A Comparative Study of Solid Alkaline Materials for Ocean Alkalinity Enhancement Using Infrared Spectroscopy

by

© **Afreen Mahiat**

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Abstract

The urgent need to minimize the effects of climate change caused by increased greenhouse gases has generated interest in Ocean Alkalinity Enhancement (OAE) as a strategy for decreasing ocean acidity. A key aspect of implementing OAE involves monitoring chemical reactions in oceanic conditions, which are complex and involve a multitude of ions and compounds. This thesis aims to utilize the Infrared (IR) Spectroscopic signatures of solid products from potential OAE reactions. It records and explains the spectral changes that could occur when an alkaline earth hydroxide is added to water, forming carbonate minerals. This work serves as an essential catalog to help future researchers in OAE keep track of spectral features to look for.

Dedicated to my beloved parents.

Lay summary

Due to the increased concentration of carbon dioxide gas in the atmosphere being absorbed into the ocean, our oceans are getting more acidic. One way to tackle this is through Ocean Alkalinity Enhancement (OAE), a method where alkaline materials are added to ocean water to raise its pH and decrease the concentration of excess CO_2.

In my thesis, I focus on a few common reactions involving solids that are essential in OAE. My approach involves using infrared (IR) spectroscopy to compare and catalog the spectral features of these reactions. This technique is used to understand the spectral data or "fingerprints" of the solids involved. These fingerprints consist of peaks in the IR spectrum, each corresponding to specific vibrational modes within the solids.

By overlaying and comparing these spectra, I identify the distinct spectral features of each compound. This comparison helps to illustrate how the same vibrational modes in different compounds can exhibit slightly varied IR spectral characteristics. Since the ocean has a dynamic and complex environment, several reactions can occur, leading to the formation of a variety of compounds. My thesis focuses on understanding the potential outcomes of Ocean Alkalinity Enhancement (OAE) through the analysis of the IR spectra of specific solid compounds rather than tracking all possible reactions or ion mixtures in seawater. By studying the infrared (IR) spectra of key alkaline solids – namely calcium hydroxide, calcium carbonate, magnesium hydroxide, and magnesium carbonate – I aim to identify and compare their spectral characteristics.

The crux of my thesis is twofold. First, I give an introductory overview of infrared spectroscopy for those new to the topic. Then, I get into the details, explaining which specific peaks in the spectra correspond to which vibrational modes in the compound

and how to distinguish them.

Acknowledgements

Completing this research would not have been possible without the encouragement and invaluable assistance of several key individuals, and I take this opportunity to express my heartfelt gratitude.

First and foremost, I extend my deepest gratitude to Dr. Kristin M. Poduska, my supervisor and distinguished professor in the Department of Physics and Physical Oceanography. Her ongoing guidance and expert mentorship have not only shaped this research but also enriched my academic journey. Her wisdom and encouragement have been invaluable at every stage of this thesis.

I extend my sincere thanks to the head of the Department of Physics and Physical Oceanography, Dr. Len Zedel, along with professors Dr. Ivan Saika-Voivod and Dr. Qiying Chen. Their insightful feedback and advice significantly improved the quality of this work.

A special nod to Dr. Friedrich Menges from the University of Konstanz, the developer of the Spectragryph software that was essential for my spectral analyses. He generously provided access to his software at no cost and was always available for technical guidance. His generosity has had a profound impact on the quality and scope of this work.

I owe a debt of gratitude to my parents, Ashek Mahfuz, Ph.D., and Nasreen Parvin, for their unwavering encouragement and emotional support throughout this journey.

Lastly, I express my gratitude to Almighty Allah, who enabled me to complete this significant body of work.

Statement of contribution

The topic for this thesis, initially titled as "Use of IR Spectroscopy in Ocean Alkalinity Enhancement (OAE)," was first suggested by my supervisor, Dr. Kris Poduska and has evolved a lot as the goal for what is studied in the thesis changed.

My research and analysis relied fully on existing spectral data sourced from an online IR spectra database called the Kimmel Center for Archaeological Science Infrared Standards Library, Weizmann Institute of Science (see Appendix B), introduced to me by Dr. Poduska. This negated the need for experimental lab work, allowing a focus on data analysis and interpretation.

I used two key software tools for data analysis: Quasar and SpectraGryph (detailed in Appendix B). These tools were essential for analyzing the spectral data and drawing comparisons, and they presented a learning curve that I successfully tackled on my own.

My role in data analysis involved conducting detailed literature research and thoroughly examining the spectral features, supported significantly by the expertise and guidance of Dr. Poduska. Her input was invaluable in deepening my understanding of the subject matter, providing direction during our discussions, and offering constructive feedback on multiple drafts of my thesis.

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List of abbreviations

A	Absorbance
CO_2	Carbon Dioxide
CO_3	Carbonate
$CO_3{}^{2-}$	Carbonate ion
Ca^{2+}	Calcium ion
$CaCO_3$	Calcium Carbonate
$Ca(OH)_2$	Calcium Hydroxide
EW	Enhanced Weathering
H^+	Hydrogen ion
$HCO_3{}^-$	Bicarbonate ion
H_2CO_3	Carbonnic acid
IR	Infrared
Mg^{2+}	Magnesium ion
$MgCO_3$	Magnesium Carbonate
$Mg(OH)_2$	Magnesium Hydroxide
O^{2-}	Oxygen ion
OA	Ocean Acidification
OAE	Ocean Alkalinity Enhancement
OH	Hydroxide
TA	Total Alkalinity
u	(unified) atomic mass unit

