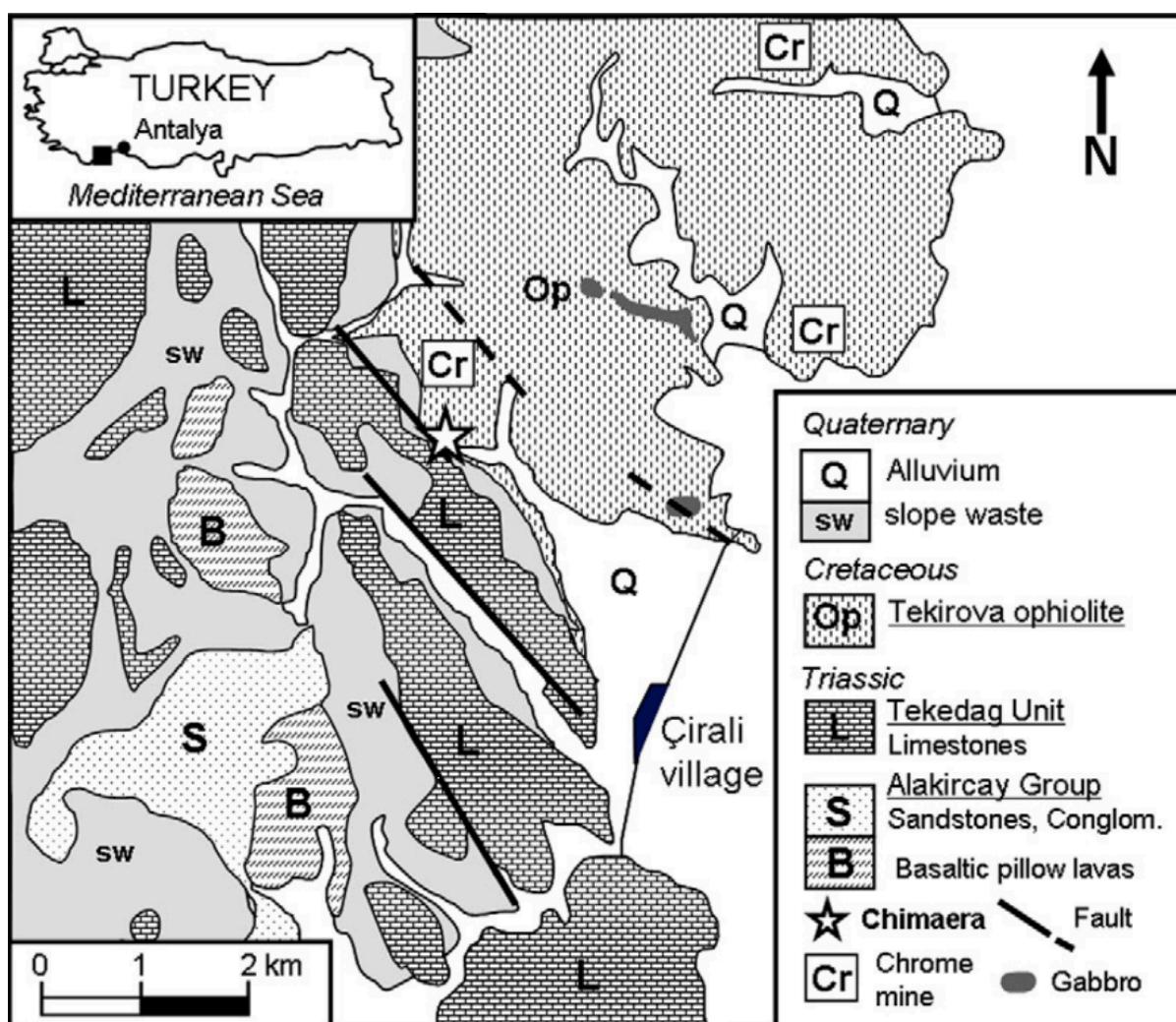


Figure 8. Lithology map of the Chimaera site. Map from Etiope et al. (2011).

There are at least fifty vents from fractures along the fault where gas is emitted (Etiope et al., 2011). The gas is produced from the serpentintized ophiolites north of the fault.

