Experimental validation of Planktic Foraminifera Fragmentation Index as Proxy for the End-Cretaceous Ocean Acidification

A Thesis

submitted to

Indian Institute of Science Education and Research, Pune
Department of Earth and Climate Sciences
in partial fulfilment of the requirements for the
BS-MS Dual degree Programme
by

Sneha Manda

IISER PUNE

Indian institute of Science Education and Research, Pune
Dr. Homi Bhabha Road,
Pashan, Pune 411 008 INDIA

April, 2019

Supervisor: Dr. Jahnavi Punekar
Assistant Professor, Indian Institute of Technology, Bombay

Declaration

I hereby declare that the matter embodied in the report entitled "Experimental validation of Planktic Foraminifera Fragmentation Index as Proxy for the end-Cretaceous Ocean Acidification" are the results of the work carried out by me at the Department of Earth Sciences, Indian Institute Technology, Bombay, under the supervision of Dr. Jahnavi Punekar and the same has not been submitted elsewhere for any other degree.

Sneha Manda

Sneha Manda

Dr. JAHNAVI PUNEKAR

DEPARTMENT OF EARTH SCIENCES
IIT BOMBAY

Certificate

This is to certify that this dissertation entitled “Experimental validation of Planktic Foraminifera Fragmentation Index as Proxy for the end-Cretaceous Ocean Acidification” towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents study/work carried out by Sneha Manda, Indian Institute of Science Education and Research under the supervision of Dr. Jahnavi Punekar, Assistant Professor, Department of Earth Sciences, Indian Institute of Technology, Bombay during the academic year 2018-2019.

Dr. Jahnavi Punekar

Committee:

Dr. Jahnavi Punekar

Dr. Gyana Ranjan Tripathy

Sneha Manda

Acknowledgements

The last five years at IISER Pune have been the most cherishable time of my life. The final year especially has been a great learning experience for me and I have many people to thank for it.

First and foremost, I would like to thank my supervisor Dr. Jahnavi Punekar for all the insightful discussions and brainstorming sessions. You have been very supportive and helpful throughout my fifth year journey. Also, thank you for making my stay at Mumbai memorable.

I would like to thank my TAC guide, Dr. Gyana Ranjan Tripathy for his advice and feedback. My sincere and heartfelt gratitude to all my professors Dr. Sudipta Sarkar and Dr. Neena Joseph. I thank you all for your advice and support throughout the entire process.

Thank you, Trupti Gurav (IIT Bombay) for helping me better understand the geochemical aspects of the project. I would also like to thank Dr. Narayan S. Punekar (IIT Bombay) for his counsel on designing the experimental protocol.

My mum and dad. Thank you for your love, unconditional support and encouragement, for which I am grateful.

And most importantly, to my closest friends. Our times spent together and endless conversations with you has me kept and strong. This journey wouldn’t be as happy and meaningful without you all.

Table of Contents

List of Figures

Abstract

The final ~50 ky of the Maastrichtian leading up to the Cretaceous-Tertiary boundary mass extinction at Bidart (France) show records of poor carbonate preservation, the final ~25 ky being critical. This event has been proposed as evidence for ocean acidification immediately preceding the mass extinction. High planktic foraminifera test fragmentation index, anomalously low bulk-rock magnetic susceptibility and peak mercury content in this same interval link this crisis interval to peak Deccan volcanism in India. New results provide experimental validation for fragmentation index as an authentic proxy of end-Cretaceous ocean acidification event.

Pristine Cretaceous planktic foraminifera morphotypes were exposed to buffers of pH 8.0, 7.5, 7.0 and 6.5 for 15 days each and their preservation state was quantified as a function of time. The critical variables affecting test vulnerability and taphonomy are morphology, pH and time of exposure. Thin-walled fragile biserial species(60%) such as Heterohelix globulosa and H. planata are the most susceptible to dissolution, followed by simple coiled forms such as Rugoglobigerina (19%) sp. and Hedbergella sp(6.4%). The globotruncanids(12%) appear to be least susceptible to chemical and physical damage. Tests exposed to low pH conditions clearly show a higher vulnerability to fragmentation. These results indicate a strong influence of chemical and physical taphonomy on planktic foraminifera census data with serious palaeoenvironmental implications. Results also indicate that an overestimation of the abundance of environmentally sensitive Cretaceous species (e.g. globotruncanids) due to taphonomic preservation bias could result in underestimation of the degree/nature of faunal crisis and tempo of extinctions in the pre-extinction acidification interval.

Chapter 1. Introduction

Understanding the premise of the research problem

1.1 Mass Extinctions and LIPs

Mass extinctions are episodic events in Earth's history where more than 50% of the biota suffer extinction over a geologically short period of time. Over the past 545 million years of Earth's history, there have been five great mass extinction events, namely: end-Ordovician (444 Ma), end-Devonian (373 Ma), end-Permian (252 Ma), end-Triassic (201 Ma) and end-Cretaceous (66 Ma). Studies reveal extinction events to be correlated to extreme environmental perturbations such as marine anoxia (Bond and Wignall 2010; C. Li et al. 2016; Paul B. Wignall et al. 2016), global warming (Gómez and Goy 2011; Joachimski et al. 2009; Y. Sun et al. 2012) and ocean acidification, (Hautmann 2004; Payne and Kump 2007) each associated with abrupt change in atmospheric and ocean chemistry (Bond and Grasby 2017).

Many of these proximal kill mechanisms can be potential effects of extraterrestrial bolide impacts as well as large scale volcanic activities. Studies have recognized the temporal correlation between extinction events, impacts and large igneous provinces (LIPs) for over thirty years. However, improvement in dating techniques reveal an absence of convincing temporal link between impacts and extinction events other than Cretaceous-Tertiary mass extinction (correlated with Chicxulub impact) (Alvarez et al. 1980; Hildebrand et al. 1991; Montanari et al. 1983). More accurate temporal correlation and multitude of paleontological and geochemical evidences suggest large igneous province (LIP) eruptions of being the ultimate cause of extinction events (Bond and Wignall 2014; Courtillot and Renne 2003; Font, Adatte, Keller, et al. 2018; Thibodeau et al. 2016; P. B. Wignall 2001). Four of the five mass extinctions are associated with LIPs, suggesting the latter to be major drivers of extinction events (Figure 1 and Figure 2). Cretaceous-Tertiary extinction stands out as it is coincident with a large extraterrestrial bolide impact (Chicxulub) (Alvarez et al. 1980; Boynton et al. 2002; Hildebrand et al. 1991) as well as LIP (Deccan Volcanism). Albeit advances in Cretaceous-tertiary studies reveal Deccan volcanism to be the ultimate causation for the fifth mass extinction (Keller et al. 2008; Keller et al. 2011; Font et al. 2018; L. Li and Keller 1998; Punekar, Mateo, and Keller 2014; Schoene et al. 2019).

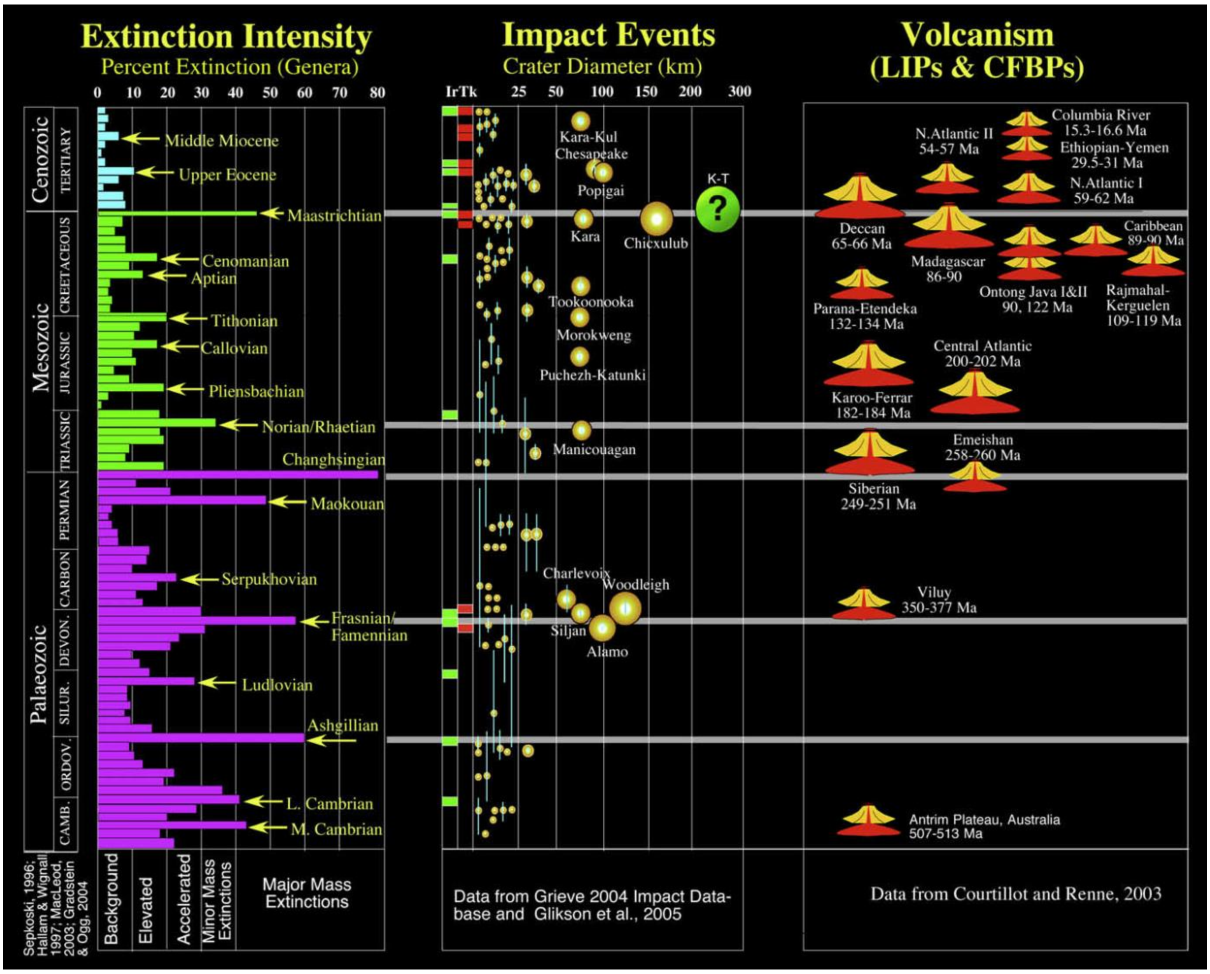

Figure 1-Extinction events, impacts and Large Igneous Provinces temporally correlated for the Phanerozoic. (Figure obtained from Keller: Cretaceous climate,volcanism,impact and biotic events, 2008)

Large igneous provinces (LIPs) represent voluminous volcanic activity occurring over periods of a few million years. Emplacement of large quantities of magma (>100,000 km^3) are correlated with environmental and biological catastrophes. The most popular hypothesis suggest that huge amounts of volcanogenic gases, released during eruptions, can drive rapid climate change that create high-stress conditions for the biota.

Extremely large volumes of magma erupting at very high rates release large amounts of volcanogenic gases that drive rapid climatic instability. CO_2 and SO_2 are the two main components of these volcanic gases that cause environmental degradation.

Increased concentration of carbon dioxide (CO_2) in the atmosphere leads to global warming over thousands to hundreds of thousands of years, while sulphur dioxide (SO_2) can lead to rapid global cooling on a decadal timescale. Such rapid fluctuations of climate are deleterious for marine and terrestrial biota.