Chapter 1

Introduction

1.1 Background

Over the last several decades, increased human activity in fossil fuel combustion, deforestation, mining, and other environmentally harmful projects have led to an increase in the release of carbon dioxide gas [1], as much as 1700 gigatonne [2], into the atmosphere. Since carbon dioxide is a greenhouse gas, its increased concentration in the air is a leading cause of global warming, causing the Earth's temperature to rise, and if this trend continues, our average global temperature is at risk of rising by nearly 4° within the next 80 years [2]. This phenomenon is well-studied, with a focus primarily on atmospheric consequences, yet comparatively little attention has been paid to the ocean. The ocean serves as our natural carbon sink, absorbing as much as 1/3 [3] of the carbon dioxide from the atmosphere. Historically, this has acted as a natural buffer, helping to maintain a balance of gases in the atmosphere. However, increased levels of CO_2 in the atmosphere also result in elevated concentrations in ocean waters. The ocean is naturally slightly alkaline, with an ideal pH of 8.2. But the rise in CO_2 level in the ocean water has caused this pH to decrease by 0.1, making the current ocean pH 8.1 instead [4]. This decrease in pH is known as ocean acidification and can be explained by the chemistry below [5]:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons 2\,H^+ + CO_3{}^{2-}. \qquad (1.1)$$
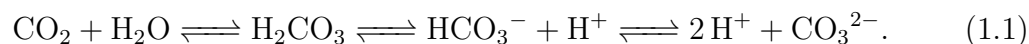
The excess CO_2 reacts with water to form carbonic acid (H_2CO_3) which then dissociates to bicarbonate (HCO_3^-) which further dissociates into hydrogen and carbonate ions. These series of reactions increase the concentration of H^+ ions in the oceans, lowering the pH [6]. This results in severe biological and environmental effects on the ocean. To address the issue of ocean acidification, several innovative approaches have been proposed, including Enhanced Weathering (EW) and Ocean Alkalinity Enhancement (OAE). EW involves the strategic placement of alkaline rocks along the sea or ocean shore that go through natural weathering processes [7], causing minerals from these rocks to erode over time and wash into the ocean, thereby increasing the concentration of alkaline materials in the water.

On the other hand, OAE aims for a similar increase in ocean alkalinity but employs a more direct method. Rather than relying on the slow process of natural weathering, OAE introduces alkaline compounds directly into ocean waters [8]. These compounds react with excess carbon dioxide and HCO_3^- ions in the ocean, reducing their concentration, rising the water's pH, and subsequently increasing the ocean's capacity to absorb CO_2 from the atmosphere.

The two most common minerals for OAE are those rich in calcium and magnesium [3] due to their alkalinity potential, such as their carbonates, hydroxides, and silicates, and much of the existing research in this field has concentrated on these two elements. The implementation of OAE is complex, with potentially positive or adverse side effects on marine biogeochemistry [9]. While this thesis primarily focuses on the IR spectral characteristics of carbonates and hydroxides involved in OAE, it is important to note that the mineral dissolution can introduce additional elements to the marine ecosystem [7]. Therefore, research into OAE needs to cover not only the immediate chemical reactions but also have a broader understanding of its ecological and biogeochemical consequences.

1.2   Thesis Objective

The main objective of this thesis is to provide guidance through example spectra, illustrating what one would observe in the Infrared (IR) Spectroscopy of solids before and after various potential OAE reactions.

The chemistry behind OAE is rooted in the ocean's carbonate system described

in Section 1.1. Alkalinity is a measure of the ocean's capacity to neutralize acids. It's primarily influenced by the concentrations of bicarbonate, carbonate, hydroxide, and hydrogen ions which sums up to give the total alkalinity (TA) [10]. We can see in equation 1.1 how these species react with each other in several steps and eventually reach a state of equilibrium in the ocean. By adding alkaline substances, such as calcium hydroxide to seawater, they are expected to partially dissociate into calcium ions Ca^{2+} and hydroxide ions OH^-, the latter of which can then react with the excess CO_2 present. The reaction we anticipate is outlined below:

$$Ca(OH)_2\,(s) + CO_2\,(g) \longrightarrow Ca^{2+} + 2\,OH^- + CO_2\,(g) \longrightarrow CaCO_3\,(s) + H_2O\,(l). \quad (1.2)$$
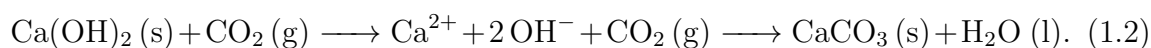
This reaction not only results in the formation of calcium carbonate but the addition of $Ca(OH)_2$ increases the concentration of OH^- ions, which are basic and can react with H^+ from equation 1.1 to increase the pH. Furthermore, the formation of the carbonates serves as a permanent sequestration mechanism for CO_2, as the carbon is locked away in the solid mineral form.

However, the real-world ocean environment is far from ideal, comprised of a diverse assortment of ions and compounds. Therefore, it is guaranteed that the presence of these ions, namely magnesium ions (Mg^{2+}), will react with the newly formed CO_3^{2-} to form compounds like magnesium carbonate ($MgCO_3$).

Upon analyzing an alkaline compound like calcium hydroxide with IR spectroscopy, we should observe peaks corresponding to the vibrational modes of the hydroxide ions. As the calcium hydroxide reacts with CO_2 in the seawater we'd expect, after studying the spectra of the resultant solid, the appearance of new peaks corresponding to calcium carbonate, with a possibility of peaks that indicate the formation of other compounds, like $MgCO_3$, which is not a direct consequence of adding $Ca(OH)_2$ but is resulted from potential side reactions.

Should these reactions occur, infrared (IR) spectroscopy can be used for post-reaction analysis to study differences in the reactants and products by identifying spectral features. A detailed discussion of the principles and techniques of IR spectroscopy and these spectral features is provided in Chapter 2 and 2.3 respectively.