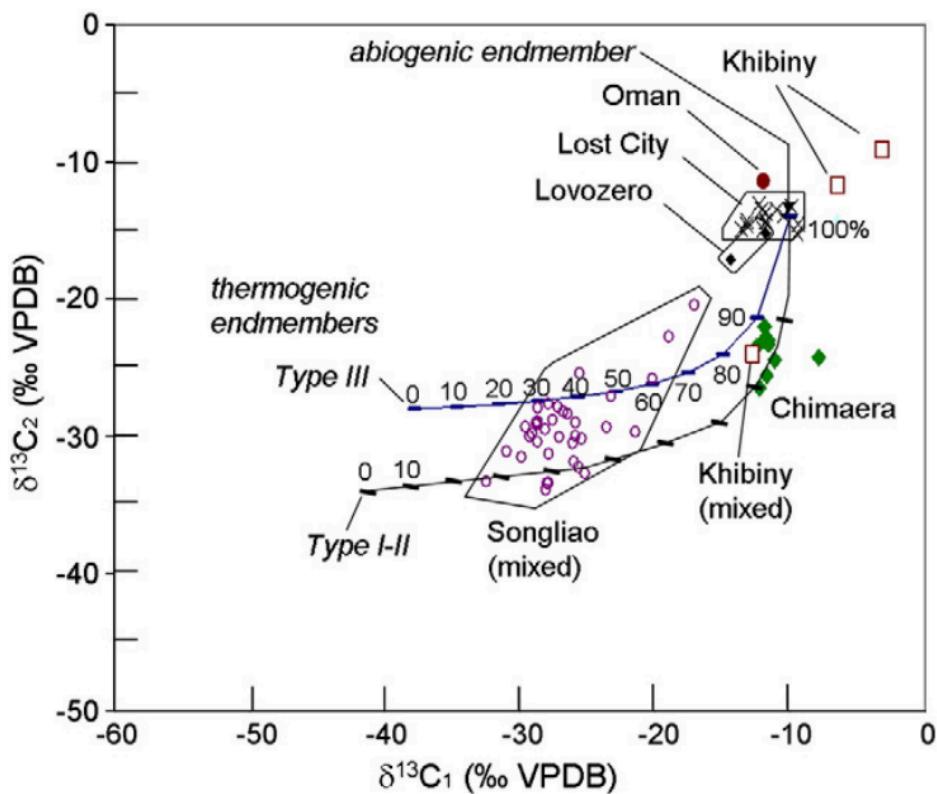


Figure 9. $\delta^{13}\text{C}_2$ vs $\delta^{13}\text{C}_1$ graph showing locations of abiotic methane sites and type of processes (thermogenic / abiogenic) found there. Graph from Etiope 2018.

The ongoing serpentization of ophiolites and gas-water-rock reactions within the fractures produce abiotic methane. From the 50 vents along the fractures in Figure 8, at least 20 burn continuously.

Data collected from the Chimaera site was compared to the global data set of abiotic and biotic methane where the molecules' endmembers indicated the source of the gas (Etiope et al, 2011). With molecular and isotopic composition of the gas, it was determined that the majority of the gas was produced abiotically, not thermogenically; however, 10–20% of the gas was produced thermogenically. A method used to differentiate between abiotic methane and biotic methane is by determining the carbon isotope present. The Schoell's plots show the zoning of methane. Shown earlier in Figure 5, it can be seen that Chimaera is located in the abiotic region on the $\delta^{13}\text{C}$ to $\delta^2\text{H}$ plot. In Figure 9, it can also be seen Chimaera methane is enriched in heavier carbon isotope and is located within the abiogenic section of the $\delta^{13}\text{C}_2$ vs $\delta^{13}\text{C}_1$ graph. The abiotic synthesis of methane produces carbon and hydrogen isotopic values enriched in heavier ^{13}C isotopes. In contrast, biotic methane shows depleted ^{13}C value.

Othrys, Greece

Othrys is a mountain in central Greece located on the ophiolite belt that cuts through east central Greece and is a location of abiotic methane production. The ophiolite belt is rich with ultramafic minerals which aid in the serpentization reaction. It was first discovered that methane was released by hyperalkaline springs in the villages of Archani and Ekkara. Seepage of methane was also found.

Ophiolites in Othrys came from orogenic events in the Jurassic which lifted the oceanic crust into the continental crust. Igneous rock is the primary make up of Mount Othrys in Greece. Flood basalts, ophilitic basalts, an intrusive sequence composed of dunites and gabbros, and tectonic peridotites including chromitite constitute Mount Othrys' lithology (Etiope, 2018). The presence of methane is found within ultramafic rock in chromitite abundant layers (Etiope, 2018).