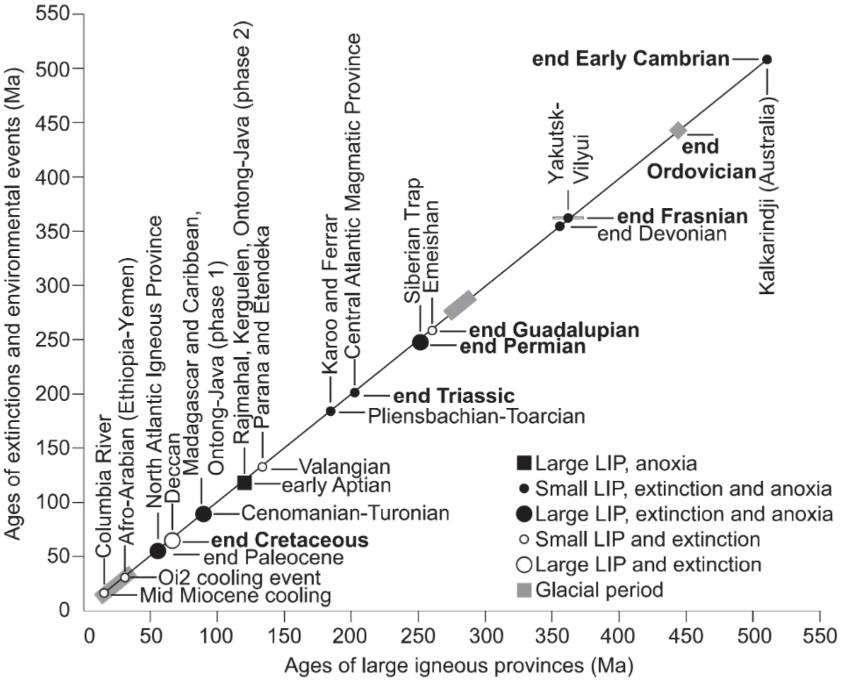

Figure 2-Temporal correlation between LIP emplacement and mass extinction and other palaeoenvironmental perturbations. From Ernst (Large Igneous Provinces, 2014)

Apart from global temperature anomalies, emplacement of tremendous amounts of volcanogenic CO_2 and SO_2 also contribute to ocean acidification: a primary contender for biotic stress in the marine realm.

1.2 Ocean Acidification: A Killing Mechanism

Every major extinction event in the Earth's geological record has been associated with interval of ocean acidification (Veron 2008). Ocean Acidification has been identified as the principal mechanism which brings about great biotic stress in the marine realm. LIPs offer an ultimate mechanism connecting these catastrophic biotic events in the marine realm to ocean acidification.

Injections of huge volume of gases by LIPs disrupt the global carbon cycle leading to severe environmental perturbations followed by episodes of colossal extinctions (Veron 2008). Release of large quantities of volcanogenic gases render natural feedback mechanisms incapable of neutralizing their effects. High rates of release of CO_2, results in excessive concentration of the greenhouse gas in the atmosphere. This perturbs the global carbon cycle leading to global warming and surface ocean acidification. The mechanism of excessive CO_2 initiating ocean acidification is explained below.

Once the air-sea CO_2 exchange equilibrates at the surface ocean, dissolved carbon dioxide reacts with water to form carbonic acid [H_2CO_3], which can further dissociate by losing H^+ ion to form bicarbonate [HCO_3^-] and carbonate ions [CO_3^{2-}].

$$CO_{2\,[atm]} \rightleftharpoons CO_{2\,[aq]} + H_2O \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2\,H^+$$

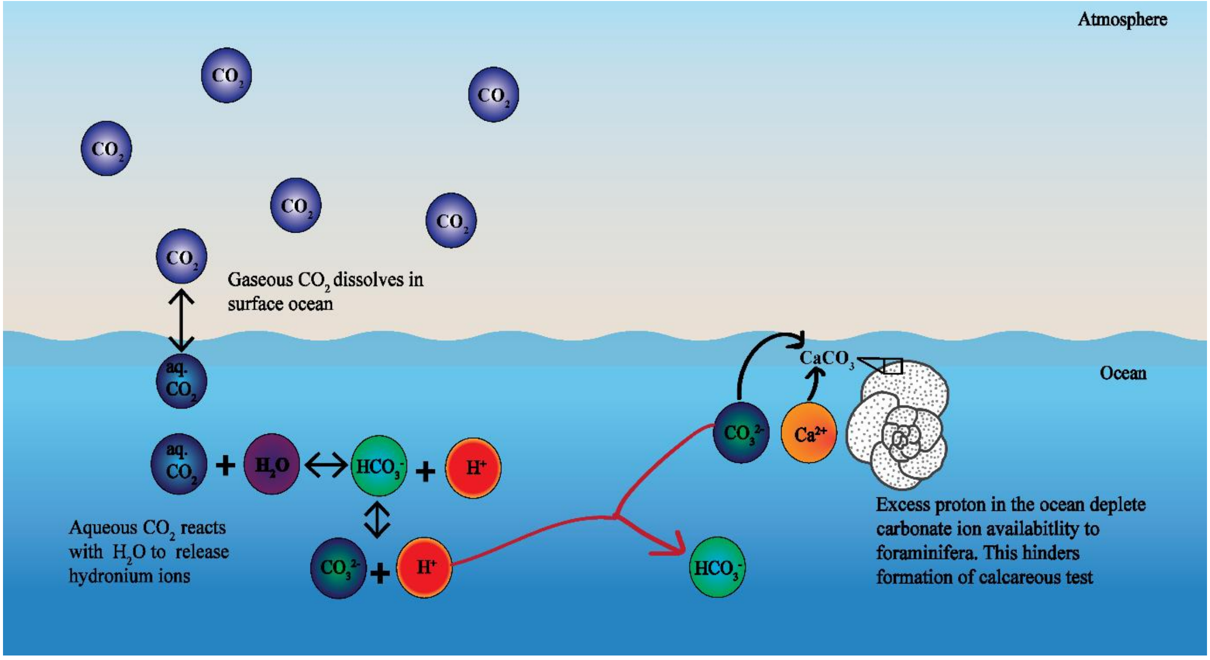

Figure 3-This figure illustrates the mechanism that leads to ocean acidification and how it can lead to a calcification crisis in the surface waters.

Increase in atmospheric carbon-di-oxide leads to higher concentrations of aqueous CO_2 in the oceans. Following chemical equilibrium principles, the chemical reactions proceeds in the forwards direction leading to accumulation of excess protons in the surface oceans. Oceans have a capacity to buffer excess proton input on a time scale of thousands of years (Hönisch et al. 2012). However, if large volumes of CO_2 is pumped into the atmosphere within shorter intervals of time, the buffering capacity of the oceans is compromised, followed by a drop in surface ocean pH values and alteration of marine carbonate chemistry.

Volcanogenic sulphur dioxide can also be a significant contributor to ocean acidification by means of a different mechanism. Sulphur dioxide released into the atmosphere reacts with hydroxyl ions in the stratosphere to form sulphate aerosols. On a decadal timescale, the aforementioned aerosols are removed from the atmosphere by precipitating as acid rain causing acidification of surface ocean waters.

Exposure to chronic high pCO_2 and low pH ocean waters have complex deleterious effects on all kinds of marine life forms. However, decreasing bioavailability of CO_3^{2-} most immediately affects marine organisms secreting calcium carbonate shells such as pteropods, coccolithophores, bivalves, gastropods, benthic and planktic foraminifera. Many studies also reveal that palaeocean acidification also influences the preservation of calcareous microfossil assemblages (Nguyen et al. 2009)(H. Berger and Piper 1972).

1.3 Cretaceous-Tertiary Mass Extinction

Cretaceous-Tertiary extinction is the last of the “Big-Five Mass extinctions” that wiped out almost three-quarters of life on Earth, including all of the non-avian dinosaurs. High resolution U-Pb dating has illuminated the age of the extinction boundary to be 66 Ma (Schoene et al. 2015, 2019).

Sedimentary layers found all over the earth at K-Pg boundary (Cretaceous-Tertiary Boundary or Cretaceous-Paleogene Boundary) show an anomalously high concentration of Iridium (Ir). Such high concentrations of Iridium led scientist to hypothesize that an extra-terrestrial asteroid impact on earth may have caused a mass extinction event (Alvarez et al. 1980). Recognition of spherule layers, shocked minerals (Bohor 1990; Montanari et al. 1983) and 180-200 km impact crater at Chicxulub at Yutacán peninsula Mexico, sustained the impact theory of the K-T extinction(Hildebrand et al. 1991). Models suggest that such a scale of impact may have released CO_2 and SO_2 from carbonate and sulphate rich rocks, that could have caused detrimental environmental effects such as acid rain, global cooling and extended darkness (Kring 2007; Toon et al. 2004).

However evidences from studies on marine planktonic fossil record and Deccan volcanism provide compelling evidence that the extinction event was caused due to Large-scale Igneous activity (Deccan Volcanism). Micropaleontological data obtained from studies illustrate that the Chicxulub impact preceded the mass extinction boundary by several hundred thousand years (Keller et al. 2003; Keller et al. 2010). Analysis of microfossil faunal turnover record with respect to the oldest impact glass spherule layer at El Penon, showed that no significant population changes and extinctions occurred below and above this layer (Keller et al. 2007).

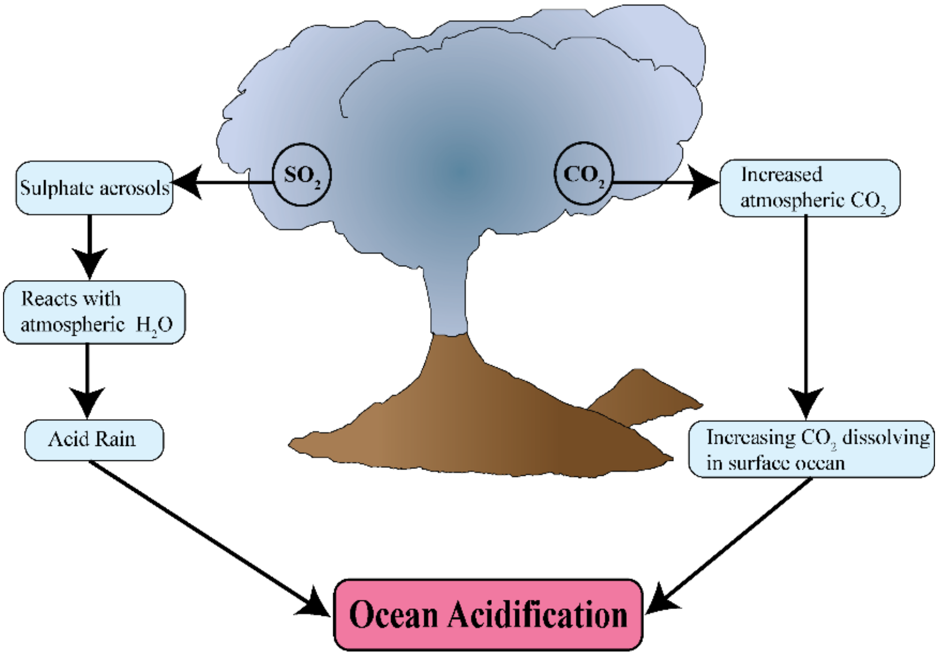

Figure 4-Illustration showing the mechanisms by which release of large amounts of CO2 and SO2 from large scale volcanic activity can lead to surface ocean acidification.