Chapter 2

Interpreting Infrared Spectra for OAE

2.1   The Principle of Infrared Spectroscopy

The underlying principle of IR spectroscopy is that when infrared radiation is passed through a sample, some of the incoming radiation is absorbed in certain wavelengths by the bonds in the sample, causing them to vibrate in specific ways, known as the vibrational modes. As a result, less radiation reaches the detector compared to the incoming light, and an absorption spectrum is produced, which is a graphical representation of how much light is absorbed at each wavenumber [11]. However, it is important to note that not all vibrational modes are IR-active. A vibrational mode is IR-active only if it results in a change in the dipole moment of the molecule [12]. Symmetrical moieties or symmetrical vibrational modes do not lead to a change in dipole moment, and as such, are not detected by IR spectroscopy. There are several textbooks and articles that describe the science behind infrared spectroscopy. Some go into detail on the background of spectroscopy, the formulas used, experimental techniques, etc. [13], while others offer a more simplified and reader-friendly approach for non-scientific audiences [11].

2.2   Spectral Features

2.2.1   Absorption Spectra: Key Concepts and Calculations

In IR spectroscopy, the types of spectra differ depending on what aspect of the substance is being studied. For the scope of this thesis, the focus will be exclusively on absorption spectra where the x-axis records the range of wavenumber, which is the number of waves in a unit distance and is proportional to the energy of the light, and the y-axis quantifies the absorbance. It's crucial to understand how this absorbance (A) is calculated. For solids, the amount of light absorbed is inverse logarithmically proportional to the transmittance and depends on factors such as the height and particle size of the sample. One example absorption formula is: **A = log(1/T) = -[h/d] log [[1-f] + f i(d)]**[14], where i(d) is the fraction of IR light transmitted by a single sample particle, which is a function of the particle diameter d and the absorption coefficient k (i(d)=exp(-kd) for cubic crystal structures) [14].

2.2.2   IR Regions and Applications

Infrared radiation itself ranges from wavenumbers of about 14000 cm^{-1} to 10 cm^{-1}, with corresponding wavelengths between 780 nm and 1000 mm [15]. The range is divided into three main regions [12]: the **near-infrared (NIR)** (fingerprint region), which ranges from 14000 cm^{-1} - 4000 cm^{-1} and is typically used in identifying functional groups, measuring moisture content, and analyzing organic compounds; **mid-infrared (MIR)**, ranging from 4000 cm^{-1} - 400 cm^{-1} particularly well-suited for the study of molecular vibrations, including stretching, bending, and torsional vibrations of various functional groups; and **far-infrared (FIR)** (terahertz region), which ranges from 400 cm^{-1} - 10 cm^{-1} and is characterized by low-frequency vibrations, lattice vibrations in solids, and rotational transitions in large molecules. FIR spectroscopy is useful for studying crystal structures, intermolecular interactions, and solid-state properties of materials.

The focus of this thesis will be on the infrared (IR) range from 400 to 4000 cm^{-1}, which falls under MIR, due to the specific vibrational modes of solids that can be observed within this range.

2.3   Understanding the Spectra

Much of the discussion in the next chapter will focus on comparing specific spectral features relevant to (OAE). These features are particularly the properties of peaks in the IR spectra of materials important in OAE. Therefore, it's essential to provide a brief overview of what these properties signify for a better understanding of the analysis that follows. For IR spectroscopy, the peaks correspond to the energy absorbed by the vibrational modes taking place within the structure. There are three main peak attributes to be mindful of:

- position of the peak maxima: wavenumber at which the radiation is absorbed/transmitted. The position is characteristic of the vibrational mode and gives information about the composition [11].

- height: gives information about the quantity of absorbance of the vibrational mode

- width: gives information about the long-range/short-range order of the solid. The broader the peak, the more amorphous and disorderly the crystalline structure throughout the solid. [14]. The sharpness of the peak suggests a higher degree of crystallinity.

The IR spectra in this thesis have relative absorbance as the y-axis and wavenumber (in cm^{-1}) in the x-axis with an x-range from 4000-400 cm^{-1}. The peaks have been normalized so that the intensity of the strongest peak is at 1 to allow a quantitative comparison of the relative intensities of different peaks within a spectrum.

The vibrational mode that caused the absorption, and therefore IR frequencies at which the peaks are absorbed, is dependent on several factors, including the mass of the atoms (the greater the mass of attached atoms, the lower the vibrational energy and thus the lower the IR frequency at which the bond will absorb and cause a peak; we can see this in Figure 2.1 and Section 3.4 when comparing spectra between magnesium and calcium compounds); and the vibrational mode (stretching, bending, twisting; we can see how different types of vibration will cause different peaks in a lot of the spectra below, but one example is of the carbonate bond in magnesium carbonate). The characteristic frequencies of a given kind of vibrational mode are often similar between two compounds that have similar crystal structures. These differences, albeit
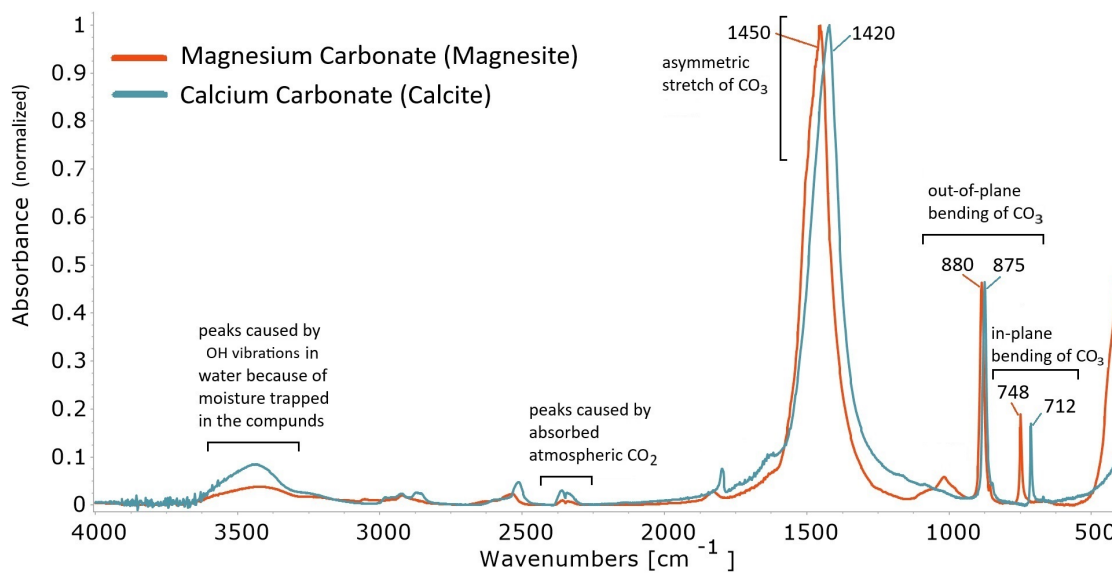
Figure 2.1: IR spectra comparison between magnesium (red) and calcium (blue) carbonate (normalized). Since calcium atoms are heavier than magnesium atoms, we can see the carbonate peaks of magnesite are shifted slightly towards higher wavenumbers, compared to calcite. We can also see from this spectral data how distinct vibrational modes corresponding to specific functional groups or moieties will have characteristic peaks.

