

**THE Mg/Ca RATIO AS A PALEOTHERMOMETER ALONG A
SALINITY GRADIENT IN THE ARABIAN GULF**

BY
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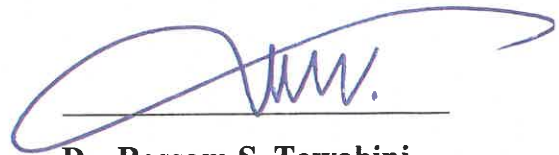
DEANSHIP OF GRADUATE STUDIES

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LIST OF ABBREVIATIONS

SEM-EDX: scanning electron microscope- energy dispersive x-ray detector

ICP-MS: inductively coupled plasma mass spectrometer

ICP-OES: inductively coupled plasma optical emission spectrometer

ABSTRACT

The ocean system is very dynamic and complex, hence there is a need to have the right assessment tools in case we have to measure the different environmental parameters like temperature and salinity. The problem is that reliable global records of climate only began in the 1880s and temperature cannot be measured directly from the past, consequently, scientists must utilize the idea of proxies. Scientists are studying the past climate of oceans to understand the past and to utilize its data to build and predict future climate for instance through models.

This study tests the utility of the proxy Mg/Ca ratio in foraminifera for use as a paleothermometer in the Arabian Gulf. The concept of this proxy is that foraminifera utilize the ions in the water to create their outer shells. However, depending on the features of the water, foraminifera will use magnesium instead of calcium to build their shells. This study is the first of its nature in the Arabian Gulf to test the accuracy and reliability of using the Mg/Ca ratio as a paleothermometer. It is important not because of the location but also because of the fact it studies benthic foraminifera as the majority of studies in the literature are for planktonic foraminifera because of the uncertainty arising between the difference in temperature of sea surface and bottom water.

The methodology used in this research follows the standard procedure for Mg/Ca ratio analysis in foraminifera, as follows: the living benthic foraminifera were isolated in the lab as per micropaleontological methods, placed in labeled microscope slides, and transferred to the geochemistry lab for analysis. The analysis includes using a scanning electron microscope (SEM-EDX) to perform elemental analysis by calculating the Mg/Ca ratio of foraminiferal shells using an Energy-dispersive X-ray spectroscopy detector in addition to imaging analysis to identify the species under study through its morphological features. The second type of analysis is Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the Mg/Ca ratio of foraminifera through the experiment of 0.3N HNO₃ digestion of the foraminifera.

The results show that the Mg/Ca ratio does not directly fit the calibration equation at high salinity in the Arabian Gulf as can be seen by the low values of R^2 (0.01-0.57), therefore we cannot rely upon the Mg/Ca ratio as a paleothermometer in the Arabian Gulf in areas where there is a high salinity gradient (51.60-79.70 PSU). Salinity impacts the paleothermometry calculations because foraminifera will absorb more Mg in their shells. My conclusion supports similar studies that the Mg/Ca ratio increases because of high salinity.

ملخص الرسالة

الاسم الكامل: أحمد أمين حسين السادة

عنوان الرسالة: نسبة المغنيسيوم/الكالسيوم كمقياس حرارة قديم على طول تدرج الملوحة في الخليج العربي

التخصص: علوم بيئية

تاريخ الدرجة العلمية: ديسمبر ٢٠٢٣م

تختبر هذه الدراسة فائدة نسبة المغنيسيوم/الكالسيوم لاستخدامها كمقياس حرارة قديم في الخليج العربي. هذه الدراسة هي الأولى من نوعها في الخليج العربي لاختبار دقة وموثوقية استخدام نسبة المغنيسيوم / الكالسيوم كمقياس حرارة قديم. إنها مهمة ليس بسبب الموقع فقط ولكن أيضا بسبب حقيقة أنها تدرس المنخربات القاعية (Benthic Foraminefra) حيث أن غالبية الدراسات العلمية هي للمنخربات العوالق (Planktonic Foraminefra) . المنهجية المستخدمة في هذا البحث هي ببساطة أن المنخربات القاعية الحية تم عزلها في المختبر وفقا لطرق علم الحفريات الدقيقة ، ووضعها في شرائح مجهرية موسومة ، ونقلها إلى مختبر الكيمياء الجيولوجية لتحليلها. يشمل التحليل المجهر الإلكتروني الماسح (SEM-EDX) لإجراء التحليل الأولي عن طريق حساب نسبة المغنيسيوم / الكالسيوم للمنخربات باستخدام كاشف التحليل الطيفي بالأشعة السينية المشتت للطاقة بالإضافة إلى بعض التصوير لتحديد النوع قيد الدراسة من خلال خصائصه المورفولوجية. النوع الثاني من التحليل هو قياس الطيف الكتلي للبلازما المقترن بالحث (ICP-MS) لمعرفة نسبة المغنيسيوم / الكالسيوم للمنخربات من خلال تجربة هضم HNO_3 للمنخربات. نتيجتي هي أن نسبة المغنيسيوم / الكالسيوم لا تتناسب بشكل مباشر مع معادلة المعايرة عند الملوحة العالية في الخليج العربي كما يتضح من القيم المنخفضة لـ R^2 ، بحيث لا يمكننا الاعتماد على نسبة المغنيسيوم / الكالسيوم كمقياس حرارة قديم في الخليج العربي في المناطق التي يوجد فيها تدرج ملوحة مرتفع (٥١,٦٠-٧٩,٧٠ PSU). يدعم استنتاجي دراسات مماثلة تفيد بأن نسبة المغنيسيوم / الكالسيوم تزداد بسبب الملوحة العالية.

CHAPTER 1

INTRODUCTION

1.1. Background

Foraminifera are microorganisms that resemble amoebas with tests (shells) made of calcium carbonate. Foraminifera utilizes the ions in the water to create their outer shells. However, depending on the features of the water, foraminifera will use magnesium in addition to calcium to build their shells. Consequently, foraminifera are good indicators of environmental variation as the ratio of magnesium to calcium in their shells can be measured to judge the environmental setup that they lived in. Also the study of foraminifera has an advantage over other microorganisms in that the group has a complete fossil record (Table 1 – The classification of the foraminifer under study).

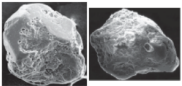
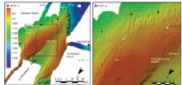
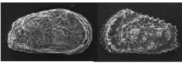
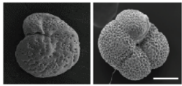
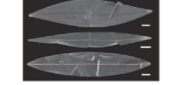
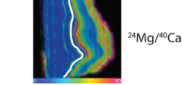
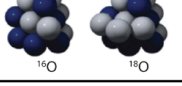
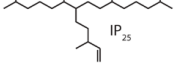
Table 1 : The scientific classification of foram under study

Domain	<i>Eukaryote</i>
Phylum	<i>Foraminifera</i>
Order	<i>Rotaliida</i>
Family	<i>Rotaliidae</i>
Genus	<i>Ammonia</i>
Species	<i>Ammonia tepida</i>

The ocean system is very dynamic and complex, hence there is a need to have the right assessment tools in case we have to measure the different environmental parameters like temperature and salinity. Scientists are studying the paleoclimatology of oceans to understand the past and to utilize its data to build and predict future climate for instance through models. Temperature cannot be measured directly from the past, consequently, scientists must find other ways by utilizing the idea of proxies. A proxy is simply a preserved physical, biological, chemical, and geological feature of the past that remains for the present that can be used for direct measurements of the different environmental

variables. Many proxies can be used to reconstruct the ocean temperature and different proxies have different geological ages in history (Table 2). In this study, I will focus on the foraminifera in the Arabian Gulf sediments as a paleoclimate proxy. And more specifically the Mg/Ca ratio of the foraminiferal calcite. The Arabian Gulf has distinctive features compared to other water bodies on earth. It is warm, saline, and relatively shallow as well as it is highly evaporative because of heat coming from the surrounding land besides the discharge of the desalination plants located in the shores of the gulf.

Table 2: Different types of proxies (Paleoceanographic Perspectives on Arctic Ocean Change. NOAA Arctic, 2017)

Proxy		Indicator Type	Explanation
Ice Rafted Debris		Sea Ice, Glaciers, Ice Sheets	Sediment-laden ice from continental margins drops terrigenous (land-based) material from melting ice and deposited on the seafloor
Bathymetry		Ice extent	Seabed features can be used to determine the extent and thickness of ice sheets and ice shelves that were large enough to scour the seafloor
<i>Microfossil Abundance</i>			Microscopic shell-building organisms that either float in the water column (planktic) or live on the seafloor (benthic) whose fossil remains are preserved in seafloor sediments.
Ostracodes		Sea Ice, Temperature	Bivalved Crustacea that secrete a pair of symmetrical calcium carbonate valves. They are found in a range of fresh and marine environments and can be planktic or benthic.
Foraminifera		Temperature, Seawater Chemistry	Single-celled organisms that secrete calcium carbonate shells (tests). They are distributed throughout the global ocean and can be planktic or benthic.
Diatoms		Sea Ice, Temperature	Photosynthetic algae that build siliceous skeletons (frustules) that are found in fresh and marine environments. They can be planktic or benthic and some species are suited to live within sea ice.
Dinoflagellate cysts		Sea Ice, Temperature	Many but not all are photosynthetic planktic organisms. They are often symbionts (e.g. corals or foraminifera). The dormant spore-life state (cysts) are excellently preserved in sediments
<i>Geochemistry</i>			The elemental and isotopic composition of foraminifera and ostracodes reflect changes in local environmental conditions. Species-specific effects require unique species proxy calibrations.
Mg/Ca		Temperature	Mg is substituted into the calcium carbonate lattice of microfossil shells as a function of temperature, with higher Mg/Ca coinciding with warmer temperatures
$\delta^{18}\text{O}$		Temperature, Global Ice Volume, Salinity	The fractionation of oxygen-16 and -18 depends on seawater temperature and global volume of terrestrial ice.
Biomarkers		Sea Ice	The concentration of a lipid biomarker, IP25, exclusively produced by sea ice dwelling diatoms in sediment organic matter is used to reconstruct extent and concentration of sea ice

This elemental ratio is one method to find out the past ocean temperature. It is often used for Quaternary and Pliocene reconstructions.

1.2. Mg/Ca Ratio

The major concept for Mg/Ca paleothermometry is that the concentration of magnesium in the foraminiferal shell is directly dependent on the temperature of the seawater (Nürnberg *et al.*, 1995). These shells are like geochemical archives. The relation between the concentration of Mg in calcite and temperature has been studied through different approaches like culturing, sediment traps, and core tops (Ferguson *et al.*, 2008; Healey, 2008; Gray 2019). There are different processes like diagenesis, carbonate sedimentation, and weathering that control the ratio of mg/ca in seawater throughout the long geological time (Schauble, 2014). Magnesium is available in seawater in a concentration of approximately 1300 ppm as it is the most available cation in the oceans after sodium (Na) (Lenntech website).

There are many water temperature proxies like foraminiferal Mg/Ca, coralline Sr/Ca ratios, foraminiferal assemblages, and alkenones (Ferguson *et al.*, 2008). By calculating the Mg/Ca ratio in foraminiferal shells, it is possible to reconstruct water temperatures of the ocean over geological timescales, with an error $<1^{\circ}\text{C}$ (Ferguson *et al.*, 2008). Experiments suggest that salinity, carbonate ion concentration, and pH influence the Mg/Ca ratio (Ferguson *et al.*, 2008). A major advantage of utilizing the Mg/Ca ratio as a paleoclimate proxy is that it allows quantitative estimation of water salinity and ocean temperature in combination with oxygen isotope measurements. Also, there are other advantages over other proxies. First, it is directly related to temperature unlike the oxygen isotope proxy which is affected by the isotopic composition of seawater. Second, the Mg/Ca ratio has long residence time (10^6 & 10^7 years for Ca and Mg respectively) so the concentrations of these two elements do not vary much with time (Barker *et al.*, 2005). Third, this ratio is used to measure temperature in different water depths based on the habitat of the species under study. Finally, the measurement of this ratio is simple and does not take long time in contrast to the oxygen isotope proxy.

Using the Mg/Ca ratio as a temperature proxy has different implications and applications, these implications include: reconstructions of the past oceans temperatures, validation of

the climate models through comparing the outputs of the models with the Mg/Ca ratio reconstructions so that researchers can validate the accuracy of these models, and climate variability by studying changes in the ratio in different locations and time periods scientist can study natural climate variability and assess the impact of human activities on the climate system.

1.3. Na/Ca Ratio

Salinity and temperature are the most important factors in studying the past circulation of oceans because they determine the ocean water density and consequently the thermohaline circulation (Wit, 2013). The importance of thermohaline circulation lies in the fact that it is playing a fundamental part in the redistribution of heat on the planet. As stated earlier, many water temperature proxies have been applied. In contrast, there is a shortage of proxies for salinity. Recently, one proxy for salinity has been suggested (Wit, 2013; Bertlich *et al.*, 2020; Watkins, 2021; Pacho *et al.*, 2023). This is the ratio of sodium to calcium in foraminiferal shells despite that it has been noted the ratio is regional and species-dependent as a reply to the salinity variations (Wit, 2013; Bertlich *et al.*, 2020; Watkins, 2021; Pacho *et al.*, 2023).

Similarly, the Na/Ca ratio has its own applications which include: reconstructions of the past oceans salinity, water mass dynamics as different water masses have different chemical compositions which include varying amounts of sodium and calcium, the dynamic environments of coastal areas and estuaries as these areas are affected by both terrestrial and oceanic processes leading to variations in salinity, and more integrated understanding of palaeoceanographic parameters as salinity is closely related to factors like evaporation, precipitation, river runoff, and ice melt (Mezger, 2016).

The purpose of the current study is to test the accuracy and reliability of using the Mg/Ca ratio of the foraminiferal species *Ammonia tepida* as a paleothermometer in the Arabian Gulf where a large salinity gradient is present. This species is available worldwide in shallow and brackish intertidal marine environments. It can tolerate a wide range of salinity and temperature. It has a Mg/Ca ratio ranging from about 20 to 150 mmol/mol as can be seen in Figure 1 under the *Rotaliidae*. The other objective of this study is to investigate the reliability of using the Na/Ca ratio of foraminifera as a direct and

independent salinity proxy taken in consideration that studying paleosalinity is more challenging than temperature as salinity of seawater is affected by different processes. These processes are sea ice formation, river discharge, balance between precipitation & evaporation, and waxing and waning of continental ice sheets.