Advances in Cretaceous studies demonstrate Deccan Volcanism in India to be the primary cause for the mass extinction. Ocean anoxia, sea level changes, global warming followed by subsequent global cooling and ocean acidification are few of the kill mechanisms associated with LIPs. Deccan volcanism took place in four phases. Phase 2 of eruptions that occurred during the late Maastrichtian palaeomagnetic chron C29r, contributed to tremendous volumes magmatic eruptions (80%) occurring over a relatively short interval of time. This phase of volcanic activity emplaced 15,000-35,000 Gigatons (Gt) of CO_2, 6500-17,000 Gigatons (Gt) of SO_2 (Chenet 2008; Chenet and Courtillot 2009) along with other toxic volcanogenic gases. Such an excessive loading of atmosphere with CO_2 and SO_2 may have contributed many proximal mechanisms resulting in extreme biotic stress and eventual large-scale extinction. Surface ocean acidification is a proximal killing mechanism that can explain the high biotic stress and eventual extinction, as recorded in the fossil record of marine calcifers such as planktonic foraminifera.

.

1.4 Planktic foraminifera as a palaeoenvironmental proxy

Foraminifera are marine heterotrophic organisms belonging to class of amoeboid protists. Based on habitat and ecological niches foraminifera are often divided into two classes: benthics and planktics. Benthic foraminifera communities dwell on or near the seabed whereas planktonic species are free-floating in surface waters. Generally, benthic foraminiferal tests are larger and flatter compared to globular form of planktonic foraminifera. All Foraminifera are characterized by ectoplasm for catching food particles and protective hard outer layer (test) made up of varied materials and forms. Most foraminifera tests are made of calcium carbonate ($CaCO_3$) (Ecology of Benthic Foraminifera, B.K. Sen Gupta).

Planktic foraminifera are often used as tracers of past oceanic conditions due to high diversity, abundance and global occurrence. This qualifies planktic foraminifera to provide continuous evidence of evolutionary and environmental change through time making them an ideal microfossil of palaeoceanographic studies. Owing to taxonomic diversity, abundance and relatively easier extraction processes, planktic foraminifera are utilized for biostatigraphic, palaeoclimatic and palaeoceanographical studies. Stable isotope signatures preserved in calcium carbonate tests are used to reconstruct palaeotemperature and palaeoproductivity. Foraminifera assemblage composition also make useful palaeobathymetric indicators.

Planktic foraminifera biostratigraphic approaches have been used to understand the tempo and trend of the Cretaceous tertiary Mass extinction (Abramovich and Keller 2002; Keller et al. 2008; Keller et al. 2011; L. Li and Keller 1998; Punekar, Mateo, and Keller 2014) because they suffered a near total extinction, leaving only one long term survivor. In the deep sea sections (DSDP 525A) of the South Atlantic, it has been recorded that there is a 65% decline in planktic foraminifera species richness from Late Maastrichtian leading up to the Cretaceous-Tertiary Boundary (L. Li and Keller 1998). Apart from studying faunal turnovers for reconstructing the extinction event, foraminfera associated proxies such as Fragmentation

Index have also been applied to the planktonic record to interpret changes in marine environment. Bad preservation of planktic foraminiferal assemblages(fragmentation index) is interpreted as a result of low pH conditions in the Maastrichtian ocean (Punekar et al. 2016).

1.5 Ocean acidification of the Upper Maastrichtian (End-Cretaceous)

Multi-proxy studies for the KPB transition at Bidart (France) and Gamsbach (Austria) document an interval of poor carbonate preservation [low Percent Calcium Carbonate and enhanced Fragmentation Index] in the final ~50 ky of the late Maastrichtian biozone CF1 immediately preceding the KPB. This interval neatly coincides with the chemical benchmark for Deccan volcanism defined by anomalously low bulk-rock magnetic susceptibility and peak bulk Hg content (Font et al., 2011, 2014, 2016, 2018; Punekar et al., 2016).

Planktic foraminifera test fragmentation is one of the many proxies used to discern an ocean acidification interval in the upper Maastrichtian section (Punekar et al. 2016). Several taphonomic factors affect the preservation quality of foraminifer tests. Calcareous tests when exposed to dissolution in low pH conditions (water coloumn, bottom waters, post-depositional) may undergo enhanced fragmentation. Intervals of enhanced fragmentation has been studied to infer acidic conditions in the Cretaceous paleoocean (Punekar et al. 2016). Although Fragmentation Index can quantify poor carbonate preservation in fossil planktic foraminifera assemblages, discerning the mechanism and degree of taphonomic distortion of the original biocoenosis remains a challenge. This warrants an elaborate study of experimentally induced taphonomic damage on common planktonic foraminifera morphotypes that dominate late Maastrichtian assemblages to authenticate poor carbonate preservation as evidence for Deccan related ocean acidification event prior to the Cretaceous-Tertiary mass extinction.

For the thesis study, dissolution experiments were performed on pristine Maastrichtian planktic foraminifera from DSDP 525A (South Atlantic) with the following specific objectives: (1) to evaluate effects of pH (6.5, 7.0, 7.5,8.0) on typical Maastrichtian morphotypes, (2) to evaluate effects of physical abrasion on Maastrichtian planktic morphotypes, (3) to understand the most vulnerable and most resistant morphotypes, (4) to provide a theoretical basis for explaining robustness of morphotypes, (5) understand the temporal framework of dissolution and (6) apply the observations to real datasets and assess their true palaeoenvironmental interpretation.

Experimental dissolution studies on Maastrichtian foraminifera are crucial to validate the pre-extinction ocean acidification of the end Cretaceous and understand the potential connection with Deccan volcanism in India as a trigger for this acidification (Punekar et al. 2016).

Chapter 2. Methodologies

Strategizing and designing the experiments

2.1 Maastrichtian Planktic Foraminifera

Near-pristine Late Maastrichtian planktic foraminifera were carefully handpicked from DSDP Site 525A washed residues using a standard binocular light stereomicroscope. DSDP 525A is known for excellent preservation of Late Maastrichtian specimens/assemblages that have been used for stable isotopic reconstruction of the end-Cretaceous chron C29r global warming event (d^{18}O) and the isotopic depth ranking of Late Maastrichtian planktic foraminifera (habitat) (Li and Keller, 1998; Abramovich et al., 2003). Preliminary qualitative taphonomic observations suggest that the shape and architecture of tests is a fundamental factor influencing the dissolution and breakage of planktic foraminifera. Based on their morphology and size variation, the Late Maastrichtian planktic foraminifera morphospace was broadly subdivided into three major "*morphogroups*" as follows:

- **i.** **Globotruncanids** - species of genera *Globotruncana, Globotruncanita, Gansserina, Rosita* e.g. *Globotruncana arca, G. orientalis, Globotruncanita falsostuarti*. They are generally larger trochospirally coiled planktic foraminifera >150µm with relatively thick walled tests and keeled chambers (Figure-5).
- **ii.** **Rugoglobigerinids** – species of genus Rugoglobigerina e.g. *Rugoglobigerina rugosa, R. hexacamerata*. These are thinner walled trochospirally coiled forms with perforated inflated chambers and rugose ornamentations. They are common in the 63-150 µm size fraction.
- **iii.** **Biserials** consist of planktic foraminifera of genera *Heterohelix, Pseudoguembelina and Pseudotextularia.* Relatively thin walled species such as *Heterohelix globulosa* and *H. planata* common in the 63-150µm size fraction were selected for analyses.

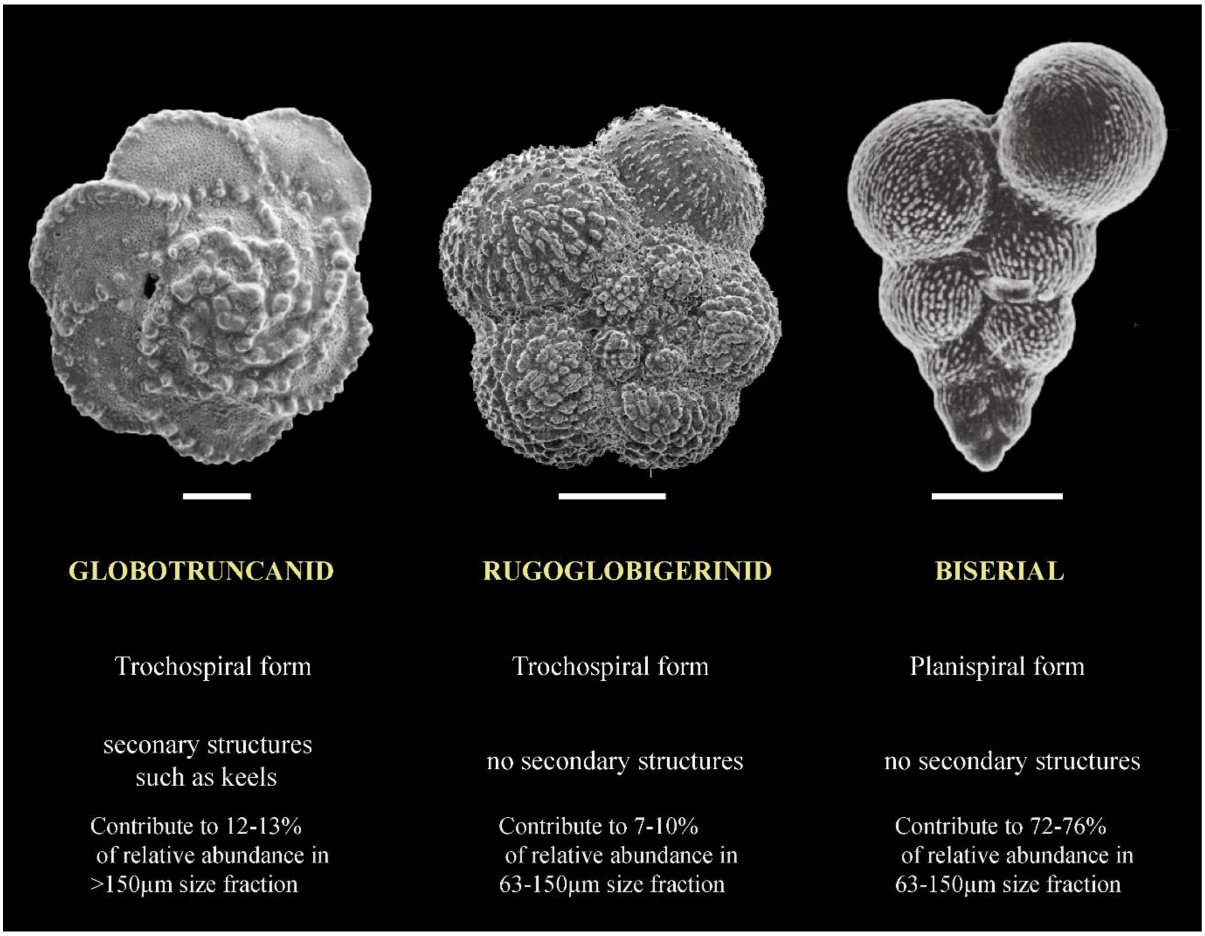

Figure 5-Morphogroups Globotruncanids, Rugoglobigerinids and Biserials collectively contribute to >90% abundance in the Cretaceous planktic foraminifera. Also, their individual shell morphology and architecture span the entire Cretaceous planktic foraminifera morphospace.

Foraminifera tests used in experimentation could not be photographed by Scanning Electron Microscopy (SEM) because the chemical treatment rendered the tests fragile. Transferring the specimens to an SEM stub using a brush led to further fragmentation of tests.