subtle, are significant enough to distinguish between these two carbonate minerals. Therefore, IR spectroscopy can provide unique identifiers for each substance, allowing us to differentiate between similar compounds like magnesite and calcite, particularly when considering their most definitive spectral features.

Chapter 3

Analysis

3.1 Materials used in OAE

Even though this thesis is on specific forms of magnesium and calcium compounds, in OAE, several other minerals are also considered due to their specific properties. A few that are of interest include:

- magnesium-rich minerals

  - brucite, $Mg(OH)_2$
  - periclase, MgO
  - forsterite, Mg_2SiO_4

- calcium-rich minerals

  - quick lime, CaO
  - hydrated lime, $Ca(OH)_2$
  - limestone rocks, $CaCO_3$
  - calcium silicates, Ca_2SiO_4 from rocks and wastes (olivine)

The preference of minerals used in OAE is often influenced by factors such as local availability. However, hydroxides are preferred more than oxides since they are more stable and easier to transport [10].

3.2 $Ca(OH)_2$ in OAE

3.2.1 Steps in a calcium hydroxide OAE reaction

Calcium hydroxide is one of the most popular candidates in OAE due to being a strong base, meaning it can react readily with dissolved CO_2 in water. The reaction for ocean alkalinity enhancement that we expect to take place involving calcium hydroxide is:

$$Ca(OH)_2 + 2\,CO_2 \longrightarrow CaCO_3 + H_2O \tag{3.1}$$
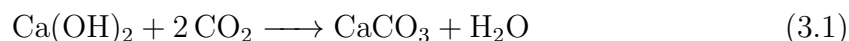
As we can see, adding hydroxide to water results in it reacting with the H^+ ions produced by the dissolved CO_2 (equation 1.1 and 1.2), reducing its concentration.

To recreate this reaction in a lab, one would start with a white solid of the reactant, which is $Ca(OH)_2$. As the reaction continues and the IR spectrum is monitored, the spectrum would evolve from one of the reactants to that of the product, with new peaks showing up and old peaks diminishing (see Figure 3.1). More notably, (assuming the final product is $CaCO_3$), there will be new peaks at 1420 cm^{-1}, 875 cm^{-1}, and 712 cm^{-1} for the new CO_3 moiety and reduced/diminished peaks at 3640 cm^{-1}, which is caused by OH bending, since calcium hydroxide should be fully dissolved and $CaCO_3$ does not have any OH. Such a reaction will give an IR spectrum like in Figure 3.1.

Thus, using Infrared spectroscopy, we were able to analyze the spectral features and compare the reactant and product spectra of one of the most common reactions in OAE. This method can be repeated for different reactions using different starting compounds (like different hydroxides or other sources of carbonates) and their IR spectra can be used to monitor the speed of reactions and study the products/by-products left behind

3.2.2 Analysis of the Spectral Differences between $Ca(OH)_2$ and $CaCO_3$

The Kimmel Centre provides multiple spectra variations for calcium carbonate (24) and hydroxide (3). I compared the 24 spectra for calcium carbonate and canceled out all the ones that show a peak at 1050 cm^{-1}, namely the 10 clay, 1 chalk, and 2