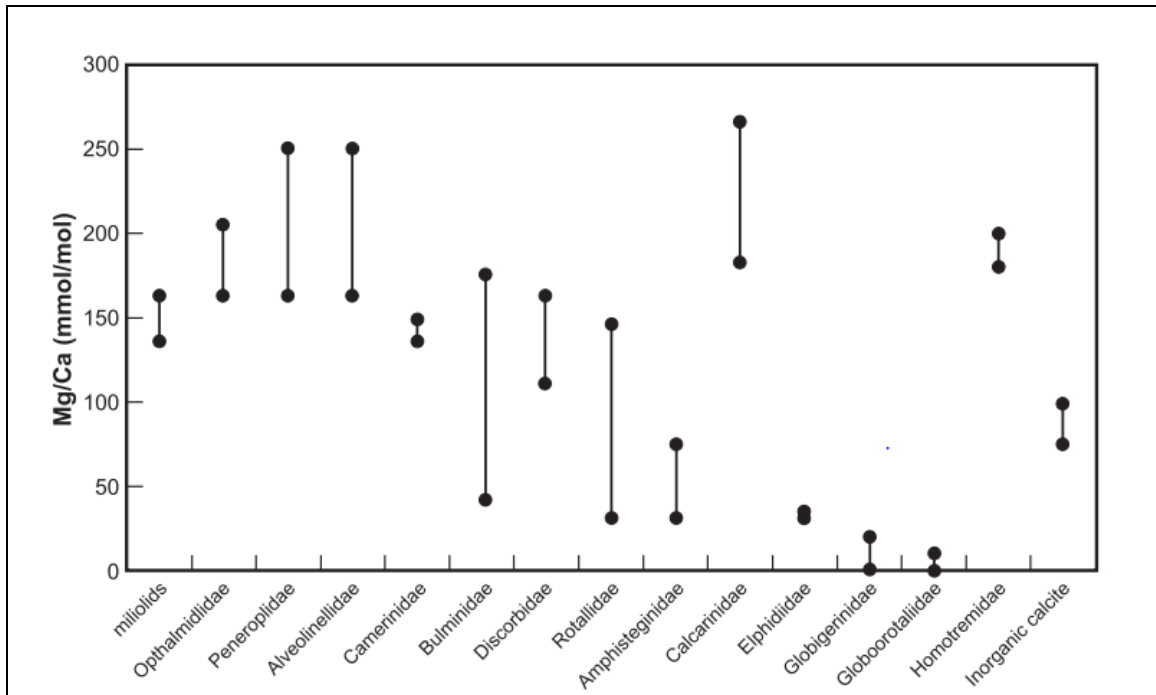


Figure 1: The Mg/Ca ratio of different groups of foraminifera (*Austin & James (eds), 2008*)

CHAPTER 2

LITERATURE REVIEW

It is important to first mention that this is the first study that examines the Mg/Ca ratio of foraminifera shells for use as a paleo thermometer taking into consideration the effects of a salinity gradient in the Arabian Gulf. This study is similar in scope to a study that has been done in the Mediterranean Sea (*Ferguson et al., 2008*).

Previous studies in this subject investigate the Mg/Ca ratio for use as a paleo thermometer and the importance of reconstructions of sea temperature to understand the past climate, however, the ratio is dependent on several factors such as salinity, dissolution, pH, and carbonate concentration (*Ferguson et al., 2008*).

Also, there are other proxies like Sr/Ca used for seawater carbonate chemistry as well as Na/Ca used for salinity (add citations). Consequently, to rely on the Mg/Ca ratio as a temperature proxy, one should study the effect of these parameters carefully. The effect of salinity on Mg incorporation into foraminiferal calcite is not well understood as per the literature. One common problem with the Mg/Ca as a temperature proxy as stated earlier is the dissolution of foraminifer shells. This lowers the Mg/Ca and causes miscalculation of ocean temperature. Benthic foraminifers which are the subject of this study are more resistant to dissolution than planktonic foraminifera.

One important parameter that should be stated is that all Mg/Ca studies that have been done on calcite older than Pleistocene must consider the Mg/Ca of the seawater from which it precipitated as per one study.

Mathematical equations have been established to quantify temperatures based on the Mg/Ca information (*Ferguson et al., 2008*). However, the equations disagree with one another and differ from one region to another. A single equation needs to be calibrated to the temperature and salinity conditions so that the method can be used regionally or globally.

There are many studies that investigated the effect of cleaning procedures on the Mg/Ca measurement. As per these studies, the removal of silicate contamination is the most

crucial step in the cleaning process. This is besides the oxidation of organic material step which may cause a reduction in the Mg/Ca ratio by about 10% (*Barker, 2003, Zarkogiannis et al., 2020, Martin and Lea, 2002*).

As a summary of literature, There are three approaches to generate the Mg/Ca temperature calibrations. Sediment trap (mainly used in the ocean), core top, and by culturing the foraminifera in the lab. Our study is similar to the core top as we are scouping the top layer of seawater sediment.

After reviewing the available literature, some research gaps have been identified:

- a) There needs to be more studies related to the paleoclimate proxies, there is a vital need to perform this kind of work in the Arabian Gulf. As stated earlier, this is the first study of its kind in the Arabian Gulf.
- b) Regression equations have been calculated to calibrate temperatures based on the Mg/Ca information. However, equations disagree with one another and differ from one region to another. A single equation needs to be calibrated for the proxy so that a unique method shall be used either globally in the open ocean or regionally in restricted marine basins such as the Arabian Gulf.
- c) Most of the calibrations developed in literature are for planktonic forams not benthic, because of the uncertainty arising between the difference in temperature of sea surface and bottom water (see Table 3 - The calibrations available in literature for benthic foraminifera). Consequently, this study is new not only because of the location but also because of the fact it utilizes benthic foraminifera.
- d) There are many studies in different locations in the world, but with different methodology (for example by using different instruments) as well as different species. Every study examines different species that are abundant for that particular location. Therefore, one should make an attempt to standardize the method and use same species that is available globally, like *Ammonia*.
- e) There is a need to perform field studies that examine the proposed direct independent salinity proxy Na/Ca, as the available studies in literature are lab culture based.

Table 3: The calibrations available in literature for benthic foraminifera

Species	B	A	Material	Region	Temperature Range (°C)
Exponential equations $Mg/Ca = B_{exp}(AT)$					
<i>C. pachyderma</i>	1.36	0.100	Low-Mg calcite	Little Bahama Banks, Hawaii	4.5–18
<i>C. pachyderma</i> , <i>C. wuellerstorfi</i>	0.85	0.11	Low-Mg calcite	Atlantic and Pacific	0–18
<i>C. pachyderma</i> , <i>C. wuellerstorfi</i> , <i>C. compressus</i>	0.87	0.11	Low-Mg calcite	Atlantic and Pacific	1–18
<i>Planulina spp.</i>	0.79	0.120	Low-Mg calcite	Pacific	2–12
<i>O. umbonatus</i>	1.01	0.114	Low-Mg calcite	Atlantic and Pacific	1–10
<i>O. umbonatus</i>	1.53	0.09	Low-Mg calcite	Atlantic	3–10
<i>Melonis spp.</i>	0.98	0.101	Low-Mg calcite	Atlantic and Pacific	1–18
<i>P. ariminensis</i>	0.91	0.062	Low-Mg calcite	Pacific	3–15
<i>Uvigerina spp.</i>	0.92	0.061	Low-Mg calcite	Atlantic and Pacific	2–18

Species	B	A	Material	Region	Temperature Range (°C)
Linear equations $Mg/Ca = B + AT$					
<i>C. pachyderma</i>	0.35	0.25	Low-Mg calcite	Little Bahama Banks, Hawaii	4–18
<i>C. pachyderma</i> , <i>C. wuellerstorfi</i>	1.28	0.16	Low-Mg calcite	Little Bahama Banks, Hawaii and Arctic	-1–18

				Ocean	
<i>C. pachyderma</i>	1.2	0.12	Low-Mg calcite	Florida Straits	6–19
<i>C. pachyderma</i>	0.7	0.14	Low-Mg calcite	Great Bahama Banks and Florida Straits	6–19
<i>Planoglabratella opercularis</i>	89.7	2.22	High-Mg calcite	Culture	10–25
<i>Quinqueloculina yabei</i>	66.0	2.9	High-Mg calcite	Culture	10–25
<i>Planoglabratella opercularis</i>	81.5	1.6	High-Mg calcite	Culture	10–25
<i>Hoeglundona elegans</i>	0.96	0.034	Aragonite	Core tops	2–18

CHAPTER 3

Materials and Methods

3.1. The Study Area

the sediment samples were collected from the lagoons in Aluqair. The distance between AlUqair and Dhahran is about 70 km from the south direction (see Fig. 2). The location consists of three connected ponds and the main beach, pond 1 is the outer one that is directly connected to the main beach, pond 2 is the middle one, and pond 3 is the smallest inner one. More information about the sample location are shown in Table 4.



Figure 2: Detailed map showing AlUqair Beach and the three ponds (the red dots represent the exact sample location).

Table 4: The GPS coordinates with water properties (temp, salinity, pH) at each location

Locality	GPS coordinates	Temperature (°C)	Salinity (PSU)	pH
AlUqair Beach (December)	25.706181, 50.229938	23.0	51.6	8.3
Pond 1	25.683865, 50.234768	22.0	56.5	8.3
Pond 2	25.710518, 50.177465	21.7	62.8	8.3
Pond 3	25.737776, 50.13472	21.5	65.7	8.2
AlUqair Beach (January)	25.706181, 50.229938	18.6	55.8	8.6
Pond 1	25.683865, 50.234768	17.1	59.5	8.4
Pond 2	25.710518, 50.177465	18.5	63.8	8.3
Pond 3	25.737776, 50.13472	17.6	64.4	8.3
AlUqair Beach (February)	25.706181, 50.229938	23.6	60.1	8.5
Pond 1	25.683865, 50.234768	19.6	61.4	8.4
Pond 2	25.710518, 50.177465	21.1	65.8	8.4
Pond 3	25.737776, 50.13472	21.6	70.0	8.5
AlUqair Beach (March)	25.706181, 50.229938	29.6	63.6	8.4
Pond 1	25.683865, 50.234768	24.8	65.8	8.5
Pond 2	25.710518, 50.177465	24.7	72.5	8.4
Pond 3	25.737776, 50.13472	25.4	74.4	8.5
AlUqair Beach (April)	25.706181, 50.229938	28.7	63.1	8.4
Pond 1	25.683865, 50.234768	27.0	66.0	8.3
Pond 2	25.710518, 50.177465	27.7	73.1	8.5
Pond 3	25.737776, 50.13472	27.1	76.8	8.5
AlUqair Beach (May)	25.706181, 50.229938	35.0	62.8	8.5
Pond 1	25.683865, 50.234768	31.4	66.4	8.5
Pond 2	25.710518, 50.177465	31.5	74.7	8.4
Pond 3	25.737776, 50.13472	30.8	78.0	8.3
AlUqair Beach	25.706181, 50.229938	32.8	61.2	8.5

(June)				
Pond 1	25.683865, 50.234768	30.8	68.2	8.5
Pond 2	25.710518, 50.177465	30.7	77.1	8.4
Pond 3	25.737776, 50.13472	29.8	79.7	8.4
AlUqair Beach (July)	25.706181, 50.229938	37.9	64.7	8.6
Pond 1	25.683865, 50.234768	36.1	67.9	8.6
Pond 2	25.710518, 50.177465	37.0	77.9	8.7
Pond 3	25.737776, 50.13472	36.8	79.2	8.5

3.2. Sample Collection

Eight sediment samples (four stained with Rose bengal and four unstained) were collected and preserved in closed sample jars at the end of every month for eight months. Two from Aluqair beach and six samples from the three associated lagoons with the main beach of Aluqair where we have already temperature monitoring stations so that we can compare the experimentally determined temperature with the measured temperature in the monitoring stations. Importantly, we know the temperature of the seawater in which the foraminifera secrete their shells. The reason behind collecting two sediment samples from each location is to help in picking the maximum number of the desired foram species. The sediment samples were collected by scouping the upper layer of sediment about one meter deep and about 100 meter in the main beach next to the fish traps in the sea and about 50 meters from the shore in the three ponds. The sediments samples were kept wet in glass jars with some air to keep the living foraminifera alive. Table 4 gives detailed information showing the sample collection months, coordinates, and water properties (temp, salinity, pH) at each location.

3.3. Micropaleontological Methods

After a minimum of two weeks, the stained sediment samples were washed with tap water until the pink Rose Bengal stain disappears as well as sieved with a 63-micron aperture sieve to remove the clay before drying in the oven at 60-70 °C for 6 hours. The unstained sample was transferred to a petri dish and kept wet. The foraminifera were

separated using an eye-dropper, and then sieving. After that, the living foraminifera were separated from the nonliving foraminifera (the living ones will be filled with cytoplasm and they are moving) by using a paintbrush, under a binocular optical microscope. Specimens were placed in labeled microscope slides and transferred to the geochemistry lab.

3.4. Laboratory Methods

In order to determine the Mg/Ca ratio: As per literature, the most recent analytical instruments to get the Mg/Ca ratio are Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (*Toyofuku et al., 2000*).

We separated the living benthic foraminifera from the collected samples and tested for the geochemistry part using a scanning electron microscope (SEM-EDX. The model is JEOL JCM-7000 (DESKTOP SEM) to determine the Mg/Ca ratio (see figure 3). The Inductively Coupled Plasma Mass Spectrometer (ICP-MS) to compare the results from each instrument, and based on the results from these instruments we examined the relationship between Mg/Ca ratios and temperature measured at the time of sample collection.

3.4.1. SEM-EDX method:

We picked 5 specimens from the four locations (Aluqair Beach, pond 1, pond 2, pond 3) a total of 20 samples and then analyzed the last chamber of the foram where the aperture is located (see figure 4). The reason behind pinning the last chamber is to get accurate and precise measurements of the Mg/Ca ratio since this is the last chamber that has been built when the temperature was recorded. Finally, we used the average value of the five specimens.



Figure 3: SEM/EDX System



Figure 4: SEM photos of *Ammonia tepida* species.

3.4.2. ICP-MS method

We weighed 20 specimens and placed them in a beaker. Then 10 ml of 0.3 N HNO_3 was added. Next, we heated and stirred for 10 minutes at 80 °C. Finally, we placed the sample into labeled plastic vials for the ICP-MS (Toyofuku, 2000). The ICP-MS model is iCAP RQ from Thermo SCIENTIFIC (see figure 5). The standard method used in the analysis is EPA 6020B.