2.2 Test Parameters

(i) pH

Dissolution of marine biogenic carbonate is affected by the ambient pH and calcium carbonate saturation state [Ω], which in turn depend on the combined effects of a complex array of variables such as temperature, salinity, depth, pressure and $p\mathrm{CO}_2$ (W. H. Berger 1968) (Doney et al. 2008)(Sarmeinto and Gruber 2006). An authentic simulation of oceanic chemistry in a laboratory set up is challenging; the aim of this study is to understand the morphological manifestation of combined taphonomic effects of ambient acidity (excess protons) and the net chemical corrosion. A pH bracket of 6.5 to 8 was chosen with due consideration to the reconstructed pH range for the entire Phanerozoic (based on $d^{11}B$ reconstructions; Hönisch et al., 2012), and future projections of surface ocean pH (business as usual scenario European Union IPCC). Increments of 0.5 pH units were selected for experimentation to ensure discrete pH conditions corresponding to diverse extents of acidic conditions and chemical conditions in the ocean. Buffer solutions were synthesized and consistency of pH was checked using Sartorius bench-top pH meter of Accuracy (pH) ± 0.1.

Two experimental runs were planned for the same experiment at pH 6.5 (one using HEPES buffer and the other using a sodium acetate buffer as a control) to ensure that the observed changes in the preservation state of foraminifera were truly a function of dissolution and not an artefact of the buffer used (see section 2.3).

(ii) Experimental Run-time (Exposure)

Planktic foraminifera tests are generally exposed to ambient ocean water (pH) when alive, post-death while settling down to the ocean bottom, and post-deposition prior to burial. A realistic run-time for this experiment to assess taphonomic effects of water-column pH was estimated based on numerical calculations and laboratory experimentation. Mathematically, the settling velocity for average representative specimens of the selected Maastrichtian planktic morphogroups was approximated using Stoke's Law. The average mass of one globotruncanid test (26.802µg) was approximated by the weighing 557 picked specimens on a Mettler-Toledo ultra-microbalance at IISER Pune. Weights obtained for globotruncanids had a readability of 0.1 µg and error margin of 1%. Rugolobigerinids and heterohelicids [biserials] are (mass of rugoglobigerinids: 2.439µg; mass of heterohelicids: 4.607µg) lighter than the globotruncanids based on Four-Dimensional X-ray Microscopy scan results of representative specimens; the average mass of these morphogroups used for settling-time calculations was. The calculations assume undisturbed settling through a water column of uniform salinity. Simple preliminary lab experiments were carried out to clock the settling time of selected (near-pristine) foraminifera through an 80 cm column of simulated ocean water (preset temperature, density and viscosity). The observations were extrapolated to a water column depth of 1000 m for rugoglobigerinids and heterohelicids (surface and sub-surface mixed layer dwellers; Abramovich et al., 2003) and 0-800 m for globotruncanids (thermocline dwellers; Abramovich et al., 2003) to calculate a gross settling time estimate through the surface ocean and the entire thermocline.

Experimental estimation of the lower bound settling time for Maastrichtian planktonic foraminifera is 21 hours. This preliminary result is in agreement with other studies on planktic foraminifera settling rate (Fok-Pun L. 1982). Run-time of the main experiment is finalized to 15 days to incorporating ocean current and other disturbances in the ocean water coloumn and post-depositional exposure on the ocean floor.

2.3 Chemical reagents

Pilot experimental runs were conducted using Acetic acid buffer (pH 7) and diluted Sodium Hydroxide solutions (pH 7.5 and pH 8) to simulate the desired pH. However, there were many shortcomings to the chemicals chosen for study. Crystal growth and encrustations were observed on the foraminifera specimens in the SEM images. Also, synthesized solutions had to be replaced once every 48 hours to main pH constancy. Frequent replacement of buffer solutions in experimental vials caused inadvertent damage to the foraminifera shells. Experimental design was revised to identify and ideal buffer which did not react with the calcium carbonate of the foraminifera specimens and maintain the pH value for longer periods of time.

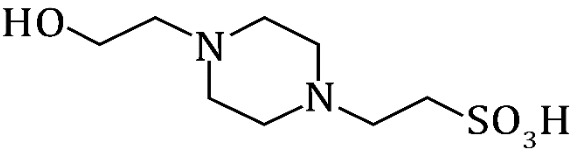

Figure 6-Chemical Structure of HEPES molecule

HEPES *[4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid]* is a zwitterionic organic buffer is chosen for the study to compensate the short comings of the pilot run. Its pKa value of 7.31 at 37°C makes it appropriate medium for experimentation due to its relevant functioning pH range [6.5-8.5]. A negligent reactivity with carbonate, calcium or other divalent cations make it an ideal buffer for the intended study as pH corrosion is compared only with respect to the net hydronium [H^+] ion availability (Good et al. 1966).

2.4 Experimental set-up

Planktic foraminifera test that settle through the ocean water column can react with ambient surface ocean waters of lowered pH leading to dissolution and enhanced fragmentation. Once deposited at the ocean bottom, they are further corroded if ocean bottom water/ pore water is undersaturated. Strong currents and bottom water energy conditions may physically damage tests by abrasion. A combination of the two processes can potentially enhance the degree of fragmentation of chemically affected tests.

(i) In vitro Evaluation of chemical taphonomic damage

Experiments were carried out at room temperature and pressure. 25 foraminifera tests of each of the three morphotype categories were carefully handpicked from the residue using a stereomicroscope. Tests of each morphotype were collected in three separate sterilized transparent acrylic petridishes. An array of four sets of three morphotype petriplates (a total of twelve) were prepared for testing the effects of pH 6.5, 7, 7.5 and 8 on each morphotype category. Using a micropipette, 6 ml of HEPES Buffer of the relevant pH was introduced to each plate such that the foraminifera tests were completely submerged in the buffer liquid. The plates were then sealed airtight to prevent evaporation and exchange with atmospheric CO_2, and allowed to stand undisturbed for 15 days. The pH 6.5 runs were carried out for a shorter run time of 6 days as the rate of dissolution is higher than that for pH 7, 7.5 and 8. The preservation state of each test was assessed and noted once every 48 hours for pH 7-8 as a shorter sampling interval did not yield observable changes in the preservation state.

(ii) In vitro Evaluation of physical taphonomic damage

a. Pure Physical Damage

In order to evaluate fragmentation of foraminifera tests when exposed to purely physical abrasion, 10 tests of each morphotype group, submerged in pH 8 solution, were immediately subject to arbitrary 5 send high energy shock on an Ultrasonicator. Preservation score for each morphogroup were noted thereafter.

b. Combined chemical and physical damage

10 foraminifera of each morphotype category were submerged in 6 ml of pH 7 and 8 HEPES Buffer for 4 days. 3 replicate petridishes with predefined number of foraminifera of each morphogroup were submerged in 6ml of buffer solution were prepared for a single pH condition (refer Figure 7). The each pH-morphotype combination was carefully introduced to an Ultrasonicator once every 24 hours, where it was exposed to higher energy conditions for an arbitrary 5 seconds. The same petri plate was retained to be exposed to 5 second high energy shock after another 24 hours. The preservation state of foraminifera tests was noted after every 24 hours (after energy shock) to assess the progress of damage with respect to time.

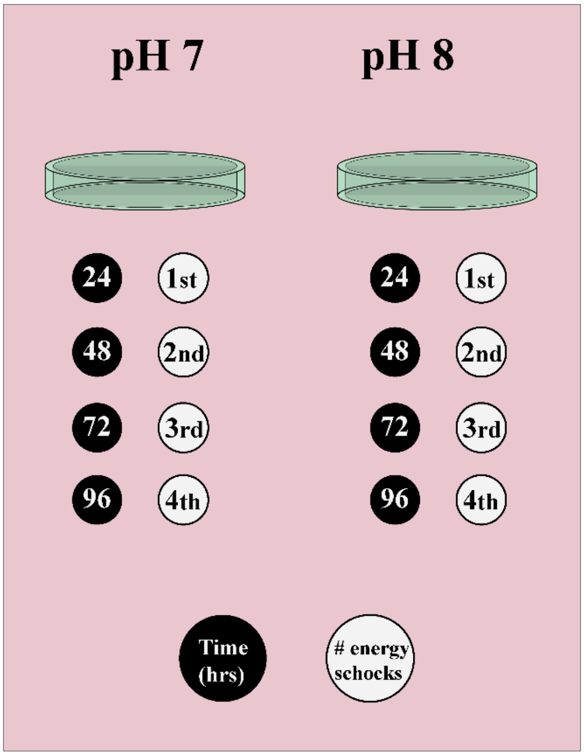

Figure 7-Graphic illustrating the experimental setup for class-2.4 (ii)(b) experiments [combined physical and chemical damage]

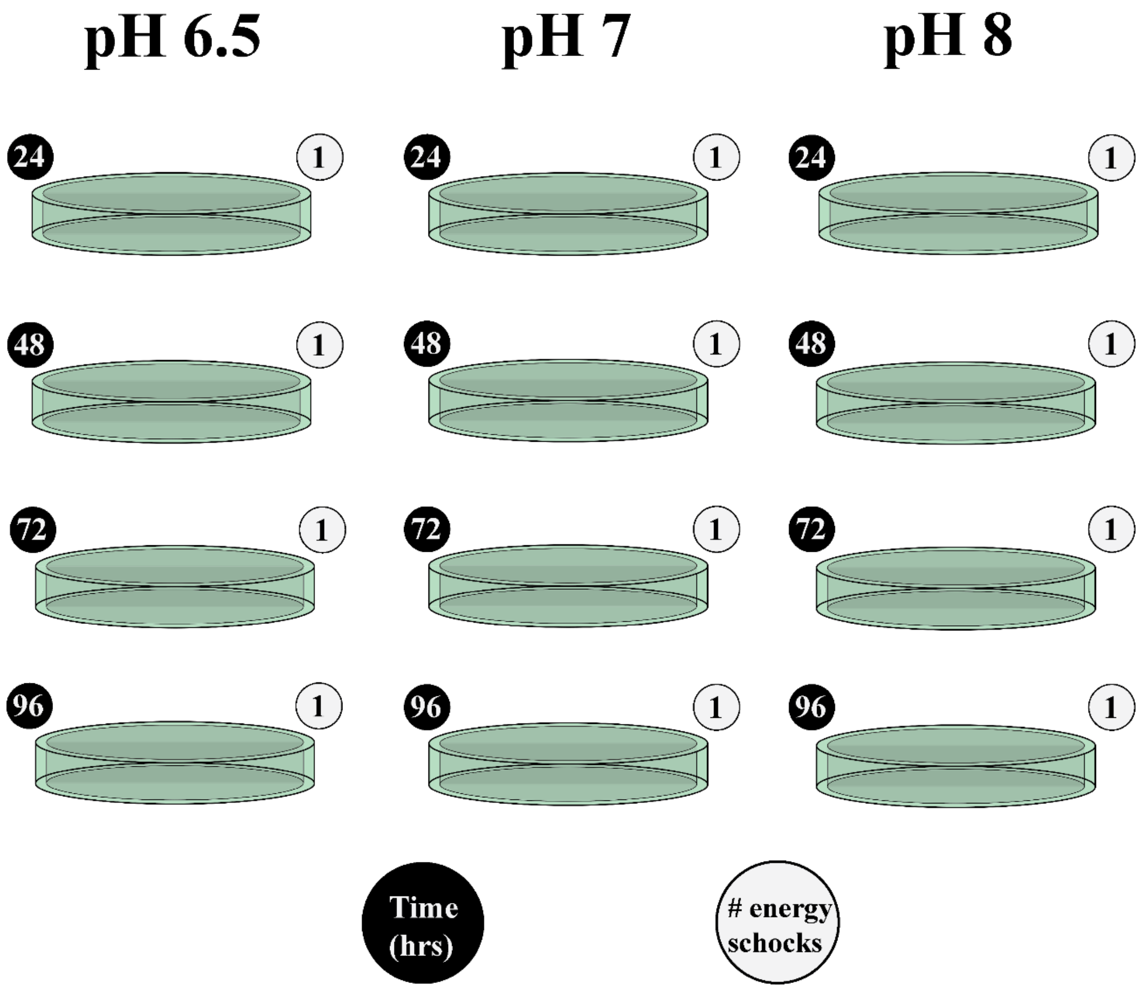

Figure 8-Graphic showing experimental set-up form class 2.4(ii)(c) studies [Time-Lapse of combined damage]

c. Time-Lapse of Combined Damage

10 foraminifera tests of each of the three morphotype categories were submerged in 6 ml of pH 6.5, pH 7 and pH 8 HEPES buffer for 4 days. 12 Replicate petridishes were prepared: once each for 24 hour, 48 hour, 72 hour and 96 hour time points and the corresponding pH respectively (experimental set-up illustrated in Figure 8). After completion of the respective time periods for each petri dish, they were subject to 5 second high energy shock. Preservation state of foraminifera was noted thereafter.