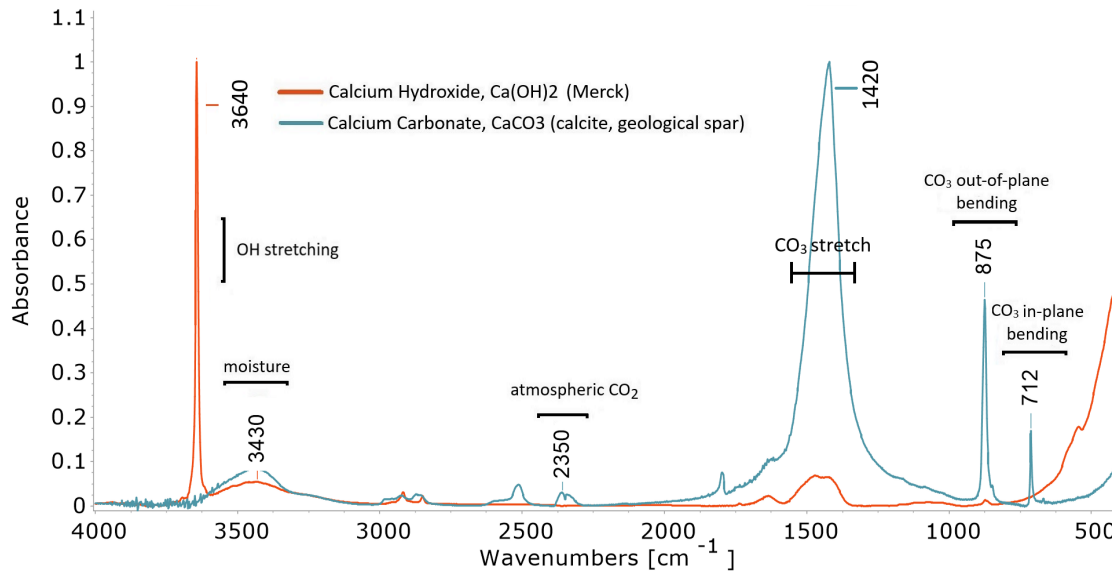Figure 3.1: IR spectra of $Ca(OH)_2$ (red) and $CaCO_3$ (blue) overlaid for comparison (normalized to set the highest peaks at a value of 1).
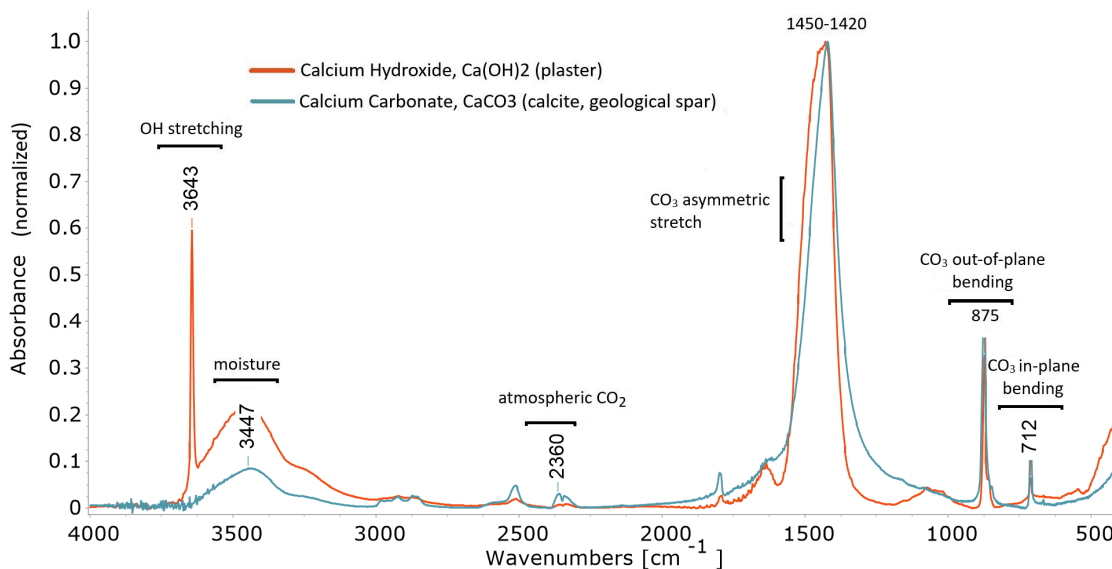

Figure 3.2: IR spectra of $Ca(OH)_2$ in plaster (red) and $CaCO_3$ (blue) overlaid for comparison (normalized to set the highest peaks at a value of 1). The spectrum with plaster shows strong CO_3 peaks, indicating the presence of both hydroxide and carbonate in the material.

ash variants. I also ignored the spectra for amorphous calcium carbonates (ACC), aragonite, and vaterite, as I wanted to focus on calcite in this thesis. Among the 4 calcite variants remaining, I dismissed the spectra for 2 biogenic calcites as I do not consider them appropriate sources of $CaCO_3$ for OAE. With the last two spectra of calcite (Aldo) and calcite (geological spar), I chose the latter as this spectrum has strong peaks suitable for further comparisons and the source aligns well with the real-life applications of OAE. For 3 calcium hydroxide variations in the database, I excluded Portlandite as its spectrum showed more peaks than expected for $Ca(OH)_2$, complicating further analysis. I initially chose the spectrum for plaster with $Ca(OH)_2$ (Figure 3.2) since it visualized a natural conversion of hydroxide to carbonate with prominent CO_3 peaks. However, as the thesis developed, the spectrum for $Ca(OH)_2$ (Merck) (Figure 3.1) became more suitable for the type of analysis I wanted to conduct.

A detailed table of the peaks and the vibrational modes to which they correspond can be found in Appendix A. To identify these peaks for this thesis, I referred to several sources. Information on the peaks for moisture, atmospheric carbon dioxide, and calcium carbonate was sourced from Chapter 12 of 'Microarchaeology' [11]. The assignment of the calcium hydroxide peak was based on research by Khachani et al. [16]. For magnesium carbonate, I figured out the peaks by comparing them to those of calcium carbonate, while the magnesium hydroxide peaks were identified with the help of Ansari et al.'s [17] and Kumari et al.'s [18] works. All these deductions were verified with IR spectrum tables in [19] and [20].

In the spectra of calcium hydroxide, various peaks at specific wavenumbers are present which can be categorized based on their vibrational modes. The broad peaks at around **3400** cm^{-1} will keep recurring in all our spectra. It shows the presence of moisture and is caused by OH in H_2O. Another recurring group of peaks are the one near **2350 cm^{-1}**. This recurring peak indicates that the compound has atmospheric CO_2 and is caused by the stretching of the C=O bond. These peaks arise from the presence of CO_2 gas in the air through which the IR beam passes during the measurement. Variations in the amount of atmospheric CO_2 in the path of the IR beam can cause these CO_2 gas peaks to increase or decrease.

The sharp peak at **3643** cm^{-1} is one of the most characteristic peaks of hydroxides, caused by the OH stretching in $Ca(OH)_2$. We will see a similar peak for magnesium

hydroxide, but the distinction in their wavenumber will be apparent.