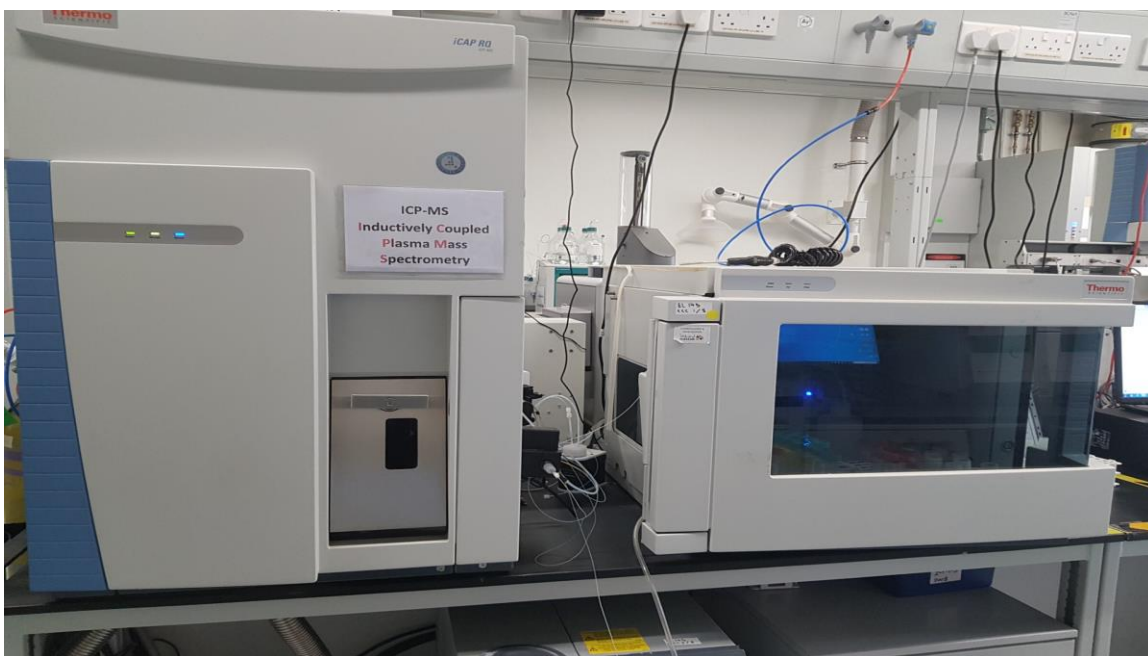


Figure 5: ICP/MS System

CHAPTER 4

RESULTS

The results section is arranged per month starting from December to July. In every month, the results include SEM-EDX results, followed by the results from the ICP-MS & ICP-OES for the foraminifera. Also, a sample calculation (an example of how to convert from mass % and ppm into mmol/mol) has been made based on which the rest of the calculations are done. The SEM-EDX results are mainly include Mg & Ca concentrations in mass % as these two elements are of particular concern for this study. To be more accurate and precise 5 samples (forams) from every location (Uqair Beach (fs), Pond 1, Pond 2, Pond 3) were pinned in the SEM-EDX, and then the average of the five results were taken. Regarding the ICP-MS results, the results include concentrations of Mg, Ca, Na in ppm in order to calculate the Mg/Ca & Na/Ca ratios. At last, the ICP-OES results of seawater are also given. It includes the concentrations of Mg, Ca in ppm in the seawater. Ideally speaking, the results of SEM-EDX should match the results of ICP-MS in all months (December to July) regarding the value of Mg/Ca ratio in the foraminiferal shells, but in reality it is only matching in January, February, and to some extent in April (see Figure 6,7). Possible reasons for this mismatching are highlighted in the discussion part.

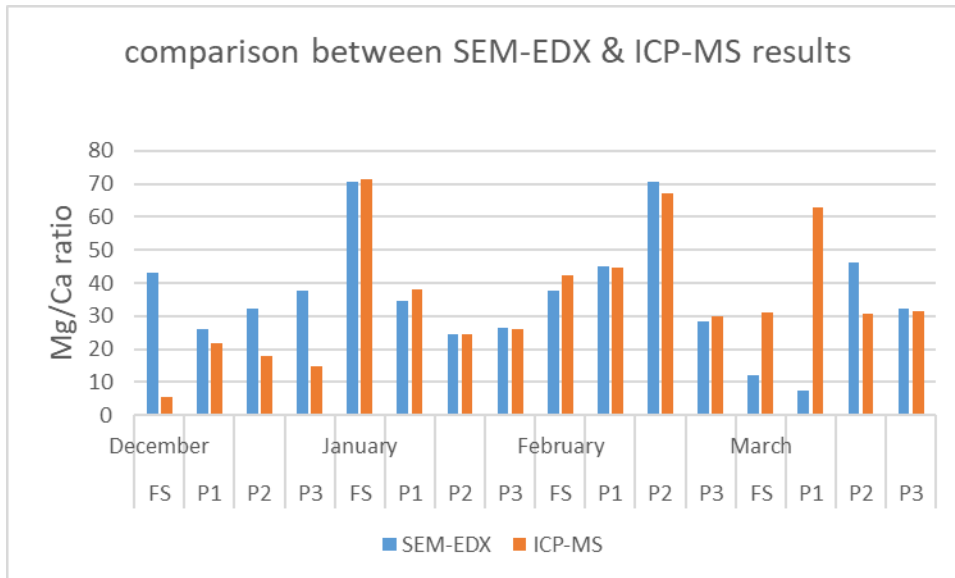


Figure 6: The SEM-EDX & ICP-MS results for (December-March).

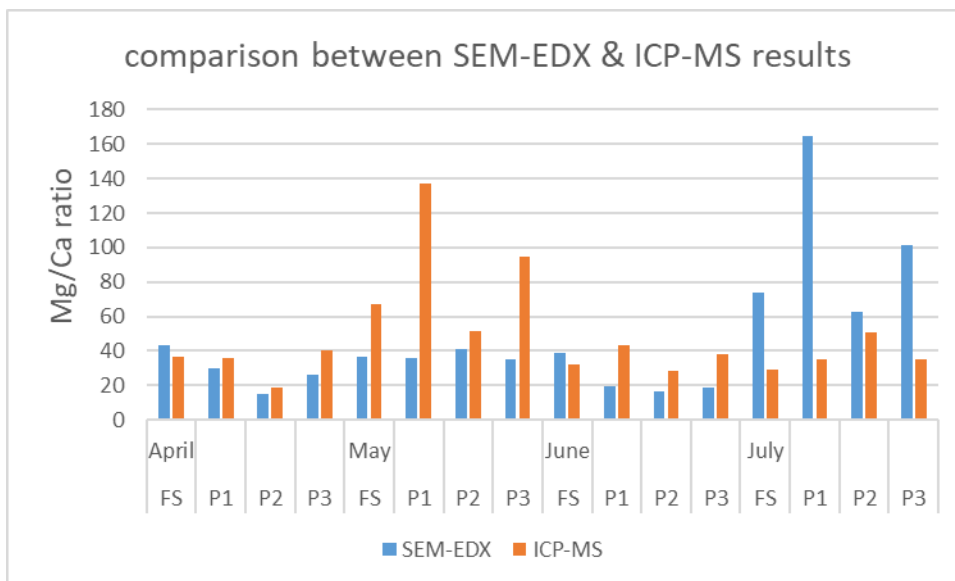


Figure 7: The SEM-EDX & ICP-MS results for (April-July).

It is good to mention here that we relied on the ICP-MS results not the SEM-EDX to generate the graphs for the months where there is a mismatch, as the ICP-MS is more sensitive. Also, the monthly results of the Mg/Ca ratio does not showing any trend from December to July at all four locations under study (Uqair Beach (fs), Pond 1, Pond 2, Pond 3). For example, in Uqair Beach the values of Mg/Ca ratio is 5,72,42,31,37,67,32,29 from December to July respectively. Consequently, there is no monthly increment in the value of Mg/Ca ratio in contrast to the literature. Possible justifications for this are mentioned in the discussion part. The maximum value of Mg/Ca ratio was 137 and it was recorded at first pond in May at 31.4°C and 66.4 PSU. Whereas the minimum value of Mg/Ca ratio was 5 at Uqair Beach in December at 23°C and 51.6 PSU. The average value was 42 at Uqair beach at 23.6°C and 60.1 PSU in February. The maximum value of Na/Ca ratio was 1645 and it was recorded at third pond in January at 17.6°C and 64.4 PSU. Whereas the minimum value of Na/Ca ratio was 2 at first pond in December at 22°C and 56.5 PSU. The average value was 333 in second pond at 30.7°C and 77.1 PSU in June (see Figure8-Figure13).