Only pH 7 and pH 8 were predominantly chosen for the second set of experiments (2.4 (ii)) because the dissolution trend observed in chemical taphonomy experiments were very similar for pH 7.5 and pH 8. pH 6.5 experimentation was introduced for class of 2.4 (ii)(c) experiments as an additional control

2.5 Quantification of preservation state

(i) Fragmentation Index and Scores

Calcareous tests of foraminifera can undergo fragmentation due to multitude of taphonomic processes. Exposure of calcium carbonate tests to ambient low pH ocean water leads to chemical dissolution rendering the foraminifera tests more fragile. These fragile tests when exposed to higher energy condition, undergo enhanced fragmentation.

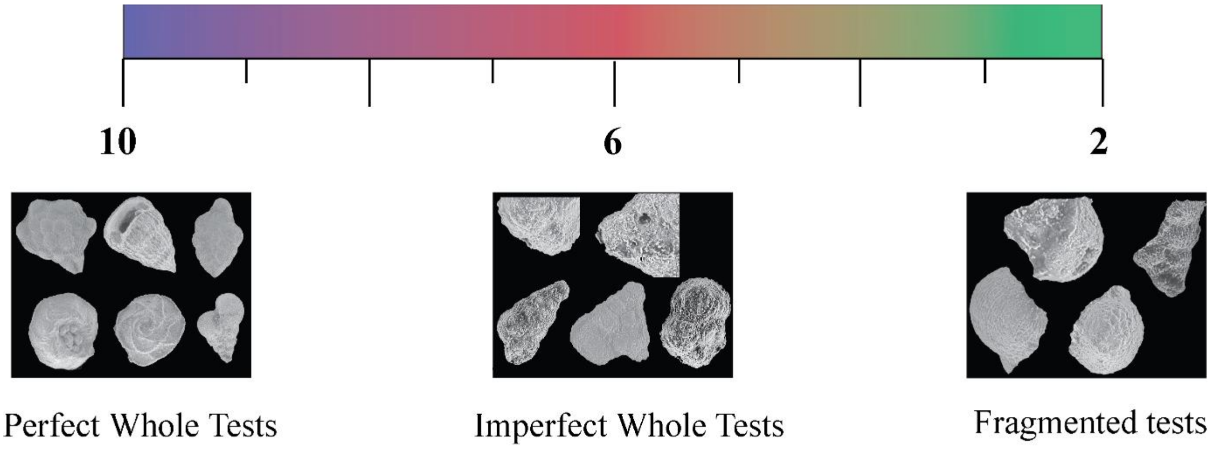

Figure 9-A score is assigned for a given foraminifera shell based on its preservation state (Si). For an assemblage or morphogroup, scores are normalized in accordance with the given formula. "Good" represent the preservation of "Perfect whole tests", with scores ranging from 10-8. "Bad" represent "Imperfect whole tests", 2/3rd or more than 2/3rd of a test, showing broken chambers or punctures. Their score ranged from 6-4. "Fragmented tests" are those that are extremely damaged and only less than 2/3rd of a foraminifera test is identifiable.

Fragmentation index is a measure of preservation state of foraminifera assemblage. Higher fragmentation index for a geological time interval corresponds to more acidic ocean chemistry.

Preservation state of select planktic morphotypes was monitored for (1) chemical and (2) physical taphonomic processes. Planktic foraminifera tests were observed under a light microscope to evaluate the preservation state. They were classified as Perfect Whole Tests [Score 10-8], Imperfect Whole Tests [Score 6-4] and Fragmented Tests [Score 2]. Perfect Whole tests are completely intact shells that do not possess any punctures on dissolution texture on the shells. Imperfect whole tests retain at least two-thirds of the intact shells exhibiting punctured chambers and sugary texture indicating dissolution. The range of this group of classification ranges from few punctures and minimal sugary texture to heavily punctured and dissolved. Tests categorized in the fragmented range exhibit extreme fragmentation and punctured chambers. Enhanced dissolution is seen in the form of extremely sugary structure of the calcium carbonate tests. Some ideas for the classification of tests are in accordance with Punekar et al. (2016).

For the each shell, the scores are normalized with respect to the total number of planktic shells.

Preservation state of a test/morphogroup is quantitatively represented as Score[S] defined as:

$$S = [\sum_{i=1}^{n} S_i]/n$$

Where S_i is the preservation score for individual foraminifera tests
n is the total number of foraminifera in a given morphogroup

(ii) Fragility Index

Studies have indicated that rate of dissolution varies for different morphologies of foraminifera tests (W. H. Berger 1968). This leads to sediments becoming more enriched in dissolution resistant morphotypes. More recent studies have strengthened this argument by showing that size of the foraminifera tests play an important role in the rate of dissolution (Nguyen et al. 2009).

My thesis study proposes a mathematical constraint that predicts the robustness (degree of resistance to dissolution) of a given planktic foraminifera test morphology. It is suspected that chamber arrangement in a foraminfera test is a chief factor that determines robustness of a morphotype.

Biserial, trochospiral and planispiral are the most dominant test arrangements in Cretaceous planktic foraminifera. Cretaceous planktic foraminifera morphospace can be classified into different groups based on test morphologies and average sizes.

Based upon observations, a theoretical concept named Fragility Index of a calcareous planktic foraminifera species has been defined for each planktic foraminifera species. It aims at quantifying the robustness of a given species to fragmentation. The definitions of Fragility Index have been defined upon the basis of the morphology of given species.

Fragility Index [F_g] is defined as

$$\mathbf{F_g = CW / SC}$$

Where CW is the width of the chamber along the growth direction, and SC is the septal contact with respect to each chamber.

Fragility Index and Fragmentation Index of each morphogroup has been compared to study a correlation between the two parameters.

Chapter 3. Results

collating data

3.1 Chemical Taphonomy

Planktic foraminifera dissolution experiments conducted at four discrete pH values (6.5, 7.0, 7.5, 8.0) clearly illustrate progressive dissolution of calcite tests of all morphotypes with time. Lower pHs result in increased corrosion of tests per unit time as hypothesized. The dataset acquired consists of (1) total number of tests remaining in the plate and (2) preservation quality of the tests quantified as preservation scores (see section 2.5 (i)) assigned to every planktic foraminifera test in each petridish of the experimental set up. The observations for each pH are spaced at regular 48 hour intervals and plotted as a function of time (Figure-10).

pH 8: Tests exposed to pH 8 yield the best preservation scores for all the three major morphogroups of Maastrichtian planktic foraminifera. The globotruncanids retain a "perfect whole test" score (9.83 post 336 hours) throughout the experimental run whereas the rugoglobigerinids yield scores (4.16 post 336 hours) equating to "imperfect whole tests" beyond 336 hours. The biserial group (score: 3.84 post 336 hours) is the most susceptible to dissolution damage and their scores indicate poor preservation equivalent to "fragmented tests" after 288 hours (score 3.92) (Figure 10.D). 95% of the globotruncanid tests did not exhibit any change in texture or holes indicating that they were unaffected by dissolution in pH 8. Five percent (5%) of the tests started to show early signs of changing surface texture. These tests looked comparatively more yellow under the microscope. This is due to enhanced visibility of secondary calcite as a result of dissolution. Rugoglobigerinids and biserials were more to dissolution. The last chambers of both the morphotypes (rugoglobigerinids and biserials) started developing holes as a consequence of dissolution. It has also been observed that entire surface of the tests displayed a sugary texture.

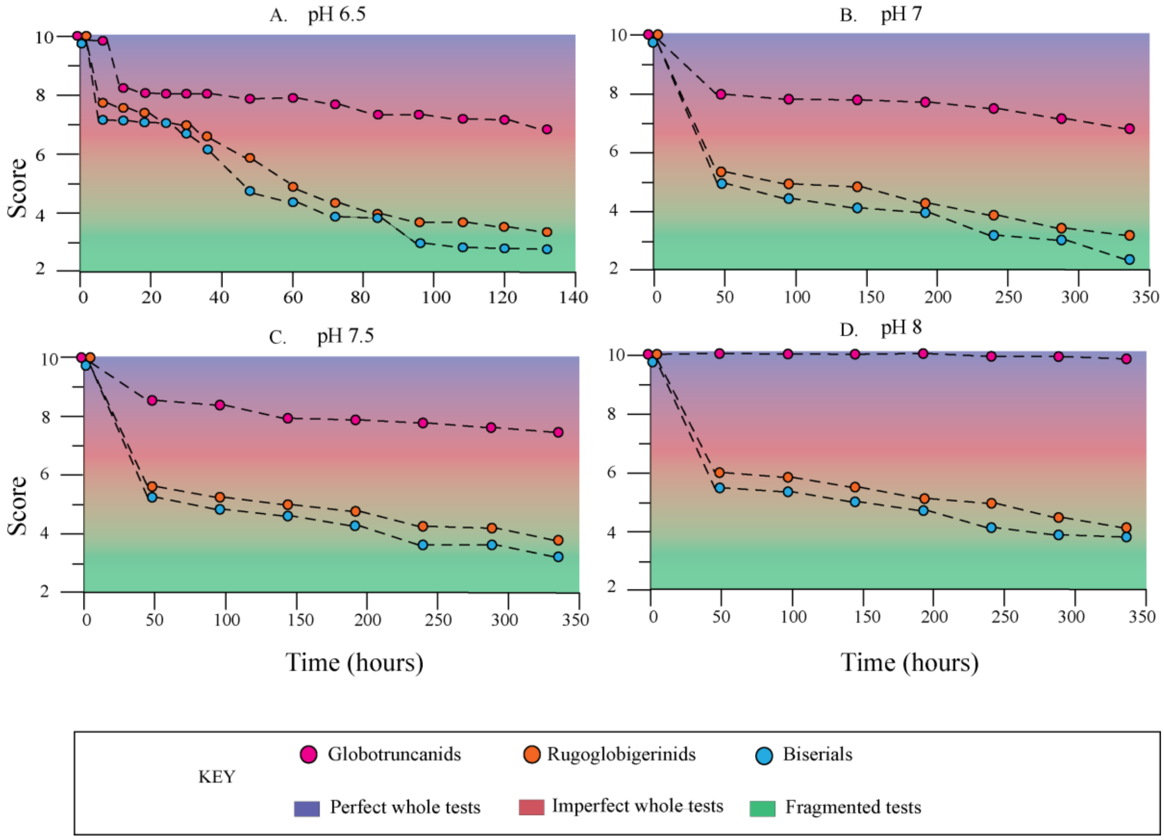

Figure 10-Each plot represents time-series data for dissolution of all three morphotypes (globotruncanids, rugoglobigerinids, and biserials). Fig 10.A, 10.B, 10.C and 10.D represent the data for pH 6.5, 7, 7.5 and 8 respectively.

pH 7.5: In general, the planktic foraminifera tests exposed to pH 7.5 exhibit observable changes marking higher degrees of dissolution within the first 48 hours of the experimental run. Preservation scores equivalent to "imperfect whole tests" are attained by both biserials (score: 5.4) and rugoglobigerinids (score: 5.6) by the 48 hour mark. However, the more resistant globotruncanid group takes three times longer (144 hours) to achieve a similar degree of corrosion (score:7.9). It is interesting to note that the preservation state of globotruncanids does not drop below a score of 7.4 ("imperfect whole tests") for the entire run. Scores indicating poor preservation equivalent to "fragmented tests" are attained by rugoglobigerinids (score: 3.8) at the 336 hour time point and by biserials (score: 3.6) at the 240 hour time point (Figure 10.C). 40% of the globotruncanids in pH 7.5 run exhibited small punctures and sugary texture of the test surface. Dissolution features of rugoglobigerinids included leeched out last chambers and punctures on the test surface. Biserial morphogroup exhibited damaged last and penultimate chambers and corrosion of the first chambers due to dissolution. Several holes, punctures and patches of leeched calcium carbonated were observed on the test surface.