Calcium carbonate or calcite crystallizes in a trigonal system and has a rhombo-hedral lattice structure [21]. In the solid state each calcium ion Ca^{2+} is surrounded by six oxygen (O^{2-}) ions in an octahedral coordination [22]. The CO_3 moiety itself is of particular interest in the context of IR spectroscopy. In solid calcite, the CO_3 moieties are planar and occur in layers, with alternating orientation of CO_3 from one layer to the next. The peaks caused by calcium carbonate are at **1420** cm^{-1} (caused by asymmetric stretch of CO_3 moiety), **875** cm^{-1}(out-of-plane bending of CO_3, where the oxygen atoms move out of the plane of the carbonate) and **712** cm^{-1} (in-plane bending of CO_3, where the oxygen atoms stay within the plane of the carbonate, but they move toward and away from the central carbon atom) [11].

3.3 Mg(OH)$_2$ in OAE

3.3.1 Steps in a magnesium hydroxide OAE reaction

Magnesium hydroxide, $Mg(OH)_2$ is another popular contender for adding alkalinity in seawater.

When a compound of magnesium hydroxide, such as those found naturally in brucite, is added to seawater, it dissolves into Mg^{2+} and OH^-. The former reacts with the $CO_3{}^{2-}$ resulting from the dissolved CO_2 (equation 1.1) to produce $MgCO_3$, and the latter reacts with H^+ ions (similar to the reaction for calcium hydroxide discussed in 3.2.1) :

$$Mg(OH)_2 + CO_2 \longrightarrow MgCO_3 + H_2O \tag{3.2}$$
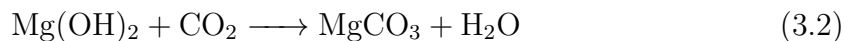
We would expect to see a similar trend in the spectral data (Figure 3.3).

3.3.2 Analysis of the Spectral Differences between Mg(OH)$_2$ and MgCO$_3$

As stated before in Section 2.3, the difference between the spectra of magnesium vs calcium isostructural compounds is caused by the difference in their mass and size
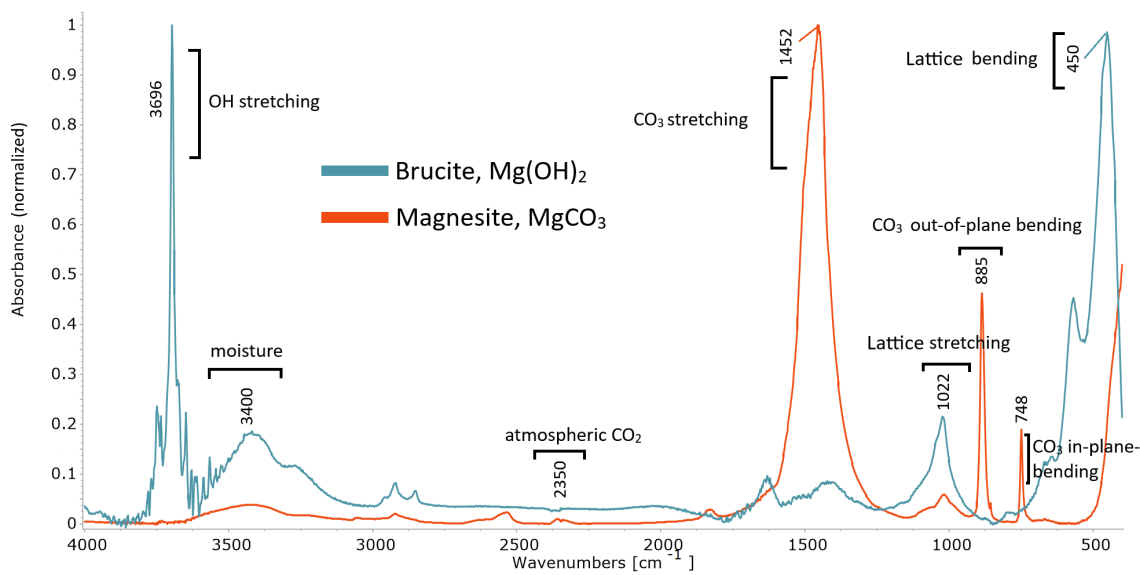
Figure 3.3: IR spectra of $Mg(OH)_2$ and $MgCO_3$ overlaid for comparison (normalized to set the highest peaks at a value of 1).

which results in the structure of the crystals being slightly altered. This alteration in the structure modifies the mode of vibration which causes the range of light they absorb to be changed. This change is what we can distinguish when comparing spectra.

We know from Section 3.2.2 the peaks at around **3400** cm^{-1} and **2350** cm^{-1} are caused by moisture and atmospheric CO_2, respectively. A closer examination of the infrared (IR) spectra of magnesium hydroxide $(Mg(OH)_2)$ shows two specific peaks that serve as distinctive markers, aiding in the identification and characterization of brucite. The intense sharp peak at **3696** cm^{-1} is, as discussed in 3.2.2, primarily caused by the stretching vibration of the OH [17] and indicates the presence of these hydroxyl groups. The peak at **450** cm^{-1} in the IR spectrum of $Mg(OH)_2$ can be attributed to the bending vibration of the lattice [18].

The infrared (IR) spectrum of magnesium carbonate $(MgCO_3)$ also reveals several distinctive peaks. The very intense and sharp peak at **1452** cm^{-1} represents the asymmetric internal stretching vibration of the carbonate moiety (CO_3) within $MgCO_3$. Moving down the x-axis, the intense and very sharp peak at **885** cm^{-1} corresponds to the out-of-plane bending of CO_3 within the crystal lattice of $MgCO_3$ and is seen in our spectra for $Ca(OH)_2$. The less intense but still very sharp peak at **748** cm^{-1} is attributed to the in-plane bending vibration of the carbonate CO_3 in $MgCO_3$ [23].

Although slightly less intense than the 885 cm^{-1} peak, it remains a prominent feature in the IR spectrum and provides further evidence of the carbonate ions' presence in the compound.