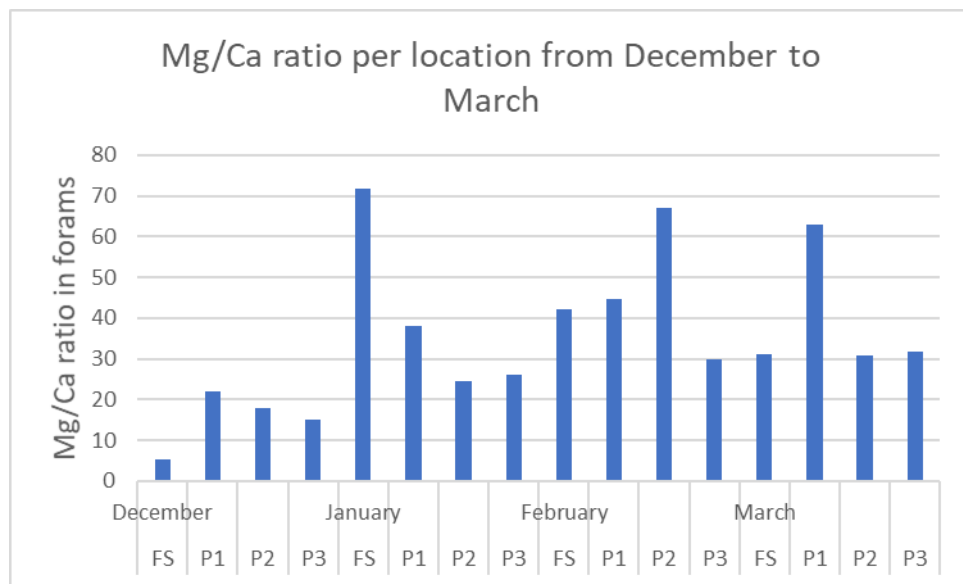


Figure 8: Mg/Ca ratio per location from December to March Based on ICP/MS

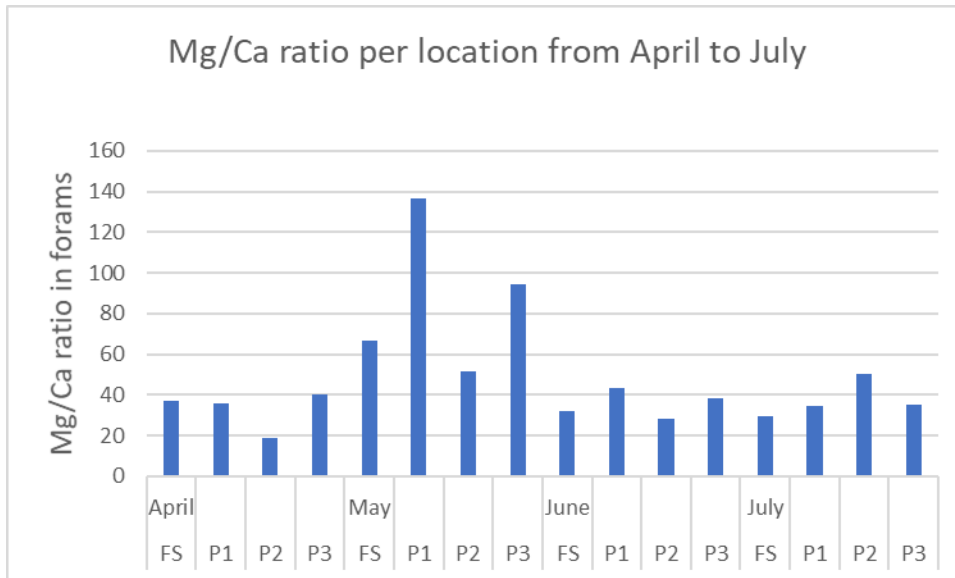


Figure 9: Mg/Ca ratio per location from April to July Based on ICP Results

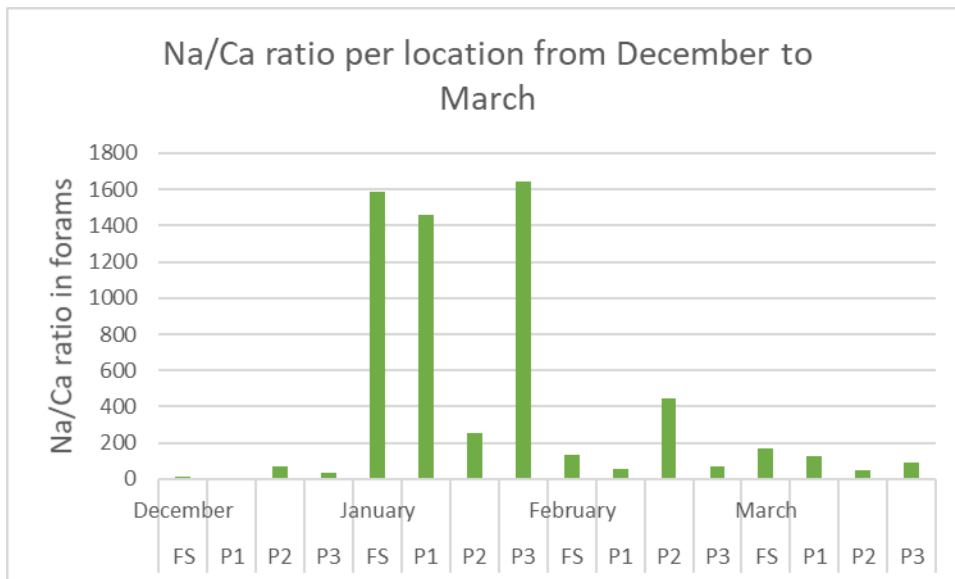


Figure 10: Na/Ca ratio per location from December to March Based on ICP Results

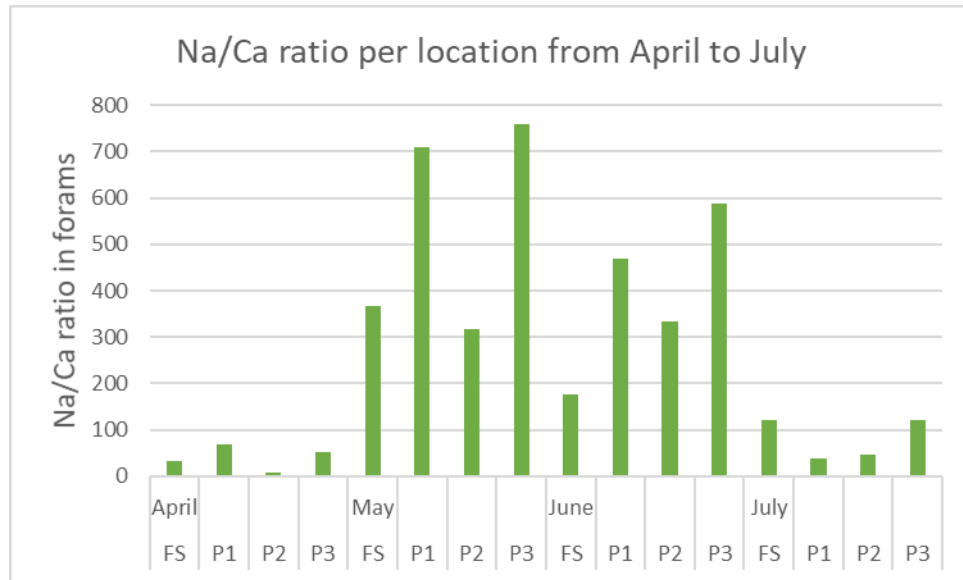


Figure 11: Na/Ca ratio per location from April to July Based on ICP Results

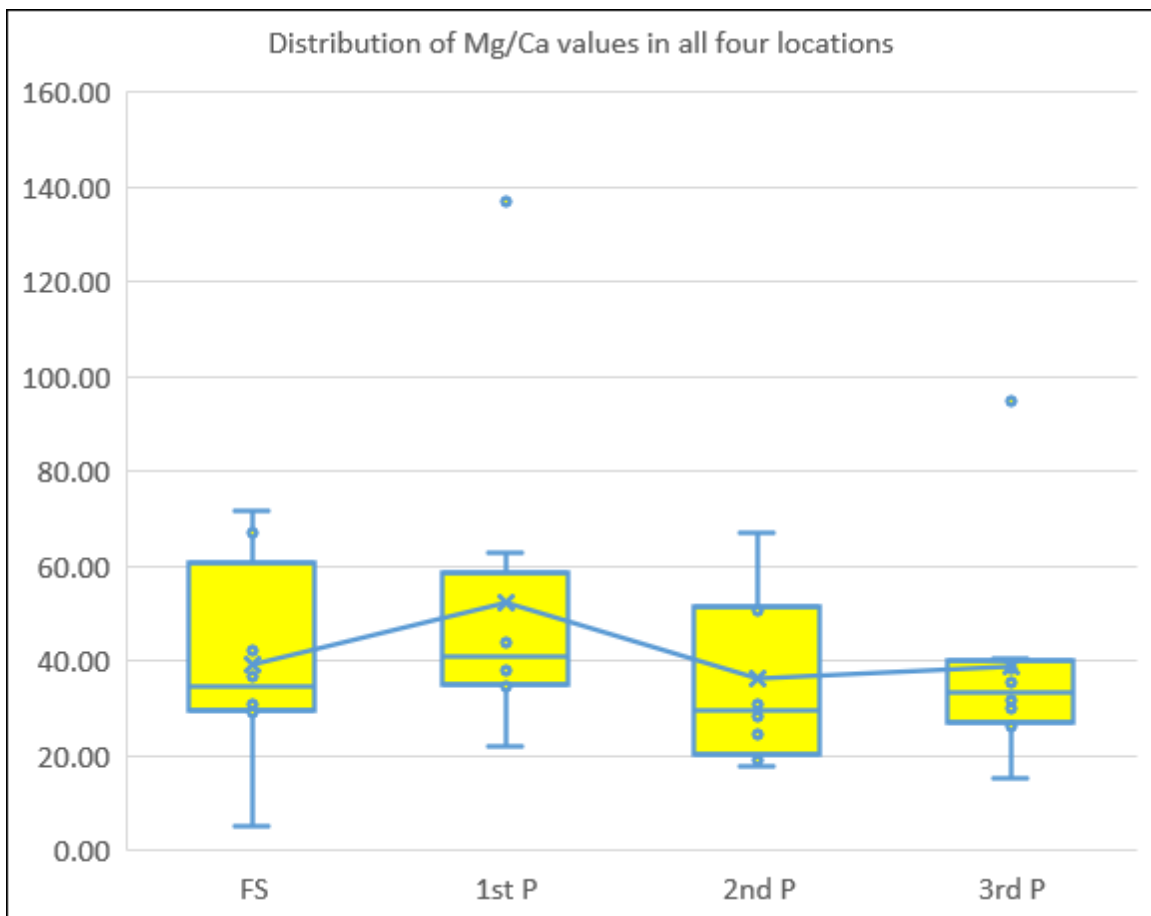


Figure 12: Distribution of Mg/Ca values in all four locations.

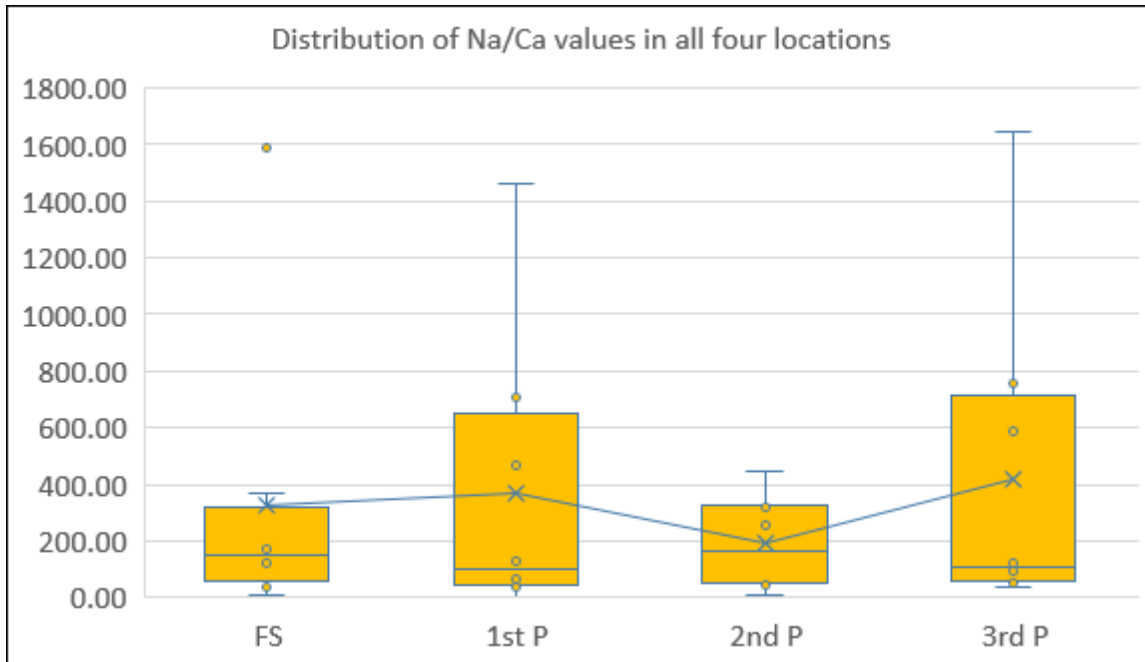


Figure 13: Distribution of Na/Ca values in all four locations.

The maximum temperature in this study was 37.9°C and it was measured by the multi-meter probe in July at Uqair Beach. Whereas the minimum temperature was 17.1°C in January at first pond. The average temperature was 27.7°C in April at the second pond.

The maximum salinity in this study was 79.7 PSU and it was measured by the multi-meter probe in June at the third pond. Whereas the minimum salinity was 51.6 PSU in December at Uqair Beach. The average salinity was 65.7 PSU in December at the third pond. The maximum pH in this study was 8.7 and it was measured by the multi-meter probe at pond 2 in July. In contrast, the minimum pH was 8.2 in December at pond 3.

The monthly results of the ICP-OES regarding the concentrations of Mg & Ca in seawater (see figure 14-15) are about 2126 ppm for Mg, and about 875 ppm for Ca in all months as an average. The maximum concentration of Mg was 2960 ppm at P3 in February. In contrast, the minimum concentration of Mg was 1291 ppm at Uqair Beach in

July. Regarding the Ca concentration, the maximum value was 1322 ppm in July at Uqair Beach. Whereas the minimum concentration was 428 ppm in February at Uqair Beach.

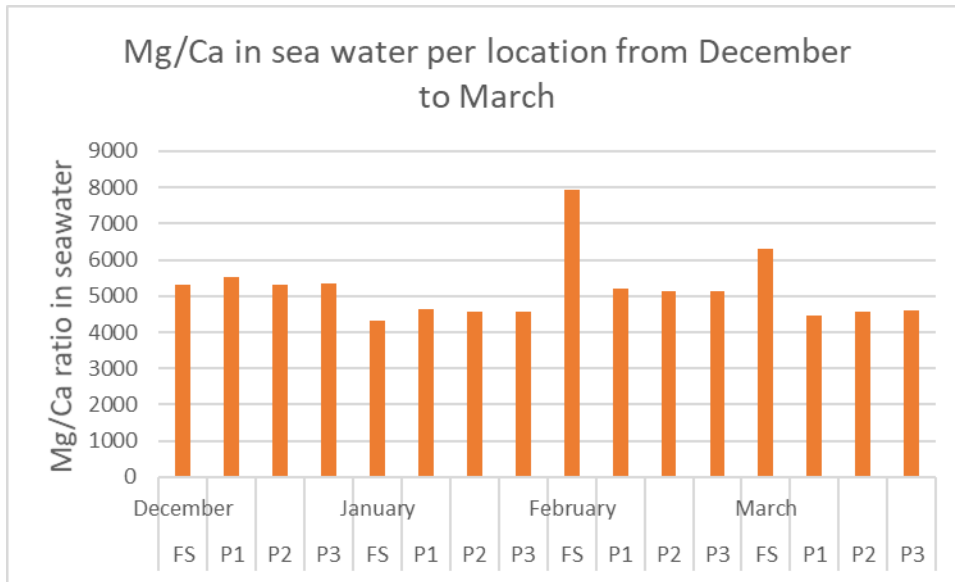


Figure 14: Mg/Ca in sea water per location from December to March.

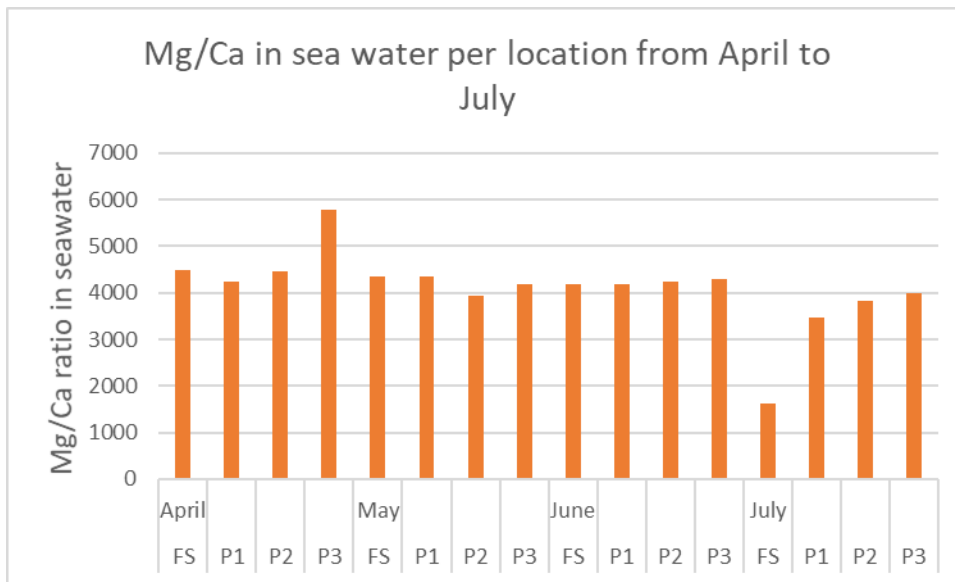


Figure 15: Mg/Ca in sea water per location from April to July.

The graph (figure 16) of Mg/Ca (mmol/mol) vs Temperature(°C) shows poor correlation (< 0.70) as can be seen by the low values of the R^2 . The range of R^2 is between 0.01 and 0.57. Consequently, the ratio of Mg/Ca can not be used as temperature proxy in all months.

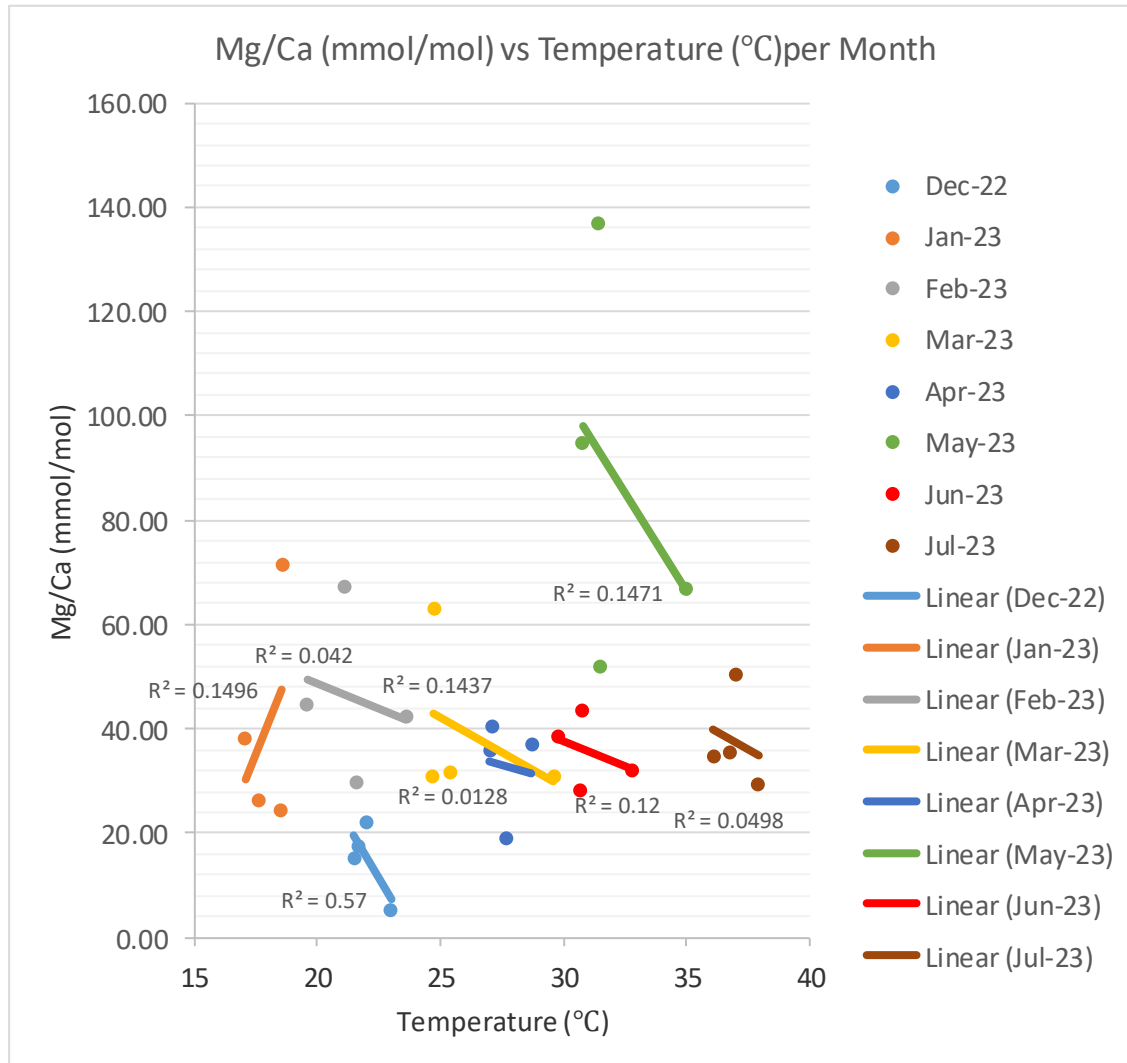


Figure 16: Mg/Ca (mmol/mol) vs Temperature(°C) [Per Month]

According to the graph (figure 17), the Uqair beach (fs) shows the lowest correlation ($R^2=0.01$) between Mg/Ca ratio and temperature. This is compared to the P3 which shows highest correlation ($R^2=0.22$). while P1 & P2 are in the middle with $R^2 = 0.1$ & 0.06 respectively.