Approximately 36% of the rugoglobigerinids and biserials exhibited severe dissolution of the tests with only less than two-third of the test remaining intact.

pH 7.0: For pH 7, the average scores for all the three morphotype groups transitioned to a poor preservation within the first 48 hours of the experiment. At the 48 hour time point, the globotruncanids show best preservation with the score of 7.83, whereas the rugoglobigerinids and biserials yield scores 5.36 and 5.29 respectively, equivalent to "imperfect". At the 240 hour time point, the scores for rugoglobigerinids (3.92) and biserials (3.2) clearly fall under the "fragmented tests" category indicating very poor preservation. However, the resistant globotruncanids are the least damaged and remain at an "Imperfect whole tests" score (6.8) even after 336 hours into the experiment (Figure 10.B). Few globotruncanids (16%) exhibited collapsed chambers walls while the rest of them displayed a sugary texture and few holes to exhibiting different levels of chemical leeching. Greater than 60% of rugoglobigerinids and heterohelicids showed enhanced dissolution with punctured and broken chambers. Remainder 40% of them showed extreme dissolution with less than two-third of the shell intact.

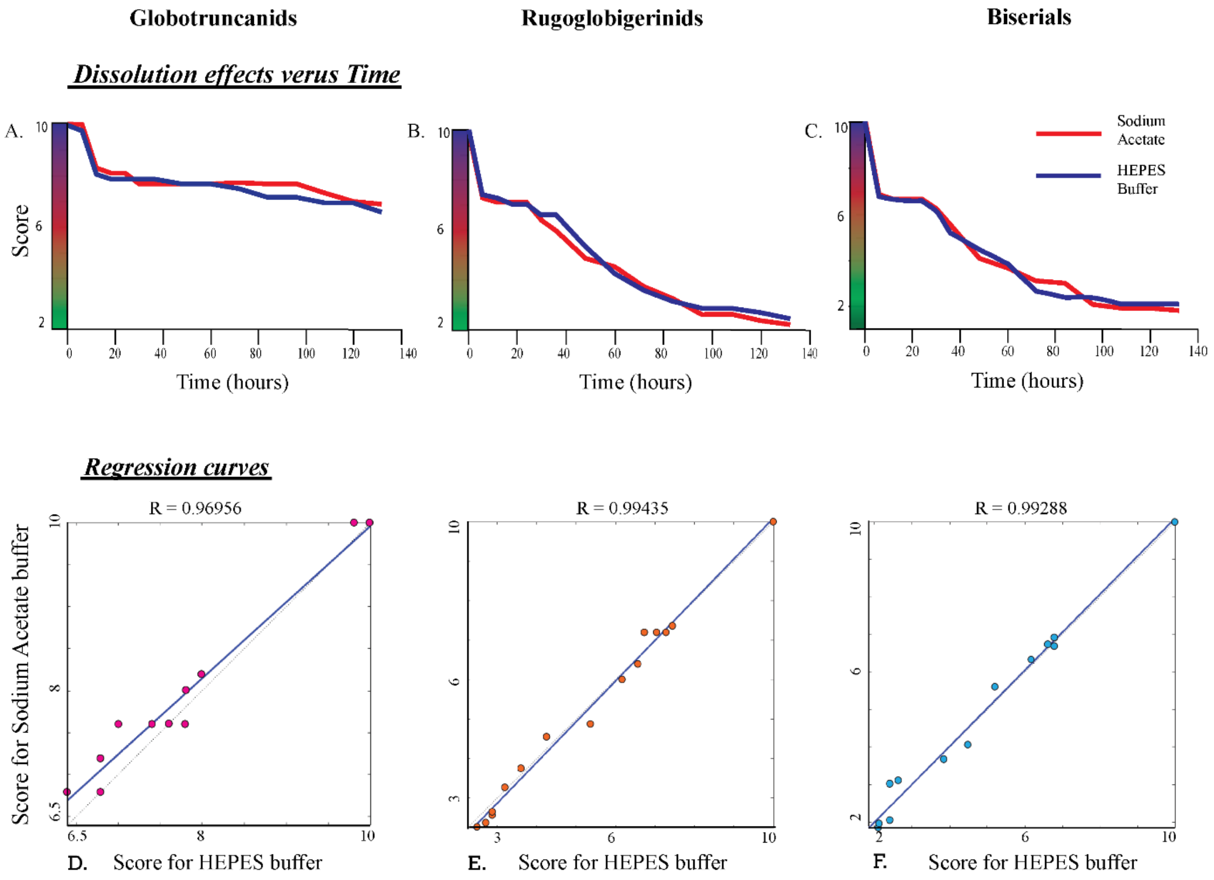

Figure 11-Plots in the first row [A, B, C] compare the dissolution effects of pH 6.5 for HEPES and Sodium Acetate buffer for each morphogroup. Figures D, E and F show regression plots for effects of both the buffers. Regression values very close to 1 indicate the dissolution effects during experimentation are not effected by any unprecedented chemical property unique to the buffers.

pH 6.5: Dissolution experiments for pH 6.5 were conducted in two chemical mediums : HEPES and Sodium acetate buffer. Due to rapid dissolution of all morphogroups of foraminifera in pH 6.5 solutions, experimental run-time was set to 132 hours in accordance to preliminary experimental results. Extent of dissolution of all three morphogroups in HEPES and sodium acetate buffer was comparable at each of the time points [Figure 11]. Regression plots for dissolution effects in both media show extremely comparable trends [R=0.97 (for globotruncanids); R=0.99 (for rugoglobigerinids); R=0.99 (for biserials) where R is the regression value] indicating that apart from the pH, no other chemical properties of the buffering agent played a significant role in dissolution (Figure 11).

The preservation state of the globotruncanid group is comparable to “imperfect whole tests” for the 132 hours of experimental run for HEPES (score: 6.4) as well as for sodium acetate buffer (score: 6.8). The rugoglobigerinids transition from “imperfect whole tests” score to “fragmented tests” score within 72 hours of the experiment for both the pH 6.5 media (HEPES buffer score: 2.48, sodium acetate buffer score: 2.24). By the 60th hour of the experimental run, the biserial morphotypes attain a preservation state of “fragmented tests” (HEPES buffer score: 3.84 and sodium acetate buffer score: 3.86). The preservation state by the end of the experiment (132 hours) for the globotruncanids, rugoglobigerinids and biserials are indicated by scores 6.4, 2.48 and 2.08 for HEPES buffer runs, and 6.8, 2.24 and 1.84 in sodium acetate buffer runs. 20% of the globotruncanids exhibited collapsed chambers, whereas >65% of rugoglobigerinids and biserials showed extreme chemical dissolution (represented by “fragmented test” score) by the end of the 132 hour experimental run. (Figure 10.A)

Trends in preservation state of tests was unique to each morphogroup. Dissolution of the heterohelicids predominantly starts with leaching away of the last two chambers of the test and extreme sugary texture of the first pair of chambers; for globotruncanids, the center of each chamber begins to collapse as the extent of dissolution aggravates. Dissolution of rugoglobigerinids morphogroup typically starts with leeching and puncturing of the final chamber of the test.

3.2 Physical Taphonomy

Effects of physical abrasion by high energy conditions were tested by two sets of experiments. The first set of experiments were carried out in pH 7 and pH 8 whereas the second set of experiments were conducted for pH 7, pH 8 and pH 6.5 (pH 6.5 was tested to serve as an additional control).

a. Purely physical damage

   As a control, a set of experiments were performed without the effect of chemical dissolution. 10 foraminifera of each morphotype were exposed to high energy conditions immediately after submerging them pH 8 buffer. Observations indicate that the three morphotypes of foraminifera do not respond differently to physical agitation, i.e., they could not be clearly ranked according to their response to purely physical taphonomy.

b. Combined physical and chemical damage

   Three morphotypes of Maastrichtian planktic foraminifera (10 of each group) were submerged in 6 ml of pH 7 and 8 buffers. After every 24 hours, the experimental set up was exposed to an arbitrary high energy condition for a duration of 5 seconds. At the end of 96 hours, Biserials are found to be more susceptible to damage in both the pH conditions with a score of 1.2 and 2(“fragmented tests”). Rugoglobigerinids rank as the second most vulnerable morphotype with score of 4 in pH 7 and pH 8 buffers. Globotruncanids (pH 7 score: 5.2, pH 8 score: 7.2) follow the trend of being the morphotype most resistant to physical as well as chemical damage (Figure 12).

c. Time-lapse of combined damage

   This round of experiments was conducted for pH 6.5, 7 and 8. All petridishes contain 10 foraminifera of each morphotype. Four petriplates are assigned to each pH value. They are labelled 24-hour, 48-hour, 72-hour and 96-hour (total of 12 petriplates) After chemical treatment of the designated time period, the shells were exposed to 5 seconds of high energy condition. The trend of Preservation state reaffirms to globotruncanids being the most robust morphotype under all pH conditions (pH 6.5 score: 4.4, pH 7 score: 6, pH 8 score: 7.2). Simple coiled foraminifera like Rugoglobigerinids (pH 6.5 score: 2, pH7 score: 2.4, pH 8 score: 3.2) and thin walled Biserials are the most prone to damage. However, heterohelicids (pH 6.5 score: 1.6, pH 7 score: 2, pH 8 score: 2.8) are the most vulnerable of the two (Figure 13).