By analyzing the unique patterns of peaks in the IR spectra, we can differentiate between magnesium hydroxide and magnesium carbonate and gain insights into their chemical compositions. This highlights the significance of IR spectroscopy in the field of ocean alkalinity enhancement (OAE), as it enables us to track the reactions and transformations of alkaline materials, such as hydroxides and carbonates, in the context of CO_2 absorption and ocean acidification mitigation. The specific peaks observed in the IR spectra serve as valuable fingerprints, aiding in the characterization and monitoring of these compounds, and ultimately contribute to our understanding of their potential role in OAE strategies.

3.4 Comparing Magnesium and Calcium Compound Spectra

It is important to note that the following discussion is exclusively for the IR spectra used in this thesis specifically.

The fundamental goal of OAE is to decrease the absorbed carbon dioxide with alkaline materials. However, we are only focusing on the IR spectra of **solids** and the sections above show that the solids (calcium and magnesium carbonates/ hydroxides) often have similar peaks. It is very important to understand and identify which peaks are caused by which specific vibrational modes and how we can use the spectra to distinguish between the compounds. It is easier to group the important peaks that show up in our solids and then analyze them.

In Figure 3.4, the presence of a peaks at around **1420-1450** cm^{-1}, **875-880** cm^{-1}, and **700-760** cm^{-1} indicates that the compound is a carbonate. One way to differentiate between calcium and magnesium carbonates is by analyzing the accurate wavenumber at which these peaks show up. The peaks for $MgCO_3$ will appear to be at a higher wavenumber than that for $CaCO_3$ because of the difference in structures. Magnesium atoms (24u) are lower in mass than calcium atoms (41u), making $CaCO_3$
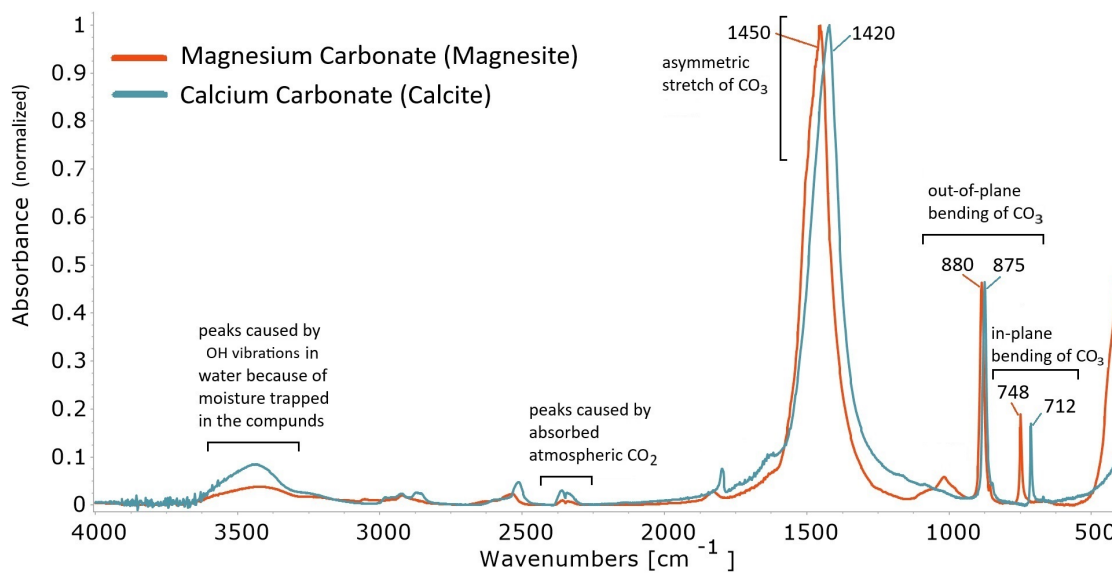
Figure 3.4: IR spectra comparison between $CaCO_3$ and $MgCO_3$ (normalized to set the highest peaks at a value of 1)
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heavier than $MgCO_3$. Since larger mass corresponds to lower vibrational energy, a compound that is heavier than another with a similar structure will have a peak at a lower wavenumber in the infrared spectra. This is a reliable way to distinguish between $MgCO_3$ and $CaCO_3$.

In the case of hydroxides (Figure 3.5), the major difference between $Mg(OH)_2$ and $Ca(OH)_2$ is the peak at around **3640** cm^{-1} for $Ca(OH)_2$, which is caused by OH stretching in $Ca(OH)_2$ [24]. This peak appears at **3700** cm^{-1} for $Mg(OH)_2$. It is at a higher wavenumber, which indicates higher vibrational energy, which is expected for the lighter $Mg(OH)_2$. Once again, the method of determining if the product we get from the reaction is part of the magnesium or calcium compound is to note the position of the characteristic OH or CO_3 peaks. The peaks for magnesium compounds tend to be in a higher wavenumber than those for calcium compounds. In the context of OAE, while it's challenging to predict precisely which products will form due to the complex mixture of ions and minerals in ocean water, informed predictions can still be made based on the initial alkaline material used. There are several reasons why this identification can be important when it comes to actual OAE application:
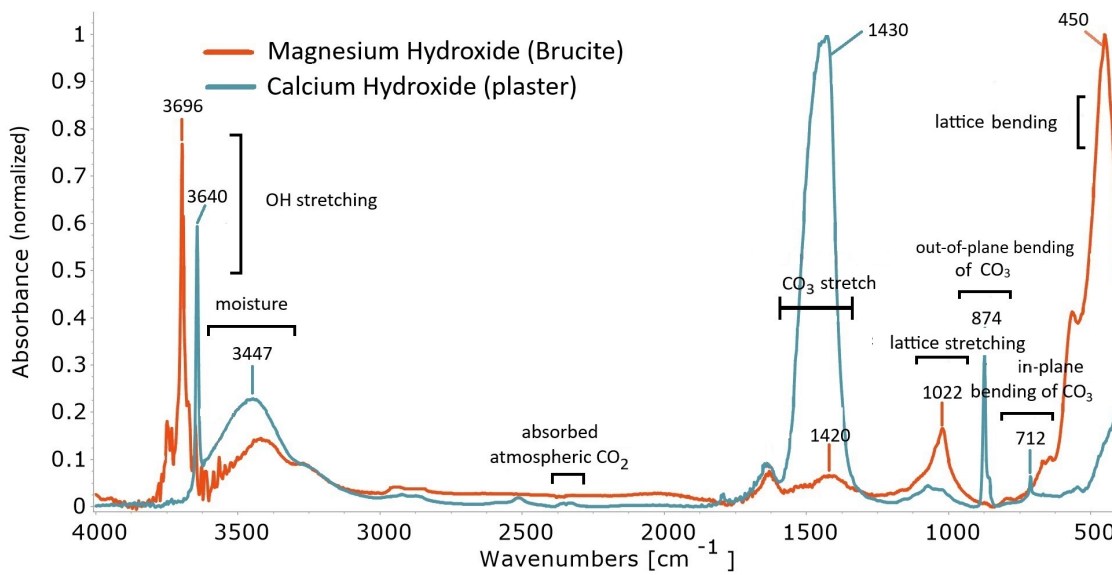
Figure 3.5: IR spectra comparison between $Ca(OH)_2$ and $Mg(OH)_2$ (normalized to set the highest peaks at a value of 1)
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- verifying the reaction taking place is the desired one. This is not necessary but can help us have an idea of what is going on underwater.