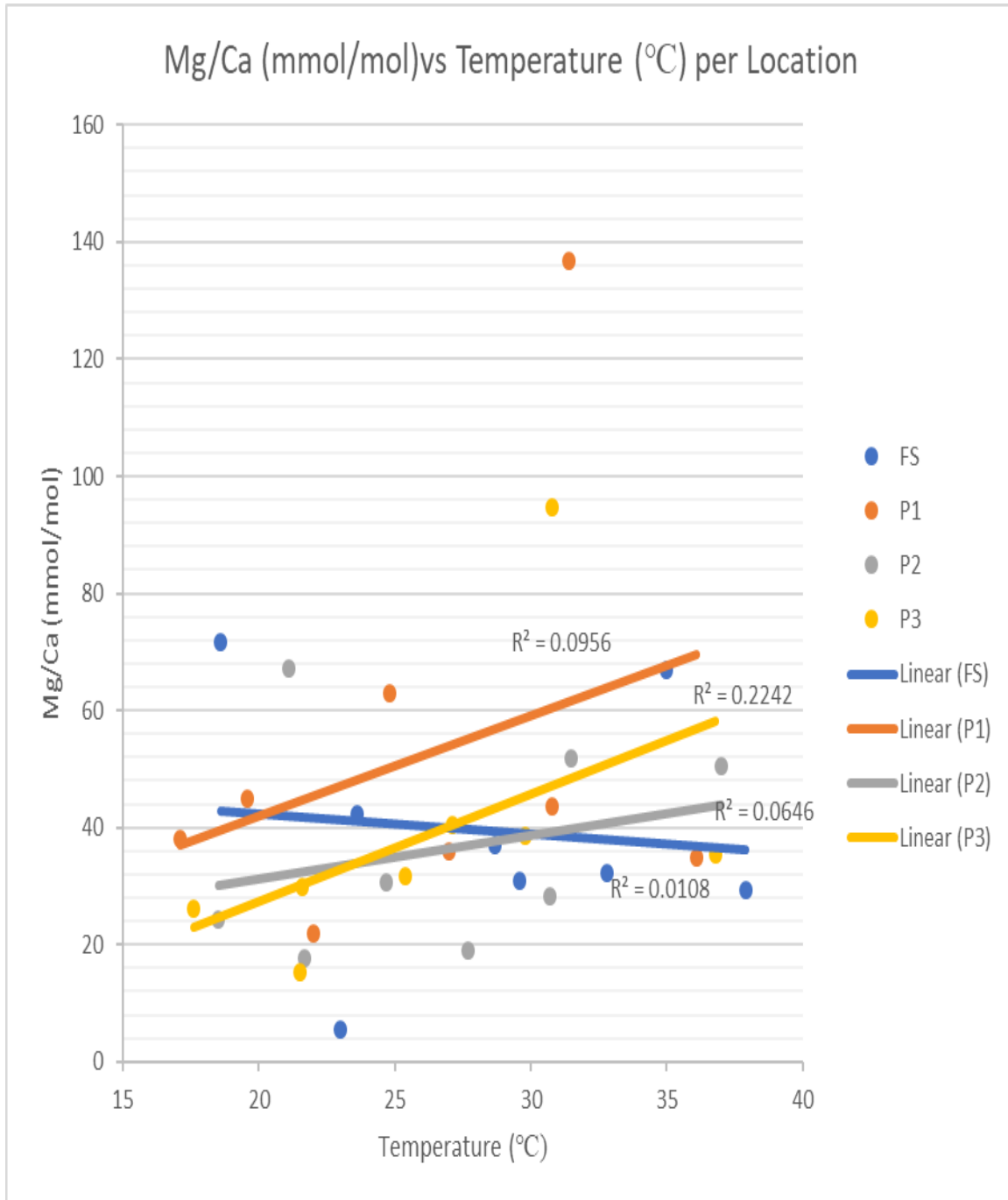


Figure 17: Mg/Ca (mmol/mol) vs Temperature(°C) [Per location]

The graph (figure 18) of Mg/Ca (mmol/mol) vs Salinity (PSU) shows poor correlation (< 0.70) except for the month of January where $R^2=0.908$. The range of R^2 is between 0.003 and 0.908.

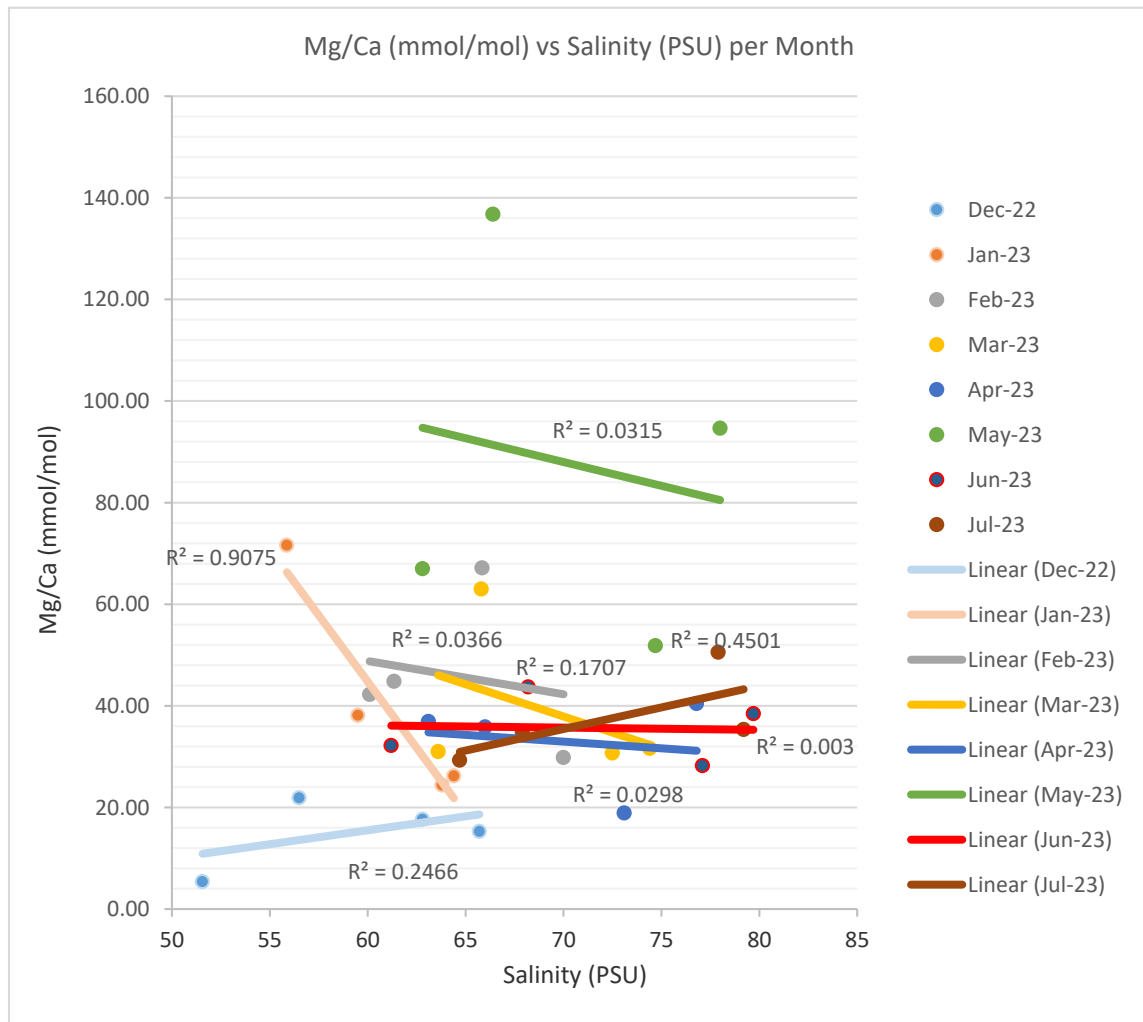


Figure 18: Mg/Ca (mmol/mol) vs Salinity (PSU) [Per month]

The graph (figure 19) of Mg/Ca (mmol/mol) vs Salinity (PSU) shows poor correlation (< 0.70) in all four locations. The range of R^2 is between 0.035 in P2 and 0.303 in P3.

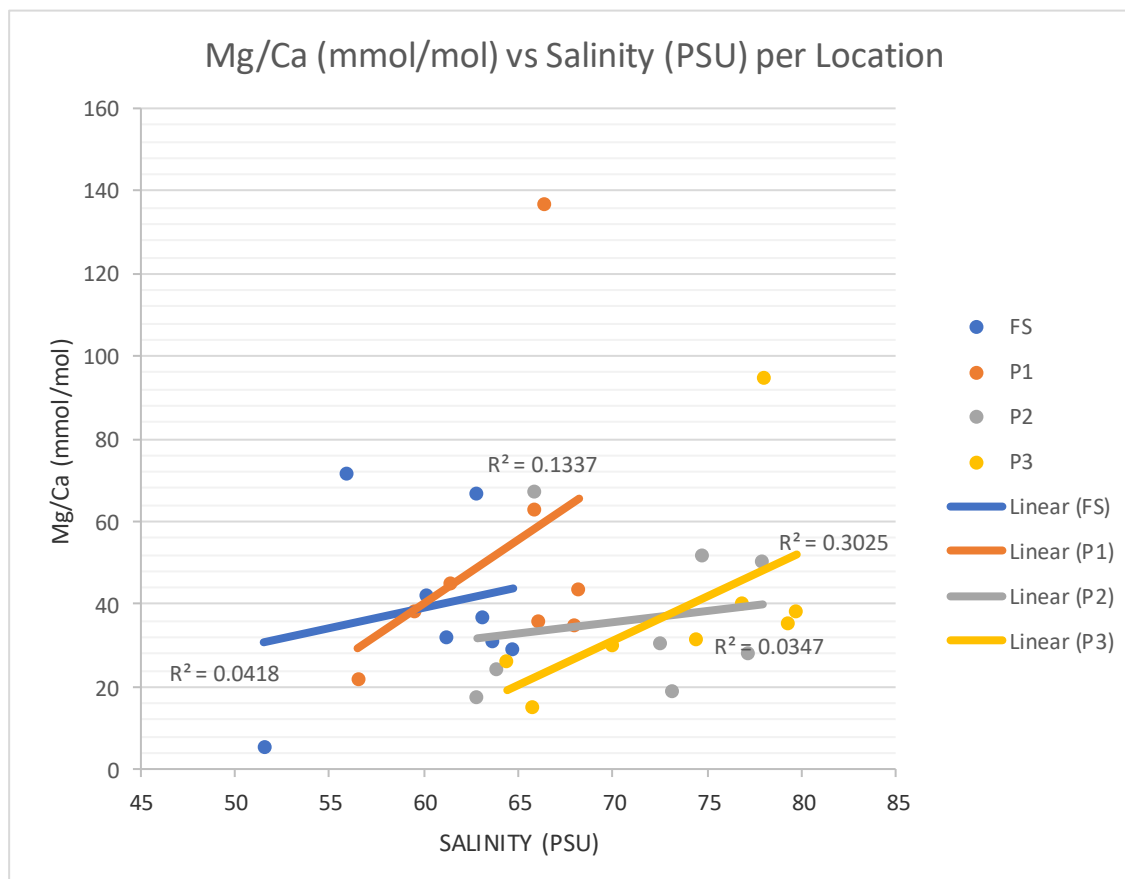


Figure 19: Mg/Ca (mmol/mol) vs Salinity (PSU) [Per location]

The graph (figure 20) of Na/Ca (mmol/mol) vs Salinity (PSU) shows poor correlation (<0.70) as can be seen by the low values of the R^2 . The range of R^2 is between 0.003 and 0.763. Hence, the ratio of Na/Ca can not be used as salinity proxy except for the month of May when value of R^2 was 0.763.

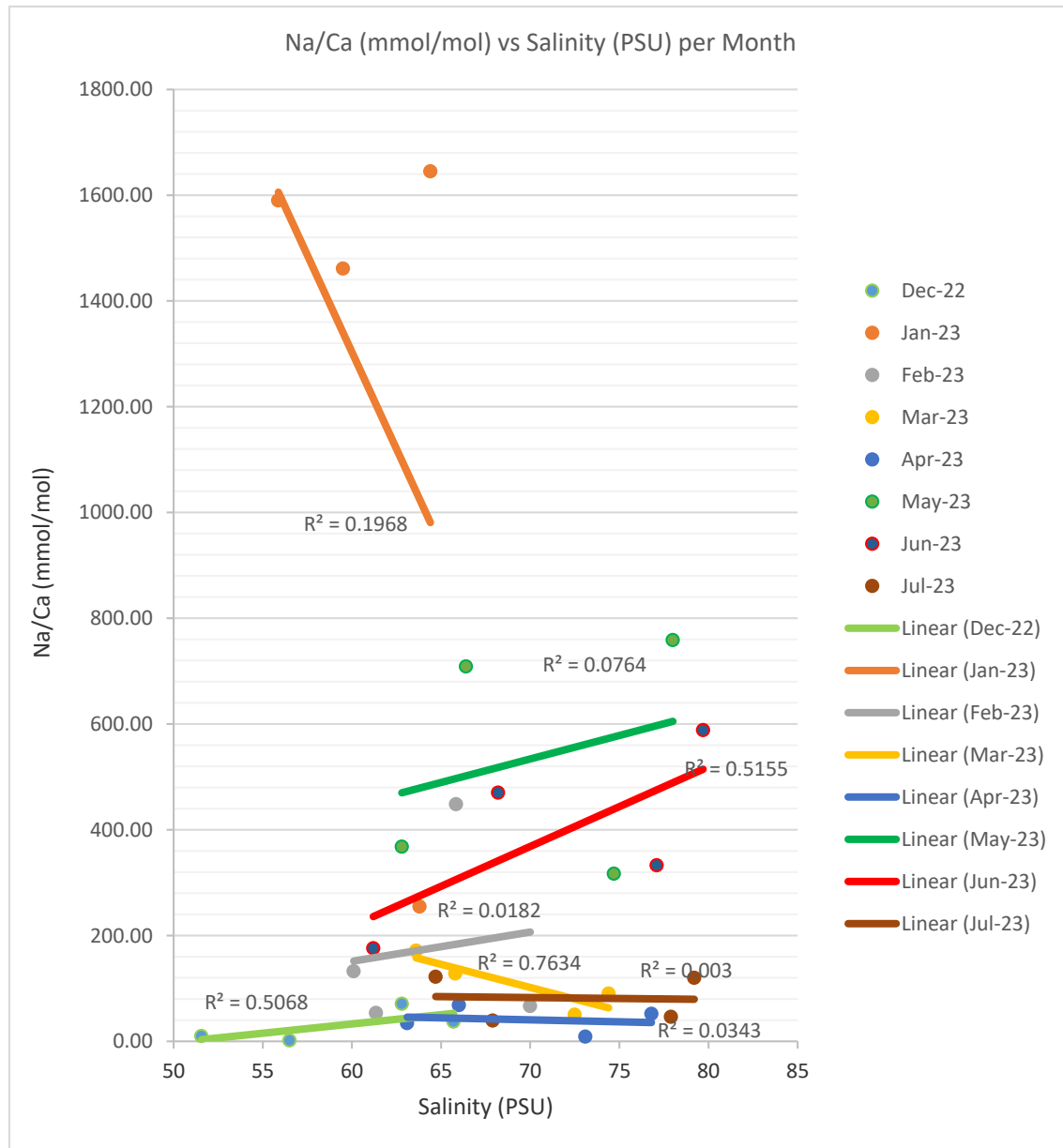


Figure 20: Na/Ca (mmol/mol) vs Salinity (PSU) [Per month]

According to the graph (figure 21), the Uqair beach (fs) and P3 shows the highest correlation ($R^2=0.09$) between Na/Ca ratio and salinity, while P1 & P2 shows the lowest correlation ($R^2=0.02$).