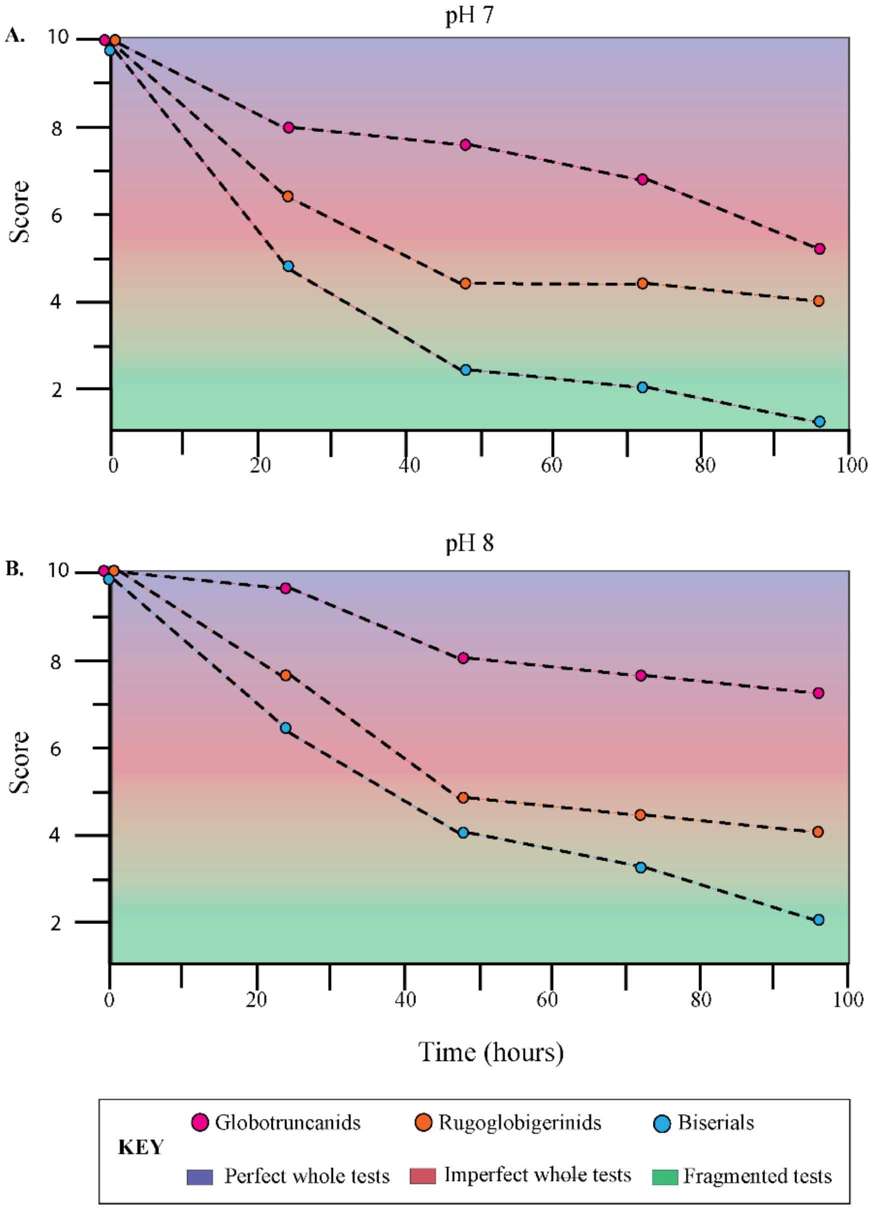

Figure 12-Plots 6.A and 6.B characterize the cumulative effects of physical agitation on preservation potential of all three morphotypes of planktic foraminifera for pH 7 and pH 8 conditions respectively.

Results from experiments clearly indicate that a combination of chemical dissolution and physical abrasion results in a severely worse preservation of foraminifera compared to the only chemical taphonomic factors acting on them [3.2 (b) , (c)]. Chemical dissolution can render Maastrichtian planktic foraminifera more prone to fragmentation, and as a consequence, lead to worse preservation in low pH conditions.

The trends of preservation potential of each planktic morphogroup in experiments evaluating physical taphonomic damage remains the same as those of chemical taphonomy. Globotruncanids are the most resistant morphotypes, followed by rugoglobigerinids and heterohelicids.

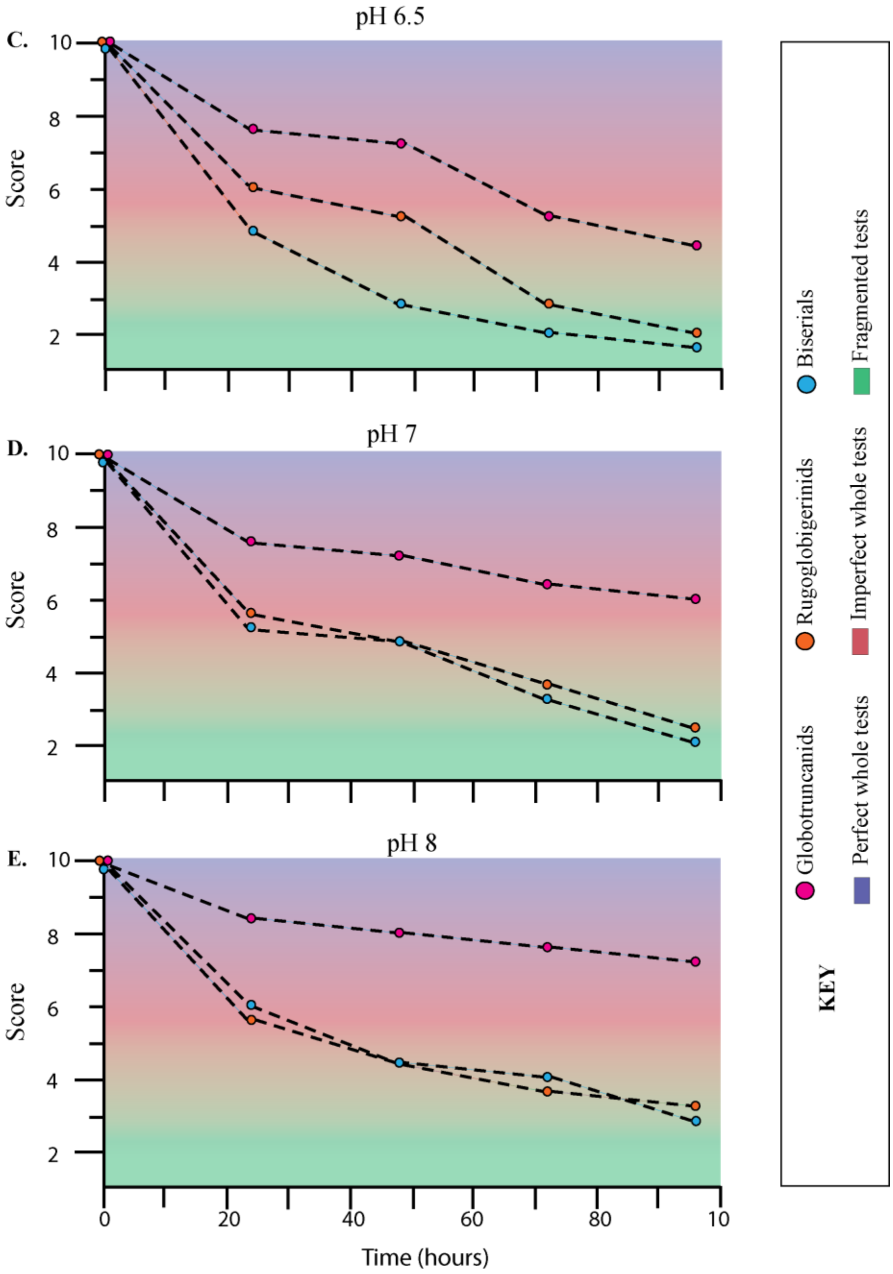

Figure 13-Plots 13.C, 13.D and 13.E characterize the effects of physical agitation [incubatory] on preservation potential of all three morphotypes of planktic foraminifera for pH 6.5, pH 7 and pH 8 conditions respectively.

3.3 Fragility Index

Based on the test morphology and Fragility Index values, the end-Cretaceous morphospace has been broadly divided into eight morphogroups. Populations studies of faunal datasets of Bidart, France (Punekar et al. 2016) and Elles, Tunisia (GSSP Section) (Abramovich and Keller 2002) Maastrichtian sections indicate that three of the eight morphogroups: heterohelicids(light biserials as indicated in Figure-14), simple coiled trochospiral (rugoglobigerina sp. and Hebgerella sp.) and Globotruncanids span >95% of the planktic morphospace. Analysis of Fragility Index for all species point to light biserials such as *Planoheterohelix globulosa* and *Planoheterohelix planata* to be the most vulnerable to taphonomic damage. The average fragility index for Light Biserials is 1.85 followed by *Hedbergella sp.*(1.61) and *Rugoglobigerina sp.*(1.5). *Globotruncanids* along with *Planoglobulina brazoensis* are ranked as the most robust species with a fragility index of 0.68 and 0.67 respectively [Figure 14].

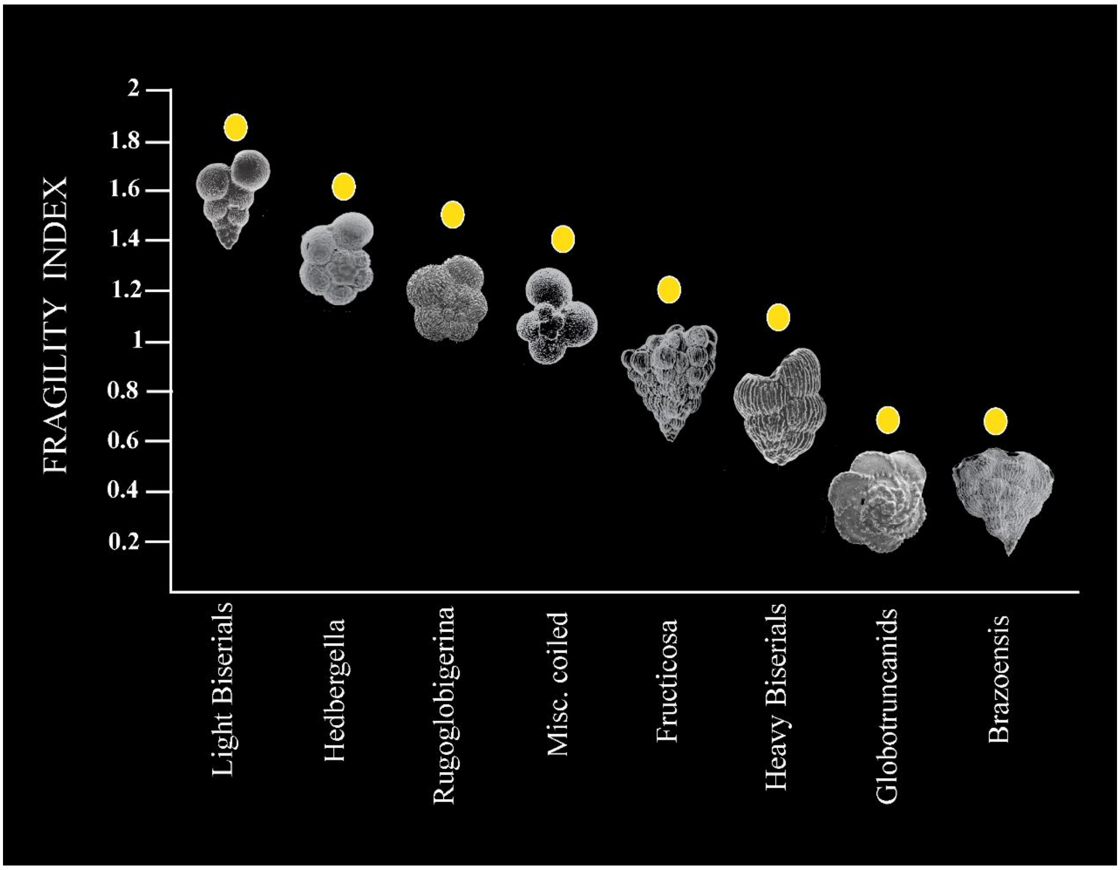

Figure 14-This illustration divides the End-Cretaceous planktic foraminifera into 8 morphogroups depending on the robustness of the test. The morphogroups are arranged in increasing order of robustness (i.e. decreasing order of fragility index).