- detecting side reactions, which is beyond the scope of this thesis but is important in calculating the efficiency of the alkaline compounds.

- analyzing environmental impacts. Identifying the product produced is vital to understanding if those compounds will have any adverse impact on the environment.

- refining the method. A deeper understanding of the chemistry in the ocean will help us create better solutions/ methods for OAE.

Chapter 4

Conclusion

Ocean Alkalinity Enhancement represents a promising frontier in the fight against climate change. This study introduces the application of IR spectroscopy in OAE. As the role of OAE in climate change mitigation grows, the use of IR spectroscopy could become an invaluable asset for monitoring and optimizing this approach.

In this thesis, I have thoroughly applied IR spectroscopy to analyze the chemical reactions occurring during OAE processes, with a particular focus on alkaline magnesium and calcium compounds. While the primary emphasis has been on these two groups of solid compounds, the methodology holds the potential for expansion to other alkaline minerals that could be effective in OAE. Through this analytical approach, I was able to identify and compare distinct spectral changes of various minerals. These spectral features can be crucial in understanding the chemical environment of the oceans in future research. The results were revealing: they showed a clear pattern of how alkaline earth hydroxides and carbonates can be so similar yet so distinctly different. IR spectroscopy has been instrumental in visualizing to some extent how basic hydroxides interact with atmospheric CO_2 to form carbonates. We can also look at a spectrum and identify if there is a mixture of compounds, as highlighted in Figure 3.2, but our ability to delve into these phenomena in detail is constrained. This limitation is particularly apparent in this thesis, where the focus has solely been on solid materials and we couldn't use IR spectroscopy to analyze ions and molecules that are prevalent in the oceanic environment and play a crucial role in OAE reactions.

Nevertheless, the understanding gained from this study can significantly contribute to the ongoing efforts to apply OAE as a viable strategy for mitigating climate change,

offering a new lens through which we can optimize these crucial reactions. Future research should continue to explore this promising avenue, especially given the urgent need for effective strategies to minimize ocean acidification and atmospheric CO_2 levels.

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Appendix A

Peaks Discussed in the Thesis

All the papers used to identify and analyze the moieties and their corresponding peaks are listed in Section 3.2.2. But the table below was influenced and guided by the IR Spectrum Table and Chart by Millipore Sigma [19].
https://www.sigmaaldrich.com/CA/en/technical-documents/technical-article/analytical-chemistry/photometry-and-reflectometry/ir-spectrum-table

Wavenumber (cm^{-1})	Moieties	vibration type	compound
3700-3640	OH	stretching	hydroxide
3500-3200	$O-H$, intermolecular	stretching	water/moisture
2370-2300	CO_3	bending	atmospheric CO_2
1450-1420	$C=O$	stretching	carbonate
880-875	CO_3	bending	carbonate
750-710	CO_3	bending	carbonate

Appendix B

Database and Software

B.0.1 Database

Reference: Weizmann Institute of Science "The Helen and Martin Kimmel Center for Archaeological Science", https://centers.weizmann.ac.il/kimmel-arch/infrared-spectra-library.

The Kimmel Centre Infrared Spectra database [25] can be easily accessed and downloaded via this link: IR Spectra Library or this url: `https://centers.weizmann.ac.il/kimmel-arch/infrared-spectra-library`. Clicking the download button will download the entire library to your computer. However, it is straightforward to sort through and extract the specific spectra needed for work.

B.0.2 Software

QUASAR

Reference: Quasar, Version 1.9.0, 2023, https://midir.lightsource.ca/quasar/
Homepage: Quasar Mid-IR, URL: `https://midir.lightsource.ca/quasar/`
Download link: Quasar Download, URL: `https://quasar.codes/download/`
The download page has options for both Windows and macOS installation, along with guides and user manuals on how to install and use the application.

SPECTRAGRYPH

Reference: F. Menges "Spectragryph - optical spectroscopy software", Version 1.2.16.1, 2023, http://www.effemm2.de/spectragryph/

Homepage: Spectroscopy Ninja, SpectraGryph, URL: `https://www.effemm2.de/spectragryph/`

Download link: SpectraGryph Download, URL: `https://www.effemm2.de/spectragryph/down.html`

SpectraGryph installation is easy but requires some additional steps such as reading through the licensing requirements and filling out a download form. You can download the trial version and use it as much as needed since it the trial time limit is very generous. You can also email Dr. Friedrich Menges at info@effemm2.de for an activation key for the free version of the software with unlimited uses if the purpose of the use is non-commercial.