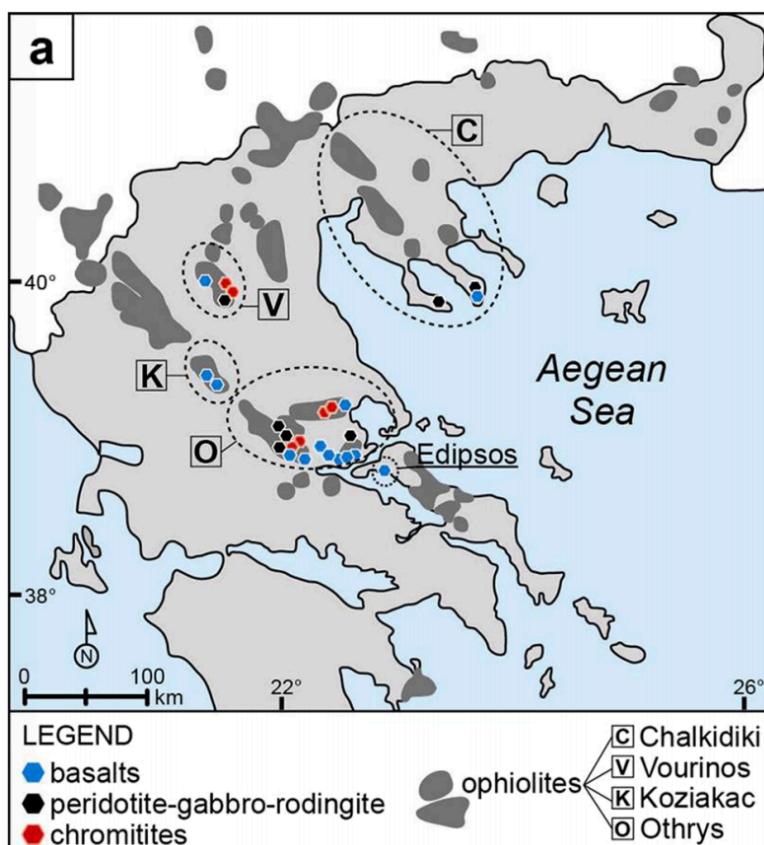


Figure 10. Map of types of ophiolites in Greece. Map from Etiope (2018).

The ophiolite rocks in Greece are made of serpentinite, peridotite, chromitite, gabbro, rodingite and basalt (Etiope, 2018). The chromitites, however, contain a significant presence of $^{13}\text{C}_2$ methane. Presence of heavier hydrocarbons is an indicator of abiotic gas. Chromitites contain ruthenium and chromium, which are metal catalysts for the production of methane.

Carbon to hydrogen ratios provide a good indication of the source of methane, be it abiotic or biotic. Methane produced from Othrys rocks has an isotopic composition of $\delta^{13}\text{C}$ ranging from

-27% to -37.3‰ and $\delta^2\text{H}$ ranging from -250‰ to -311‰ (Etiope and Lollar, 2013). Looking back at Figure 6, methane produced by Othyrs rocks have carbon to hydrogen ratios that land in the abiotic region.