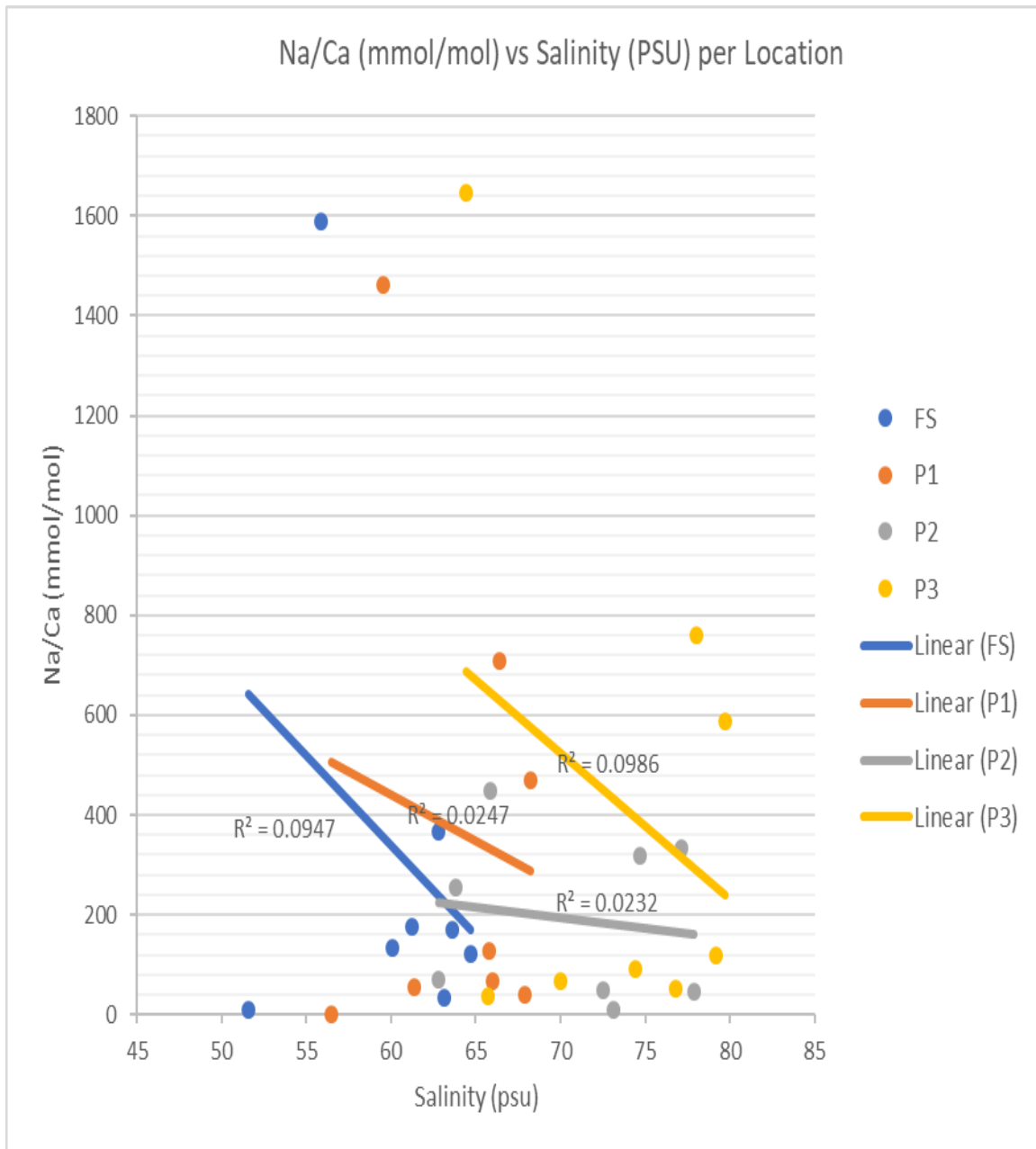


Figure 21: Na/Ca (mmol/mol) vs Salinity (PSU) [Per location]

The graph (figure 22) of Na/Ca (mmol/mol) vs Temperature ($^{\circ}\text{C}$) shows poor correlation (<0.70) as can be seen by the low values of the R^2 except for the month of June where $R^2 = 0.850$. The range of R^2 is between 0.0006 in February and 0.850 in June.

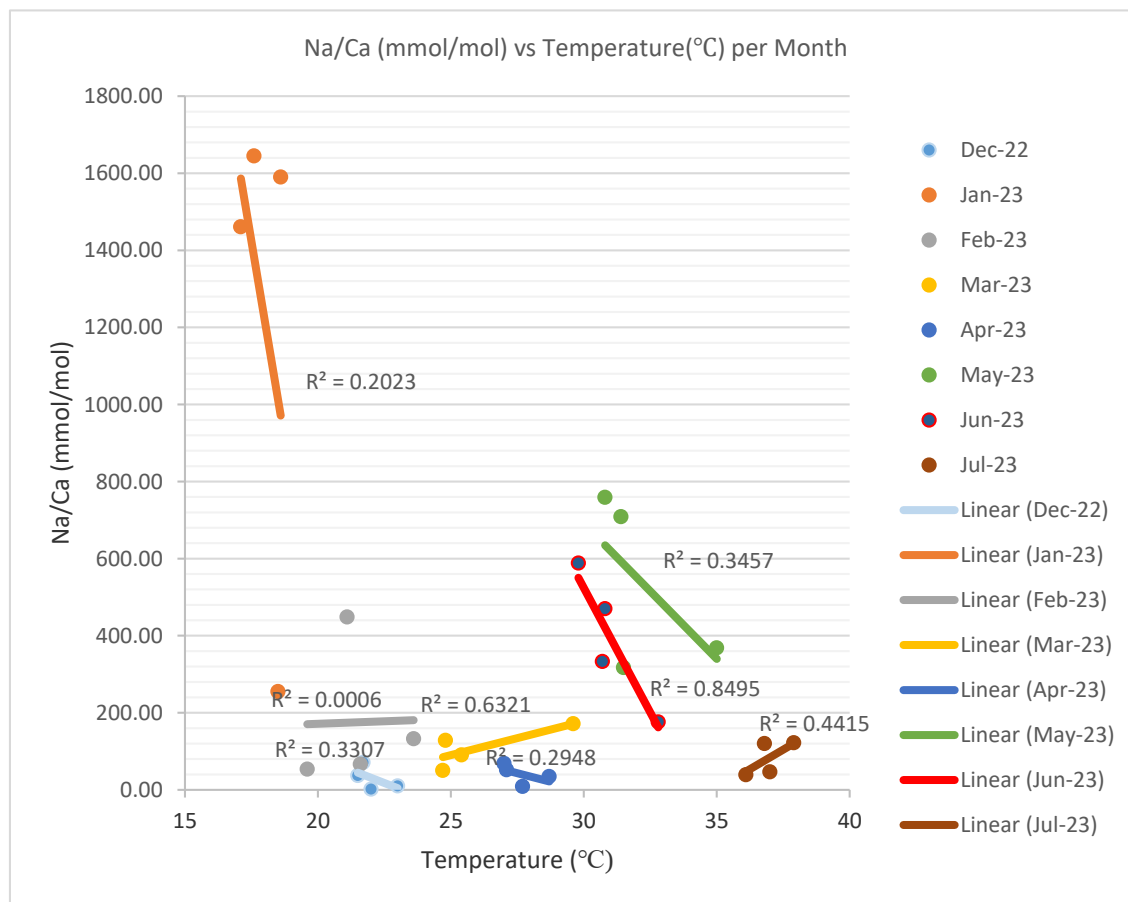


Figure 22: Na/Ca (mmol/mol) vs Temperature (°C) [Per month]

The graph (figure 23) of Na/Ca (mmol/mol) vs Temperature (°C) shows poor correlation (<0.70) as can be seen by the low values of the R^2 in all four locations. The range of R^2 is between 0.047 in P2 and 0.264 in FS.

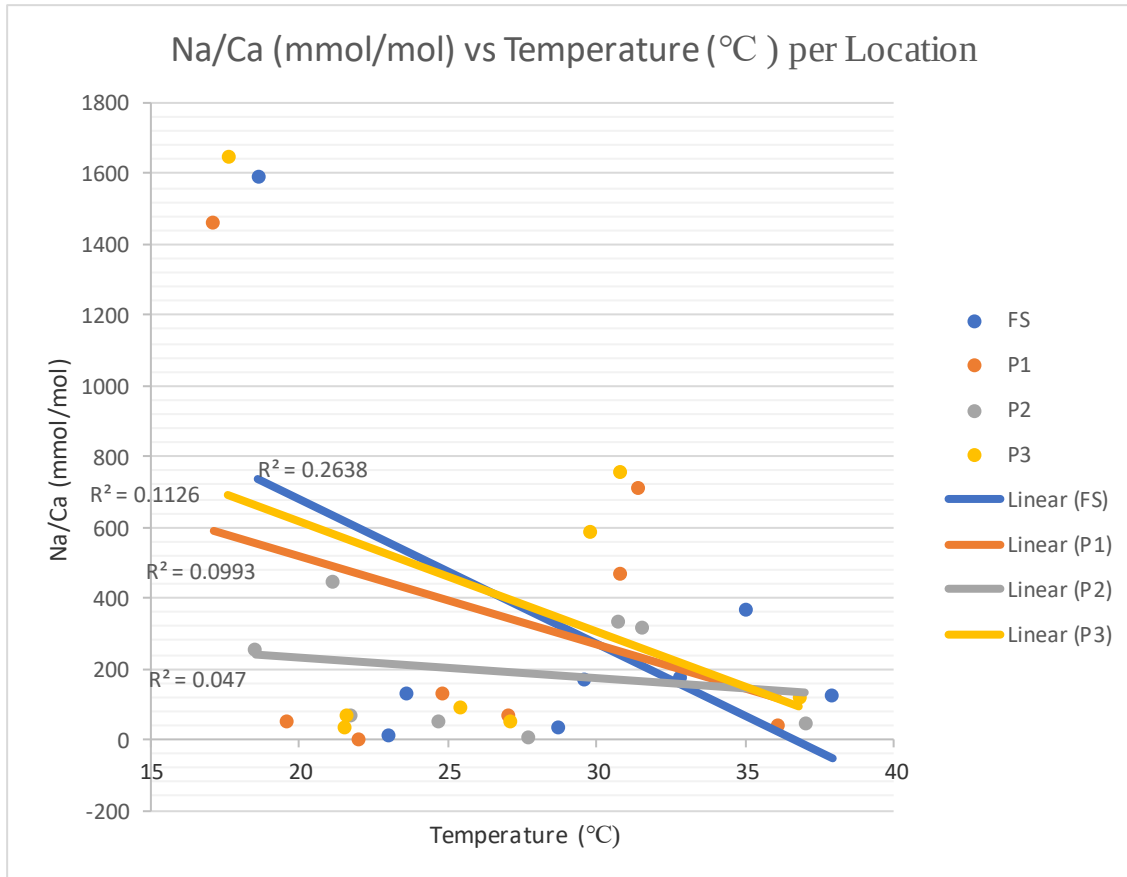


Figure 23: Na/Ca (mmol/mol) vs Temperature (°C) [Per location]

As per the graph (figure 24), the Mg/Ca ratio in forams has a poor correlation (<0.70) with Mg/Ca ratio in seawater except for the month of January where $R^2 = 0.77$. The range of R^2 in the rest of the months is between 0.015 in June and 0.38 in July.

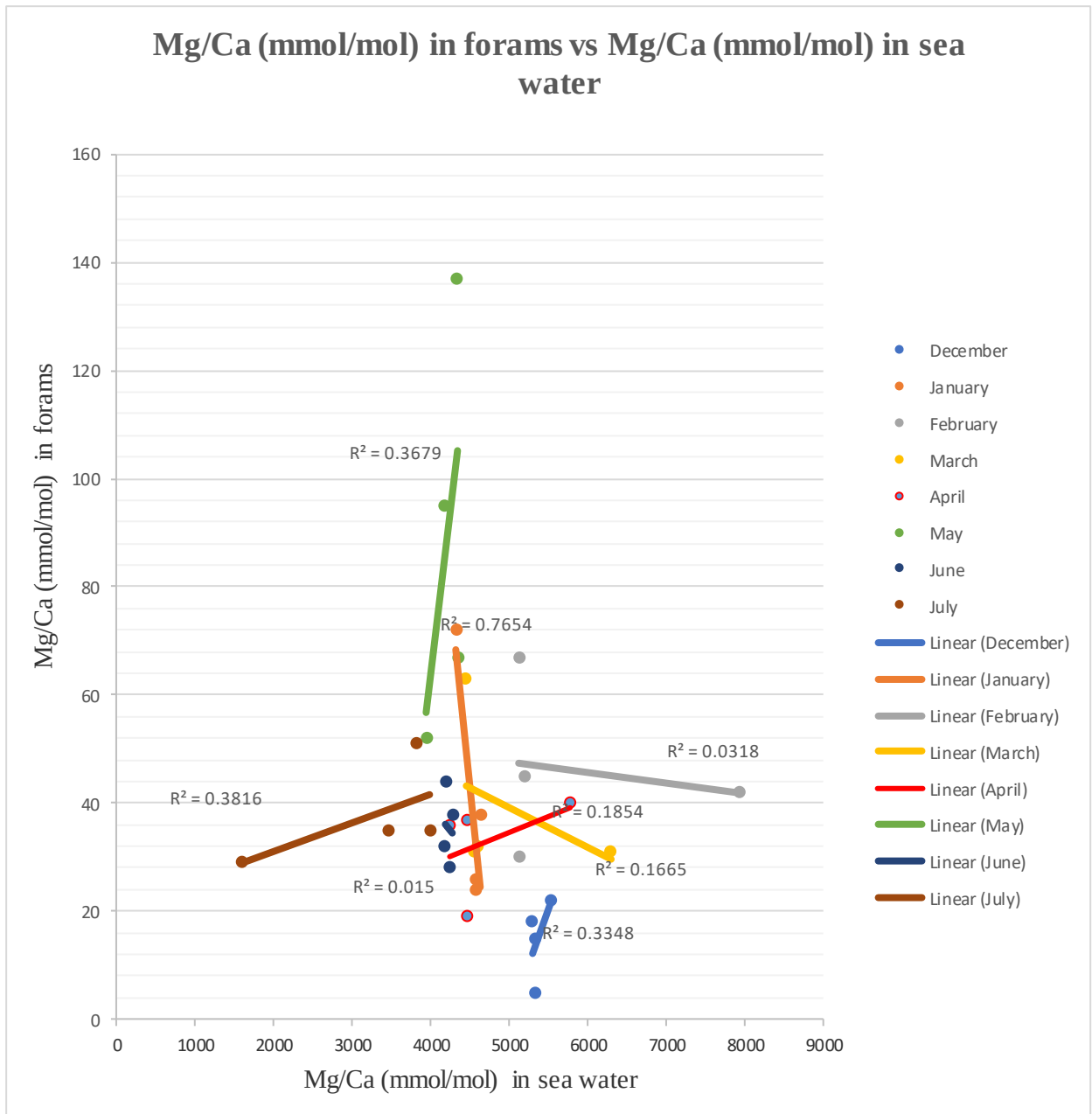


Figure 24: Mg/Ca (mmol/mol) in forams vs Mg/Ca (mmol/mol) in sea water

DECEMBER:

Table 5: SEM-EDX results of the foraminifera samples for December:

Uqair Beach (FS)	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.88	27.47	52.82
SAMPLE 2	0.18	72.42	4.10
SAMPLE 3	1.97	47.31	68.66
SAMPLE 4	0.49	76.86	10.51
SAMPLE 5	1.51	31.18	79.86
The average value of the Mg/Ca ratio is 43.19 mmol/mol			
Pond 1	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.30	48.39	10.22
SAMPLE 2	1.09	80.10	22.44
SAMPLE 3	0.41	55.53	12.17
SAMPLE 4	1.84	51.97	58.38
SAMPLE 5	1.19	70.15	27.97
The average value of the Mg/Ca ratio is 26.24 mmol/mol			
Pond 2	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.73	35.89	10.22
SAMPLE 2	0.59	35.74	22.44
SAMPLE 3	1.59	57.34	12.17
SAMPLE 4	0.96	42.11	58.38
SAMPLE 5	0.59	57.25	27.97
The average value of the Mg/Ca ratio is 32.21 mmol/mol			
Pond 3	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.63	32.30	32.16
SAMPLE 2	1.28	52.84	39.94
SAMPLE 3	0.19	78.22	4.01
SAMPLE 4	0.96	38.39	41.23
SAMPLE 5	1.27	29.76	70.37
The average value of the Mg/Ca ratio is 37.54 mmol/mol			

Sample calculation(converting mass % into mmol/mol):

$$[(0.0088/24.305) / (0.2747/40.078)] * 1000 = 52.82 \text{ mmol/mol}$$

Table 6: ICP-MS & ICP-OES results of the foraminifera and sea water respectively for December :

ICP-MS results of the foraminifera samples:	Mg (ppm)	Ca (ppm)	Na (ppm)	Mg/Ca (mmol/mol)	Na/Ca (mmol/mol)
Uqair Beach (FS)	28	8577	49	5	10
Pond 1	39	2922	3	22	2
Pond 2	162	15143	615	18	71
Pond 3	154	16631	354	15	37
ICP-OES results of the seawater:	Mg (ppm)		Ca (ppm)		Mg/Ca (mmol/mol)
Uqair Beach (FS)	2180		675		5326
Pond 1	2070		617		5532
Pond 2	2480		772		5297
Pond 3	2640		816		5335

Sample calculation(converting ppm into mmol/mol):

$$[(28*1000)/24305] / [(8577/40078)] = 5 \text{ mmol/mol}$$

JANUARY:

Table 7: SEM-EDX results of the foraminifera samples for January:

Uqair Beach (FS)	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.27	33.65	13.23
SAMPLE 2	0.23	2.46	154.17
SAMPLE 3	1.18	63.61	30.59
SAMPLE 4	0.41	39.15	17.27
SAMPLE 5	1.73	35.19	81.07
The average value of the Mg/Ca ratio is 70.78 mmol/mol			
Pond 1	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.22	54.36	6.67
SAMPLE 2	0.52	26.58	32.26
SAMPLE 3	0.83	29.47	46.44
SAMPLE 4	0.02	70.35	0.47
SAMPLE 5	0.60	39.66	24.95
The average value of the Mg/Ca ratio is 34.55 mmol/mol			

Pond 2	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.30	49.51	9.99
SAMPLE 2	0.76	60.71	20.64
SAMPLE 3	0.43	37.97	18.67
SAMPLE 4	0.98	45.28	35.69
SAMPLE 5	0.90	39.75	37.33
The average value of the Mg/Ca ratio is 24.46 mmol/mol			
Pond 3	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.47	70.27	11.03
SAMPLE 2	0.07	65.65	1.76
SAMPLE 3	0.63	53.63	19.37
SAMPLE 4	0.91	40.07	37.45
SAMPLE 5	0.61	44.29	22.71
The average value of the Mg/Ca ratio is 26.51 mmol/mol			

Table 8: ICP-MS & ICP-OES results of the foraminifera and sea water respectively for January:

ICP-MS results of the foraminifera samples:	Mg (ppm)	Ca (ppm)	Na(ppm)	Mg/Ca (mmol/mol)	Na/Ca (mmol/mol)
Uqair Beach (FS)	5754	132472	120826	72	1590
Pond 1	10251	443023	371304	38	1461
Pond 2	1597	107894	15772	24	255
Pond 3	1305	82099	77471	26	1645
ICP-OES results of the seawater:	Mg (ppm)	Ca (ppm)	Mg/Ca (mmol/mol)		
Uqair Beach (FS)	1940	738	4335		
Pond 1	2230	793	4637		
Pond 2	2370	855	4571		
Pond 3	2360	850	4578		

FEBRUARY:

Table 9: SEM-EDX results of the foraminifera samples for February:

Uqair Beach (FS)	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.85	41.24	33.99
SAMPLE 2	0.65	24.94	42.98
SAMPLE 3	0.96	39.71	39.86
SAMPLE 4	0.84	40.46	34.23
SAMPLE 5	0.68	71.51	15.68
The average value of the Mg/Ca ratio is 37.77 mmol/mol			
Pond 1	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	3.00	10.97	450.95
SAMPLE 2	0.09	80.12	1.85
SAMPLE 3	0.31	33.39	15.31
SAMPLE 4	0.43	48.39	14.65
SAMPLE 5	2.29	25.43	148.49
The average value of the Mg/Ca ratio is 45.075 mmol/mol			
Pond 2	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.32	30.50	17.30
SAMPLE 2	0.36	36.58	16.23
SAMPLE 3	0.36	64.65	9.18
SAMPLE 4	1.36	19.92	112.58
SAMPLE 5	1.95	16.28	197.51
The average value of the Mg/Ca ratio is 70.56 mmol/mol			
Pond 3	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	1.13	30.43	61.23
SAMPLE 2	0.05	78.62	1.05
SAMPLE 3	0.30	29.62	16.70
SAMPLE 4	0.39	35.15	18.30
SAMPLE 5	0.39	37.52	17.14
The average value of the Mg/Ca ratio is 28.34 mmol/mol			

Table 10: ICP-MS & ICP-OES results of the foraminifera and sea water respectively for February:

ICP-MS results of the foraminifera samples:	Mg (ppm)	Ca (ppm)	Na(ppm)	Mg/Ca (mmol/mol)	Na/Ca (mmol/mol)
Uqair Beach (FS)	10848	423608	32223	42	133
Pond 1	13492	496293	15252	45	54
Pond 2	7299	179303	46099	67	448
Pond 3	2511	138779	5299	30	67
ICP-OES results of the seawater:	Mg (ppm)	Ca (ppm)	Mg/Ca (mmol/mol)		
Uqair Beach (FS)	2060	428	7937		
Pond 1	2430	770	5204		
Pond 2	2600	836	5128		
Pond 3	2960	950	5138		

March:

Table 11: SEM-EDX results of the foraminifera samples for March:

Uqair Beach (FS)	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.35	55.77	10.26
SAMPLE 2	0.55	66.08	13.80
SAMPLE 3	1.83	38.75	7.79
SAMPLE 4	0.51	51.15	16.35
The average value of the Mg/Ca ratio is 12.05 mmol/mol			
Pond 1	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	2.42	33.32	11.96
SAMPLE 2	1.00	45.40	3.64
SAMPLE 3	1.48	34.35	7.10
SAMPLE 4	1.25	31.12	6.64
The average value of the Mg/Ca ratio is 7.34 mmol/mol			
Pond 2	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	8.95	20.17	731.94
SAMPLE 2	0.43	60.66	11.69
SAMPLE 3	0.77	46.6	27.25
SAMPLE 4	3.13	24.01	214.76
The average value of the Mg/Ca ratio is 246.41 mmol/mol			
Pond 3	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.61	52.10	19.31
SAMPLE 2	1.06	47.91	36.49
SAMPLE 3	0.80	21.69	60.83
SAMPLE 4	0.40	55.15	12.05
The average value of the Mg/Ca ratio is 32.17 mmol/mol			

Table 12: ICP-MS & ICP-OES results of the foraminifera and sea water respectively for March:

ICP-MS results of the foraminifera samples:	Mg (ppm)	Ca (ppm)	Na (ppm)	Mg/Ca (mmol/mol)	Na/Ca (mmol/mol)
Uqair Beach (FS)	7848	417346	41049	31	171
Pond 1	13358	349750	25697	63	128
Pond 2	2757	148063	4263	31	50
Pond 3	2022	105440	5440	32	90
ICP-OES results of the seawater:	Mg (ppm)	Ca (ppm)	Mg/Ca (mmol/mol)		
Uqair Beach (FS)	1970	516	6296		
Pond 1	2020	748	4453		
Pond 2	2280	826	4552		
Pond 3	2370	849	4603		

April:

Table 13: SEM-EDX results of the foraminifera samples for April:

Uqair Beach (FS)	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	1.79	38.91	75.99
SAMPLE 2	1.25	39.63	51.89
SAMPLE 3	0.87	49.25	29.03
SAMPLE 4	1.45	48.58	49.21
The average value of the Mg/Ca ratio is 43.38 mmol/mol			
Pond 1	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.75	22.46	55.29
SAMPLE 2	2.99	36.26	135.98
SAMPLE 3	0.53	38.20	22.88
SAMPLE 4	0.38	53.48	11.72
The average value of the Mg/Ca ratio is 29.96 mmol/mol			
Pond 2	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.97	32.46	49.28
SAMPLE 2	0.39	61.63	10.35
SAMPLE 3	0.43	36.85	19.11
SAMPLE 4	0.45	46.09	15.99
The average value of the Mg/Ca ratio is 15.15 mmol/mol			
Pond 3	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	1.08	40.57	43.90
SAMPLE 2	0.23	51.09	7.43
SAMPLE 3	0.47	33.69	23.01
SAMPLE 4	0.48	64.26	12.24
The average value of the Mg/Ca ratio is 26.38 mmol/mol			

Table 14: ICP-MS & ICP-OES results of the foraminifera and sea water respectively for April:

ICP-MS results of the foraminifera samples:	Mg (ppm)	Ca (ppm)	Na (ppm)	Mg/Ca (mmol/mol)	Na/Ca (mmol/mol)
Uqair Beach (FS)	3764	168215	3315	37	34
Pond 1	14036	645611	25336	36	68
Pond 2	4645	405403	2040	19	9
Pond 3	7473	304725	9078	40	52
ICP-OES results of the seawater:	Mg (ppm)		Ca (ppm)		Mg/Ca (mmol/mol)
Uqair Beach (FS)	1990		733		4477
Pond 1	2120		874		4248
Pond 2	2230		823		4468
Pond 3	2310		658		5789

May:

Table 15: SEM-EDX results of the foraminifera samples for May:

Uqair Beach (FS)	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.84	48.32	28.67
SAMPLE 2	0.66	53.45	20.36
SAMPLE 3	0.75	33.53	36.88
SAMPLE 4	0.56	47.15	19.58
SAMPLE 5	1.83	38.42	78.54
The average value of the Mg/Ca ratio is 36.81 mmol/mol			
Pond 1	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.57	51.99	18.08
SAMPLE 2	0.92	51.8	29.29
SAMPLE 3	0.75	61.74	20.03
SAMPLE 4	1.10	38.52	47.09
SAMPLE 5	1.82	46.02	65.21
The average value of the Mg/Ca ratio is 35.94 mmol/mol			
Pond 2	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	1.18	31.53	61.71
SAMPLE 2	1.19	51.63	38.01
SAMPLE 3	1.44	45.66	52.00
SAMPLE 4	0.64	38.37	27.50
SAMPLE 5	0.78	46.73	27.52
The average value of the Mg/Ca ratio is 41.35 mmol/mol			
Pond 3	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.55	42.77	21.20
SAMPLE 2	1.00	46.81	35.23
SAMPLE 3	0.78	52.12	24.68

SAMPLE 4	0.87	37.18	38.59
SAMPLE 5	1.61	48.15	55.14
The average value of the Mg/Ca ratio is 34.97 mmol/mol			

Table 16: ICP-MS & ICP-OES results of the foraminifera and sea water respectively for May:

ICP-MS results of the foraminifera samples:	Mg (ppm)	Ca (ppm)	Na (ppm)	Mg/Ca (mmol/mol)	Na/Ca (mmol/mol)
Uqair Beach (FS)	43002	1058572	223504	67	368
Pond 1	91998	1109234	451016	137	709
Pond 2	11446	364036	66189	52	317
Pond 3	14858	258914	112683	95	759
ICP-OES results of the seawater:	Mg (ppm)		Ca (ppm)		Mg/Ca (mmol/mol)
Uqair Beach (FS)	1850		701		4352
Pond 1	2090		850		4346
Pond 2	1900		793		3951
Pond 3	2295		905		4182

June:

Table 17: SEM-EDX results of the foraminifera samples for June:

Uqair Beach (FS)	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.41	36.63	18.46
SAMPLE 2	2.64	30.21	144.10
SAMPLE 3	1.67	34.49	79.84
SAMPLE 4	0.57	48.39	19.42
SAMPLE 5	1.14	49.62	37.88
The average value of the Mg/Ca ratio is 38.90 mmol/mol			
Pond 1	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.54	37.79	23.56
SAMPLE 2	0.36	45.89	12.94
SAMPLE 3	0.69	45.66	24.92
SAMPLE 4	0.23	44.71	8.48
SAMPLE 5	0.51	28.84	29.16
The average value of the Mg/Ca ratio is 19.81 mmol/mol			
Pond 2	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.21	52.59	6.58
SAMPLE 2	3.41	25.69	218.88
SAMPLE 3	0.53	51.46	16.98
SAMPLE 4	0.53	35.90	24.34
SAMPLE 5	0.62	55.60	18.39
The average value of the Mg/Ca ratio is 16.57 mmol/mol			
Pond 3	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.82	47.51	28.46
SAMPLE 2	0.39	32.95	19.52
SAMPLE 3	0.38	49.50	12.66
SAMPLE 4	0.83	52.36	26.14
SAMPLE 5	0.23	51.25	7.40
The average value of the Mg/Ca ratio is 18.84 mmol/mol			

Table 18: ICP-MS & ICP-OES results of the foraminifera and sea water respectively for June:

ICP-MS results of the foraminifera samples:	Mg (ppm)	Ca (ppm)	Na (ppm)	Mg/Ca (mmol/mol)	Na/Ca (mmol/mol)
Uqair Beach (FS)	8041	411825	41572	32	176
Pond 1	21407	807742	217795	44	470
Pond 2	17169	1002743	191409	28	333
Pond 3	26455	1134008	382759	38	588
ICP-OES results of the seawater:	Mg (ppm)	Ca (ppm)	Mg/Ca (mmol/mol)		
Uqair Beach (FS)	1712	674	4191		
Pond 1	1867	734	4194		
Pond 2	2095	815	4241		
Pond 3	2205	849	4285		

July: Table 19: SEM-EDX results of the foraminifera samples for July:

Uqair Beach (FS)	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	1.56	46.15	55.74
SAMPLE 2	0.89	44.25	33.17
SAMPLE 3	0.96	26.91	58.83
SAMPLE 4	1.42	15.73	148.86
The average value of the Mg/Ca ratio is 74.15 mmol/mol			
Pond 1	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	2.77	37.07	123.22
SAMPLE 2	0.95	29.39	53.30
SAMPLE 3	3.85	18.17	349.39
SAMPLE 4	1.81	16.26	183.56
SAMPLE 5	2.55	37.22	112.97
The average value of the Mg/Ca ratio is 164.49 mmol/mol			
Pond 2	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	1.71	21.73	129.76
SAMPLE 2	0.71	16.59	70.57
SAMPLE 3	0.89	21.70	67.63
SAMPLE 4	0.35	21.48	26.87
SAMPLE 5	0.43	40.08	17.69
The average value of the Mg/Ca ratio is 62.50 mmol/mol			
Pond 3	Mg (mass %)	Ca (mass %)	Mg/Ca (mmol/mol)
SAMPLE 1	0.44	33.98	21.35
SAMPLE 2	1.39	19.10	120.00
SAMPLE 3	0.57	16.17	58.13
SAMPLE 4	2.23	20.29	181.23
SAMPLE 5	1.46	19.11	125.98
The average value of the Mg/Ca ratio is 101.34 mmol/mol			

Table 20: ICP-MS & ICP-OES results of the foraminifera and sea water respectively for July:

ICP-MS results of the foraminifera samples:	Mg (ppm)	Ca (ppm)	Na (ppm)	Mg/Ca (mmol/mol)	Na/Ca (mmol/mol)
Uqair Beach (FS)	7369	414810	29054	29	122
Pond 1	4876	231006	5194	35	39
Pond 2	9297	303294	8056	51	46
Pond 3	5940	277204	19087	35	120
ICP-OES results of the seawater:	Mg (ppm)	Ca (ppm)	Mg/Ca (mmol/mol)		
Uqair Beach (FS)	1291	1322	1609		
Pond 1	1647	785	3460		
Pond 2	1944	840	3814		
Pond 3	2250	929	3996		

Table 21: The multi-meter probe reading of (temperature & salinity) at the Al-Uqair beach and the three associated ponds (1,2,3), with the calculated ratios of Mg/Ca and Na/Ca used to generate the graphs.

	Mg/Ca (mmol/mol)	Na/Ca (mmol/mol)	Temperature (°C)	Salinity (PSU)
Uqair Beach (December)	5	10	23.0	51.6
1st P (December)	22	2	22.0	56.5
2nd P (December)	18	71	21.7	62.8
3rd P (December)	15	37	21.5	65.7
Uqair Beach (January)	72	1590	18.6	55.8
1st P (January)	38	1461	17.1	59.5
2nd P (January)	24	255	18.5	63.8
3rd P (January)	26	1645	17.6	64.4
Uqair Beach (February)	42	133	23.6	60.1
1st P (February)	45	54	19.6	61.4
2nd P (February)	67	448	21.1	65.8
3rd P (February)	30	67	21.6	70.0
Uqair Beach (March)	31	171	29.6	63.6
1st P (March)	63	128	24.8	65.8
2nd P (March)	31	50	24.7	72.5
3rd P (March)	32	90	25.4	74.4
Uqair Beach (April)	37	34	28.7	63.1
1st P (April)	36	68	27.0	66.0
2nd P (April)	19	9	27.7	73.1
3rd P (April)	40	52	27.1	76.8
Uqair Beach (May)	67	368	35.0	62.8
1st P (May)	137	709	31.4	66.4
2nd P (May)	52	317	31.5	74.7
3rd P (May)	95	759	30.8	78.0
Uqair Beach (June)	32	176	32.8	61.2

1st P (June)	44	470	30.8	68.2
2nd P (June)	28	333	30.7	77.1
3rd P (June)	38	588	29.8	79.7
Uqair Beach (July)	29	122	37.9	64.7
1st P (July)	35	39	36.1	67.9
2nd P (July)	51	46	37.0	77.9
3rd P (July)	35	120	36.8	79.2

CHAPTER 5

DISCUSSION

This research investigates the applicability of the Mg/Ca ratio in foraminiferal calcite to be used as a temperature proxy as well as the Na/Ca ratio to be used as a direct independent salinity proxy in the Arabian Gulf. Unfortunately, there is no previous data in this body of water in terms of the range of the Mg/Ca ratio of foraminifera, the effect of salinity in this highly saline gulf, the impact of temperature in this warm sea, and the influence of Mg/Ca ratio in sea water on the Mg incorporation into foraminiferal shells. This fact complicates our task in addressing these two proxies as we will rely on field studies made in different locations around the world with colder temperature than the Gulf and less saline water bodies besides the culture lab studies available in literature that has been done mostly on planktonic foraminifera.

5.1. The Comparison Between SEM-EDX and ICPMS results:

In this study, we have calculated the Mg/Ca ratio using these two different instruments. The monthly results show that the results match in some months and mismatch in others.

Ideally speaking, both methods should give the same results in all months. The possible reasons behind this mismatching is that uncertainty in picking foraminifera that are similar in terms of morphology to *Ammonia tepida*, but may be a different species of *Ammonia*. In the SEM-EDX we picked five foram specimens, they might not be all belong to the same species of *Ammonia*. Similarly, in the ICPMS we digested different 20 specimens than the ones with SEM-EDX. One more reason behind the mismatching is that the size issue as one study suggest that the larger size forams have a higher ratio of Mg/Ca (*Elderfield, 2002*). Finally, in ICPMS we digest the whole foram whereas in SEM-EDX we analyse the surface of the last chamber of the foraminifer.

5.2. Comparison Between The Main Beach And The Three Associated Ponds

The monthly results of these four locations shows similarity in the results with slight difference in R^2 value in both (the correlation between Mg/Ca and temperature as well as the correlation between Na/Ca and salinity) as they are connected and located in the same lagoon system. This is with approximately same characteristics in terms of salinity, temperature, and pH. In theory, all studies in the Arabian Gulf should reach to the same conclusion if they are done on same temperature, salinity, pH, and most importantly on the same species as the Mg/Ca paleo thermometry is species dependent.

5.3. The Impact Of Salinity And Temperature On The Mg/Ca Ratio In The Forams

Mg/Ca ratio in foraminifera is highly affected by temperature and salinity (*Ferguson et al., 2008; Clark, 2009; Dissard et al., 2010; Mawbey et al., 2020; Geerken, 2018; Hoogakker, 2009*) as well as the possible dissolution of foram shells (*Clark, 2009*). The ratio should decrease with dissolution of foram shells. As reported in the literature, the Mg/Ca ratio should increase with increasing temperature (*de Nooijer, 2017; Fehrenbacher et al., 2017*). The Mg/Ca ratio should increase by about 3% per one °C increment in temperature as per laboratory experiments (*Bryan and Marchitto, 2008*). However, our monthly results show that there is no trend from December to July, that is from low (ca. 17°C) to high (ca. 37 °C) temperature. Possible justifications for this are the effect of high temperature, It is important to mention here that the sensitivity between temperature and the Mg/Ca ratio decreases at higher temperatures (*Bryan and Marchitto, 2008*) as the case in the warm Arabian Gulf as per the findings of one study. Also, the high salinity has an effect. It can elevate the Mg/Ca ratio (*Ferguson et al., 2008*). In fact, the extent of the salinity effect on the Mg/Ca ratio is disputed. Some authors claim the effect is minor while others suggest an 15-59% increment in the Mg/Ca ratio per psu (*Boussetta, 2012; Ferguson et al., 2008*). And finally, the possible dissolution of foram shells as previously mentioned (*Clark, 2009*).

5.4. The Mg/Ca ratio in Sea Water:

The specific mechanism by which Mg is incorporated into the foraminiferal shells is not fully understood. This incorporation of magnesium happens by a process named as the calcification. When the foram makes its shell, it takes dissolved ions from the surrounding seawater. One of these ions is Mg ion, and when the concentration of Mg in sea water increases the ratio of Mg/Ca increases as the foram tend to has more Mg into its shells (*Mewes et al., 2014; Mario et al., 2020; Segev and Erez, 2006*). The monthly concentrations of Mg and Ca in sea water at the Al Uqair area are almost constant as per our results. Consequently, the Mg/Ca ratio in the sea water has no impact on the ratio in foraminiferal calcite, as the ratio varies from December to July.

5.5. The Mg/Ca Ratio As A Temperature Proxy:

More and more studies are accumulating since the 1990s that confirm the Mg/Ca paleothermometry (*Nürnberg et al., 1996; Eggins, 2003; Elderfield, 2006; Marchitto, 2007; Lowenstein, 2012; Billups, 2003, Barker, 2005; Raja, 2007; Creech et al., 2010; Katz et al., 2010; Rosenthal, 2011; Bryan and Marchitto, 2008*), however, our results show poor correlation between the Mg/Ca ratio and temperature. This finding was expected as one similar study (*Ferguson et al., 2008*) which was conducted in the Mediterranean Sea concluded that salinity has a major impact on the Mg/Ca ratio along lower salinity gradient (36-40 PSU) than the one we have at Al Uqair (52-80 PSU). This is besides other factors which are also affecting the Mg/Ca ratio. These factors are first, biological effects (growth rate and metabolic activity) and are different from one species to another. Second, dissolution of Mg can result in losing or decreasing the Mg concentration in the foraminiferal shells. Third, the diagenesis (the post-depositional change of sediments, which can impact the chemical composition of foram shells. Finally, the ph of sea water may also influence the Mg/Ca ratio, but with less importance than salinity. Consequently, all these factors are affecting the Mg/Ca ratio and the accuracy and reliability of Mg/Ca as a temperature proxy. In fact, there are many attempts to calibrate the Mg/Ca and temperature in many areas around the world. Some are successful and some are not at hypersaline seas because of mainly salinity and other

reasons that have been mentioned previously. Scientists are continuously working on the improvement of this proxy by correcting for salinity effects and the other effects as well. They are applying the correction factor to adjust the temperature proxy values determined from the Mg/Ca ratio, accounting for the impact of salinity and by estimating the corrected temperature value.

5.6. The Na/Ca Ratio As A Potential Direct Independent Salinity Proxy:

The current studies which are mainly culture lab studies suggest that the Na/Ca ratio can be used as a salinity proxy (*Wit, 2013; Bertlich et al., 2020; Watkins, 2021; Pacho et al., 2023*), however, our monthly results shows the opposite. The possible reason is the high temperature in Al Uqair area as the only field study available in literature is suggesting (*Mezger, 2016*). Higher temperatures may cause foraminifera to uptake more sodium. But still more research is needed to investigate and confirm the impact of temperature. Also, this field study which was conducted in the Red Sea at about 40 PSU while here in Al Uqair the salinity range between 52 and 80 PSU. These higher salinity values could also have an effect to raise the Na/Ca ratio. Similarly to the Mg/Ca ratio biological factors (growth rate, genetic variations, and metabolic activity among foraminiferal species) and diagenesis should be there. In reality, the Na/Ca ratio as a salinity proxy faces calibration and interpretation challenges. Creating a strong calibration between the Na/Ca ratio and salinity requires cautious calibration against modern samples and validation against instrumental salinity measurements. Moreover, interpreting paleo salinity changes from this ratio can be complicated because of the interference of many environmental factors. In my opinion, there might be other reasons for this poor correlation between the Na/Ca ratio in foraminifera and salinity of sea water. These reasons include pH, carbonate ion concentration, nutrient availability, and the sample size used to measure the ratio by the analytical techniques. One final possible reason is that there might be a nonlinear relationship between the Na/Ca ratio in the foraminiferal shells and sea water salinity. It is possible that the ratio reaches a saturation point or plateau at higher salinities as the case in the Al Uqair lagoons resulting in poor correlation with the incremental changes in salinity. Consequently, there is a vital need to make both field and lab culture studies to investigate regarding these factors that might affect the suggested correlation.

CHAPTER 6

CONCLUSION & RECOMMENDATIONS

6.1. Conclusion

This study confirms the result of similar studies that the Mg/Ca ratio will be high because of high salinity. The Mg/Ca ratio will not directly fit the calibration equation at high salinity like in the Arabian Gulf as can be seen by the low values of R^2 . Consequently, we cannot rely on Mg/Ca ratio as a paleothermometer in the Arabian Gulf along a salinity gradient (51.6–79.7 PSU). In fact there are still challenges that we have to face in order to have successful calibration. Moreover, this study confirms that the Na/Ca ratio cannot be used as a proxy for salinity in the western Arabian Gulf as can be seen in the graphs shown in the results section due to the reasons mentioned in the discussion part.

6.2. Recommendations

Further studies need to be conducted considering the following points:

1. Calibrating Mg/Ca ratios to accurately reflect temperature needs careful analysis and consideration of the factors involved.
2. Biological variability (vital effects) needs to be accounted when using Mg/Ca ratios as a temperature proxy.
3. Preservation and diagenesis: making assessment to the impacts of diagenesis and preservation is mandatory to make reliable calibration.
4. Seasonal variability: some species of foraminifera have seasonal changes in Mg/Ca ratios, which can impact the accuracy of temperature reconstructions. Therefore, these variations need to be understood in order to build accurate calibration.
5. Expanding the temporal and geographic coverage to enlarge the representation of Mg/Ca paleothermometry results.

6. Increasing the replication (making multiple measurements on the same sample) and sample size, this will enhance the statistical strength of the results.
7. Using standard reference materials with known Mg/Ca ratios to calibrate and validate the analytical techniques used to measure the Mg/Ca ratio.
8. Performing both field studies and lab culture studies as the combination will enhance the understanding of Mg/Ca paleothermometry. while the field studies are more accurate and more representative as they make the measurements in the natural environment of foraminifera. The lab culture studies allows better experimental control over different environmental variables as well as it has stronger statistical analysis because of the replication of experiments.

6.3. Future Work

Future work in this topic might try to test other species like *Elphidium* or *Peneroplis* as they are abundant in the Arabian Gulf instead of *Ammonia* and see if they will give the same results or to keep the same species but to perform a lab culture study at different temperatures & salinities in order to better understand the Mg/Ca paleothermometry in the Arabian Gulf. Also, one may work on the effect of the calcification process of foraminiferal calcite on the ratio of Mg/Ca as the process of calcification is not fully understood.

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