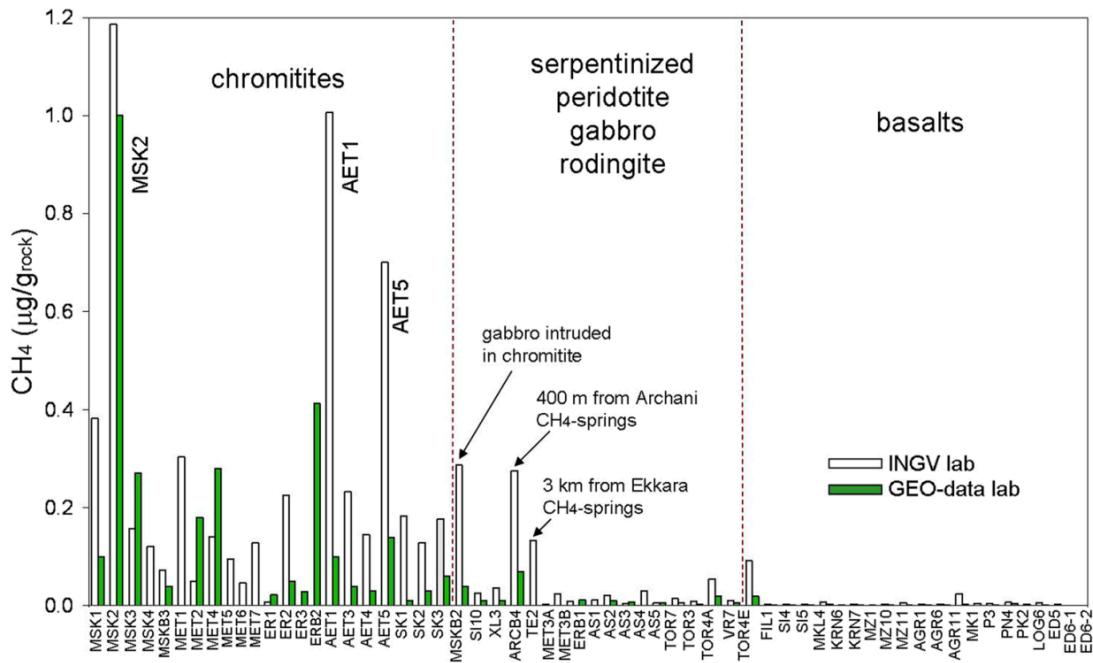


Figure 11. Graph of methane abundance in chromitites and other ophiolite rocks. Rocks are classified from the combination of macroscopic observations, microscopic observations, and SEM-EDX (spectroscopy) analysis. Figure from Etiope (2018).

The gas emitted from various igneous outcrops was analyzed to determine a relationship between the abundance of methane produced from mafic igneous rock with the abundance of methane produced from chromitites. MSK2 is abbreviated for Orthys ophiolites enriched with chromitite and AET is abbreviated for Vourinos ophiolite enriched with chromitite and peridotite. Isotope ratio mass spectrometry (GC-IRMS) and laser spectroscopy showed that the gas emitted from chromitites had a significant concentration of methane greater than 0.1 (up to 1.2) µg per gram of rock (Etiope, 2018). It was also discovered that considerably lower concentrations of methane were found in other ultramafic and mafic rocks (up to 0.05 µg) and none in non-ophiolitic rocks (Etiope, 2018).

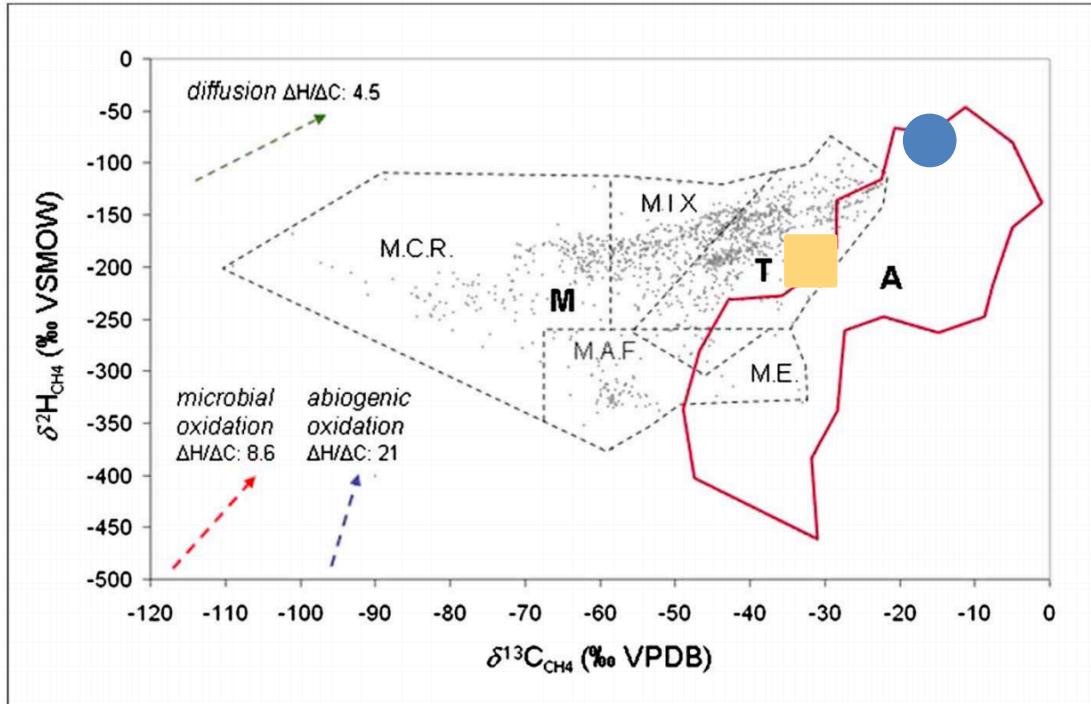


Figure 12. $\delta^2\text{H}$ vs $\delta^{13}\text{C}$ diagram showing a relationship between the hydrogen to methane ratio and carbon to methane ratio. Thermogenic, T, microbial, M, microbial carbonate reduction, M.C.R., microbial acetate fermentation, M.A.F., microbial evaporitic, M.E., and abiotic, A, are segmented on the graph (Etiope, 2013, p.290). Location of Chimarea, Turkey (blue circle) and Orthrys, Greece (yellow square) included on $\delta^2\text{H}$ vs $\delta^{13}\text{C}$ diagram. Figure 6 from Etiope and Lollar (2013).

Significance of Ophiolite Outcrops

Serpentinization is the hydrolysis of ultramafic rocks, a process which typically occurs at tectonic plate boundaries. Ophiolites, which are igneous rocks pushed up to the surface forming hydrothermal vents, also allow an environment for serpentinization to take place. Both the Chimaera seep in Turkey and Mount Orthrys in Greece allow analysis of abiotic production of methane by serpentinization and the Fisher-Tropsch type reaction to be analyzed on Earth's surface.

As shown above in Figure 12, Chimaera, Turkey and Orthrys, Greece are sites of abiotic methane. However, Orthrys also has a prominent thermogenic presence of methane. As can be seen in Figure 11, Orthrys lies within the thermogenic isotopic ratio of Schoell's $\delta^2\text{H}$ vs $\delta^{13}\text{C}$ plot. Only ophiolite regions with chromitite produced abiotic methane in Orthrys. Thermogenic methane is produced at high temperatures. Perhaps the tectonic region of Orthrys allows for metagenesis, the degradation of organic matter. Therefore, carbonate and igneous outcrop of Chimaera, Turkey most resembles the terrain on Mars.

METHANE ON MARS

Geology and Mineralogy of Mars

A principle objective for Mars rover missions is to determine evidence of life. The presence of methane, along with water vapor, carbon dioxide, nitrogen, oxygen and an ozone in the atmosphere can indicate possible life on the surface of the planet. Carbon dioxide, oxygen and methane can be produced from living organisms. Detecting their abundance in the atmosphere can lead to theorizing the existence of microbes on planets.

The geology of exposed outcrop and evidence of water are used to identify the existence of a habitable environment on Mars. Mars surface geology was explored and modeled with the use of planetary robots capturing images of terrestrial rock outcrops. Pro3D, a 3-D visualization software tool, allows for geological analysis of Martian geology (Barnes et al, 2018). The 3-D reconstruction of rover images enables the analysis of the physical dimensions of geologic features of the terrain like dips and strikes of bedding and fractures, topography, lithology of geological units, and weathering (Barnes et al., 2018).

The internal structure of Mars has also been studied to determine the planet's mineralogy. The one-dimensional models of its internal structure depended on eight parameters: thickness and mean density of the crust; the bulk volume fraction of iron and olivine; and the pressure gradient and temperature range of the mantle, and the radius and mass of the core (Verhoeven et al., 2005). Data were collected from multiple orbital space missions and from Earth-bound monitoring systems (Verhoeven et al, 2005). The bulk composition of the Mars mantle is chondritic (Zuber, 2001). Its composition is similar to that of condensing solar nebula. The rock is crystallized into igneous particles. Rocks on the surface of Mars, analyzed by one of the Mars rovers, Mars Pathfinder, were andesitic, extrusive igneous rock in composition (McSween, 2015). There were many models generated describing the mineralogical characterization of Mars' mantle. An example of the interpretations of physical and mineralogical models of the mantle is shown in Figure 12.

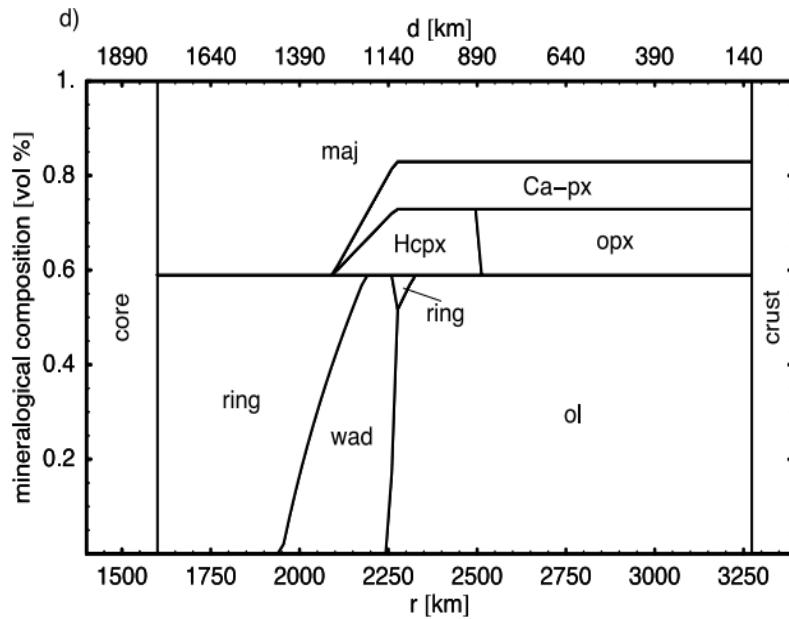


Figure 13. DW models (mineralogical composition from Dreibus and Wanke [1985] data) of synthetic data set representing Martial mantle mineralogical compositions based on fraction volume in r [km], radius, and d [km], depth. Minerals in models include: ol, olivine, wad, wadsleyite, ring, ringwoodite, opx, orthopyroxene, Lcpx, low-pressure clinopyroxene, Hcpx, high-pressure clinopyroxene, Ca-px, Ca-pyroxene, and maj, majorite. Synthetic models are from Verhoeven et al., 2005.

As can be seen in Figure 13 although the exact compositional volume of each mineral is unknown, the models indicate that there is a significant amount of olivine and pyroxenes in Mars' mantle. The simulated models of the mineralogical composition models show zones based on depth and associated with temperature. Phase are shown in the different mineral zones. For instance, the phase change for olivine to wadsleyite is at a depth of a little over 1000km (Verhoeven et al., 2005). The surface of Mars is primarily composed of igneous rock and iron-rich clays. The bulk mineralogy of surface rocks are pyroxenes.

Methane Detection on Mars

Earth's radius is about 6370 km while Mars' radius is about 3390 km. Since Mars is about half of the size of Earth, the dynamic evolution and geologic tectonism of Mars was likely much faster than Earth's. The motion of Earth's tectonic plates drives many of the geological activities on the planet. Although Mars has one single plate, Maria Zuber has speculated that "earlier in [M]artian history...the planet displayed thinner and possibly even mobile plates" (Zuber, 2001). It is still possible the plastic state of the mantle may drive tectonic activity on Mars. Because Earth and Mars are very similar planets, there is potential for life on Mars during the planet's history. In 2003 and 2004 methane was discovered in Mars' atmosphere leading to hypotheses of the possibility of life on Mars. Sources of methane include radiation from interstellar medium radiation, emittance from volcanoes, microbial activity, and geologic reactions, namely serpentinization. Inner planets are typically methane deficient whereas outer planets are methane rich from interstellar medium radiation. Earth is an exception as microbes are the most prominent source of methane. Volcanoes on Mars have been extinct for hundreds of millions of

years (Atreya, 2009), therefore, the methane detected in Mars' atmosphere was not likely to have originated from volcanic activity.

Most of Earth's source of methane is biotic. Methane is a byproduct of methanogenesis, the anaerobic respiration of organic matter by microorganisms. For Mars, in contrast, the most plausible source of methane is abiotic. Geologic sites on Earth like Chimaera, Turkey and Othrys, Greece provide clues as to how abiotic methane might be formed on Mars. As mentioned above, Mars' terrain is composed primarily of ultramafic silicate rocks. Methane was discovered in Martian regions Syrtis Major and Nili Fossae both having rocks bearing olivine (Etiope, 2011). Serpentization involves the reaction of olivine or pyroxenes and hydrogen to form methane.

Methane was detected "corresponding to serpentized olivine-bearing rocks in the Martian regions of Syrtis Major and Nili Fossae" (Etiope, 2011). The site is in a canyon displaced crust in between faults composed of igneous rock made of mafic minerals, iron and magnesium, and pyroxenes and carbonate rocks.

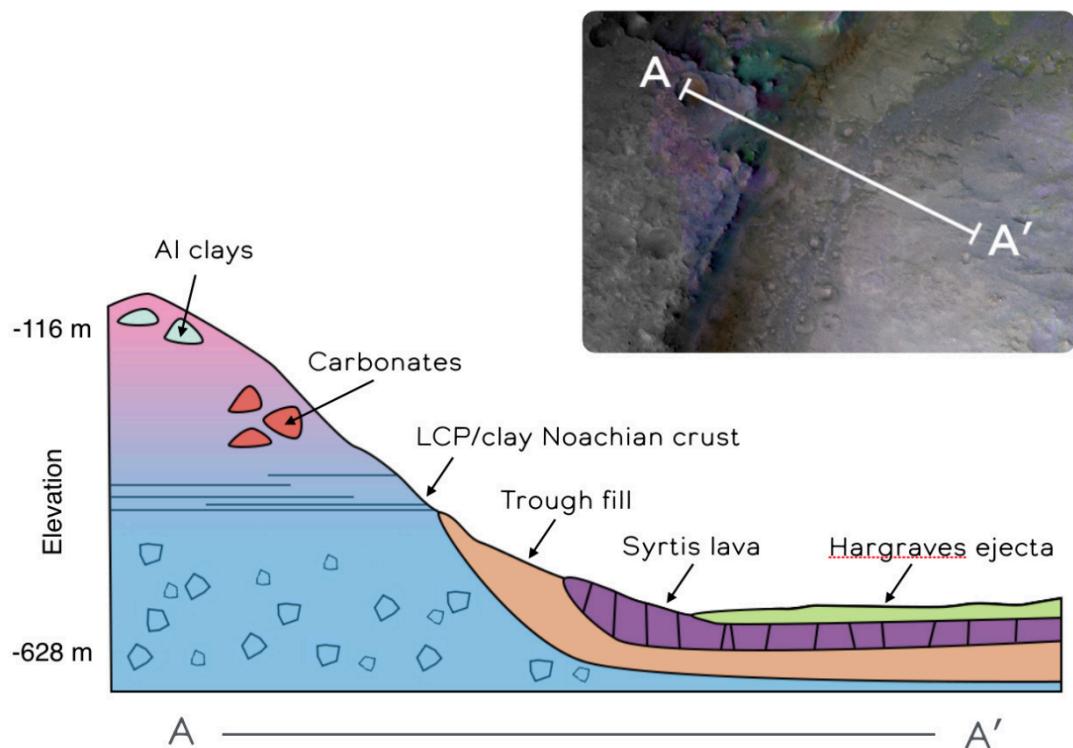


Figure 14. Stratigraphic figure of Syrtis region. Image from NASA M2020 Candidate Landing Site Data Sheets - Nili Fossae. M2020 NASA

The surface features of Mars include large volcanoes, dense craters, and plains. Because of the heavily cratered terrain, "materials near the surface are probably interbedded units of differing origins" (Carr, 1980). As shown in Figure 14, igneous Syrtis rock, carbonates, and clays are found where methane was detected. The diverse mineralogy allows for an environment conducive to serpentization. The mantle is thought to have a mafic composition as shown in Figure 13 which produces a surface mafic terrain. The olivine-clay unit may react with

carbonates in hydrothermal reaction to produce methane. The ferromagnesium minerals in the clay unit are key parts of the serpentinization reaction.

Although methane has been detected on numerous missions, the quantity of methane detected is very small and limited measurements still lead to speculation on the source of methane. NASA's Curiosity Mars rover detected 21 ppbv (Greicius, 2019) in contrast to Earth's concentration of 1620 ppbv (NASA, 2016). Ashwin Vasavada, Curiosity's project scientist at NASA's Jet Propulsion Laboratory in Pasadena, CA, said "[t]he methane mystery continues" (Greicius, 2019).

In conclusion, insufficient information is known to rule out the involvement of microbes on Mars. On Earth, isotopic differences between abiotic and biotic methane were used to determine the source of methane. Looking back to Figure 6, biotic methane tends to be more abundant in ^{12}C , whereas a higher percent of the heavier isotope, ^{13}C , classified as abiotic methane. On Earth, living organisms "contain 92 to 97 times as much carbon 12 as carbon 13" (Atreya, 2009). Isotopic classification of methane and of noble gasses on Mars has not been determined. Discovering the percentage of carbon isotopes would give more indication of whether the methane detected on Mars is from an abiotic or biotic source.

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