Experimental verification and comparison with Fragmentation Index scores for respective morphotypes validates Fragility Index as an indicator of the robustness of a species to taphonomic damage. This theoretical concept predicts that morphogroups with highest Fragility index values are more vulnerable damage by dissolution and physical abrasion; hence are more susceptible to bad preservation. Results from our study demonstrate that morphogroups with highest Fragility index showed highest Fragmentation (worst preservation state scores) and morphogroups with lowest Fragility index had the least fragmentation (best preservation state scores), hence validating the accuracy of fragility index (Figure 15).

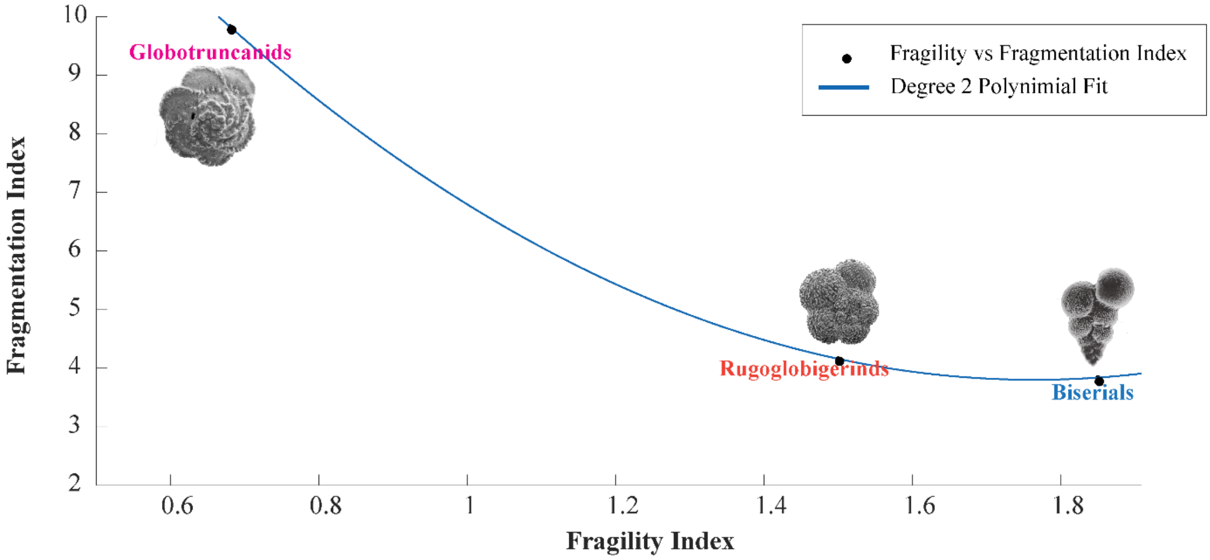

Figure 15-Average values of Fragmentation Index (experimentally derived) for morphogroups (globotruncanids, rugoglobigerinids and biserials) are plotted as a function of their respective Fragility Index (theoretically calculated). A clear trend between the two parameters can be observed.

Chapter 4. Discussion

Interpretations

4.1 Ocean Acidification towards End-Maastrichtian

Advances in Cretaceous-Paleogene studies suggest Deccan Volcanism to be the primary cause of the extinction event (Font et al. 2016; Font, Adatte, Keller, et al. 2018; Font, Keller, and Veiga-pires 2014; Schoene et al. 2019). Dating of Deccan lava flows showed that major volcanic eruptions happened in three major phases: phase-1 occurred in the late Maastrichtian emplacing 6% of total lava, phase-2 of Deccan volcanism was the largest emplacing 80% of the lava pile and occurs just below the Cretaceous-Tertiary boundary, phase-3, occurred in early Danian and contributed to 14% of the entire lava flow.

Studies on planktic foraminifera records suggest that phase-2 of Deccan volcanism, (80% by volume) in Chron 29r near the end-Maastrchitian, caused global high stress conditions leading to the extinction event. (L. Li and Keller 1998)(Keller et. al. 2008, 2009b, 2011a). Global warming, anoxia and ocean acidification are some of the major proximal killing mechanisms associated with large scale igneous activities.

Ocean acidification is a major contender for causing high-stress environment in the marine realm. Models estimate release of 15,000-35,000 Gigatons (Gt) of CO2 and 6500-17,000 Gigatons (Gt) of SO2 (Chenet 2008; Chenet and Courtillot 2009) ,from Deccan volcanism, into the atmosphere. Loading of the atmosphere with excessive volcanogenic CO_2 and SO_2 from large scale volcanic activities like phase-2 of Deccan volcanism, renders the oceans buffering capacity incapable to neutralizing surplus protons leading to ocean acidification.

Mineralogical (magnetite, akaganéite) data from K-Pg sections of Zumaia (Spain) and Magnetic susceptibility, percent $CaCO_3$ and Fragmentation Index data of planktic foraminifera from Bidart (France) sections allude to ocean acidification as being a chief killing mechanism in the Late Cretaceous marine realm (Font et al. 2018; Punekar et al. 2016).

Apart from triggering catastrophic biotic stress in the marine realm (recorded as decreasing species diversity of planktic foraminifera), ocean acidification can also tamper with preservation of planktic foraminifera assemblages by making the tests fragile and hence more susceptible to fragmentation. Maastrichtian sections of Bidart and Gamsbach located in France and Austria respectively show high fragmentation index in planktic foraminifera intervals that have been suspected to be related high stress environment (low-pH oceans) towards late Maastrichtian (Punekar et al. 2016).

Carbonate tests undergo dissolution as they pass through acidic ocean water coloumn. This would make them more fragile and susceptible to damage when undergoing post-depositional transport after settling on the ocean floor. This paints a realistic picture of the mechanisms that cause high fragmentation of planktic foraminifera assemblages in events of ocean acidification. Thesis study aims to tests the applicability of fragmentation index as a valid proxy for ocean acidification preceding the KTB.

4.2 Testing acidification hypothesis

Geological record of ocean pH and projections of future ocean pH (as a result of anthropogenic activities) have been used to constrain pH range for experimentation to replicate a more tangible scenario. Results from preliminary settling rate experimentation direct towards setting experimental run-time. Many variants of the basic experiment have been conducted to (i) generate multiple control runs to validate results (ii) evaluate (a) chemical and (b) physical taphonomy, and (c) combined effects of the two.

From experimental results it is verified that lower pH conditions correspond to higher fragmentation of the test. This result can be directly applied to foraminifer records to interpret intervals of anomalously high fragmentation with ocean acidification intervals. However, such a hypothesis should be warranted by further evidences and proxies that attest to acidic conditions.

For the same chemical condition [pH], fragmentation is observed to be the highest for biserials, followed by rugoglobigerinids and then globotruncanids. Higher fragmentation of select morphogroups alludes to a bias in assemblage preservation at times of ocean acidification. Our results show that, as dissolution proceeds, the relative abundance of globotruncanids increase as compared to that of rugoglobigerinids and biserials (Figure 10 and Figure 11). Relative enrichment in abundance of specialists (globotruncanids) in high stress environmental conditions is contradictory to expected fossilized population structure. Blooms of globotruncanids and other robust morphologies during extreme environmental degradation of the end-cretaceous in Bidart section can be explained by their preferential preservation over other species/morphogroups (Punekar et al. 2016).

Realistic scenarios in the ocean water coloumn are more likely to entail of a combination of chemical and physical taphonomic factors influencing the preservation of assemblages. Sediment transport or abrasion are results of high energy conditions in the water coloumn, whereas chemical factor such as dissolution are a result of rapid changes in the ocean chemistry. Experimental results mentioned in section 3.2 induce physical and chemical taphonomic factors on calcium carbonate tests to evaluate preservation quality. Such an incorporation of both chemical and physical taphonomic factor concurrently, enable to relate the obtained results in a tangible palaeocean acidification scenario. Apart from establishing that low pH conditions make carbonate tests more susceptible to fragmentation by physical agitation, results also make it conclusive that biserials and rugoglobigerinids are more susceptible to fragmentation as compared to globotruncanids (Figure 12 and Figure 13).

Experiments have also been conducted to quantify the how the factor of “physical agitation” independently influences fragmentation of carbonate tests. Experimental findings suggest that while physical agitation can potentially increase the fragmentation of foraminifera tests, it does not promote skewing of the population structure to the extent caused due to dissolution i.e. all three morphotypes are equally prone to fragmentation. However, further experimentation and studies are required to validate this finding.

In general, this study provides experimental proof and corresponding mechanisms that validate Fragmentation Index and anomalous abundance of robust morphologies in planktic record to correspond to low pH conditions. Validation of Fragmentation Index helps strengthen the hypothesis of ocean acidification event preceding Cretaceous-Tertiary Boundary. However, high fragmentation can also be a result of extensive physical agitation. Studying fragmentation index for benthic as well as planktic records can help resolve the causal mechanism causing anomalous fragmentation. Study of benthic records of Bidart samples reveal them to have better preservation than planktonic assemblages. This result provides conclusive evidence that causal mechanism of high fragmentation originated from process in the ocean water coloumn (prior to foraminifera tests settling on the ocean floor). This result helps interpret high fragmentation of planktic assemblages to be a result of ocean acidification. Albeit high fragmentation of planktic record can also be due to inherent robustness of benthic morphologies.

Results indicate species of globotruncanids, globotruncanita and *Planoglobulina brazoensis,* to have the least value for fragility index. This provides a theoretical basis to suspect globotruncanids and *P.brazoensis* to be the most robust of Cretaceous planktic foraminifera. The theoretical concept of fragility index is compared to experimentally obtained fragmentation index scores of the studied morphotypes. A clear correlation between fragility index and fragmentation index certify the former as a reliable theoretical measure to quantify the degree of dissolution susceptibility of each species.

Results obtained from the experiments and theoretical calculations illustrate that fragility index is a potential numerical measure that elucidate robustness of planktic foraminifera morphotypes. This concept can be applied to infer the robustness of foraminifer test morphologies to taphonomic damage. Such an inference may be valuable while studying planktic foraminifera populations for palaeoenvironmental studies. Applicability of fragility index on calcium carbonate tested microfossils belonging to different geological time is yet to be explored.

Application of fragility index metric to faunal assemblages of the Maastrichtian did not lead to any conclusive inferences or results. This may be because foraminifera fossil assemblage composition obtained for study, is a combination of taphonomic processes and the live community structure. Therefore, this theoretical quantification is inadequate when directly applied to faunal assemblage records.

4.3 Implications on geological record: Bidart

Applicability of the results of thesis study has been tested on faunal data sets of one of the best-known Cretaceous-Tertiary Boundary section. The section is exposed at a beach near Bidart, in the Basque-Cantabrian basin of Southwest France. Studies on this section have illustrated high stress condition in the upper Maastrichtian leading up to the Cretaceous-Paleogene boundary (Punekar et al 16).

Faunal datasets from the End Maastrichtian (CF1 biozone) have been tested against the results obtained from this study. Anomalous increase of fragmentation index has been alluded as a consequence of low pH conditions during the end Maastrichtian (Punekar et al. 2016). Results from experimentation validate that acidic conditions render foraminifera tests more susceptible to breakage, making fragmentation index a valid proxy to interpret palaeocean acidification. Proxies such as magnetic susceptibility, percent calcium carbonate have also been applied as dissolution proxies and attest to acidification events leading up to the end-Cretaceous.

Ocean acidification as an authentic causation of High fragmentation index has been verified experimentally through this study. High fragmentation may also be caused due to vigorous physical agitation. However, closer look at the assemblage structure of CF1 reveal that k-strategist species such as globotruncanids and brazoenesis get enhanced in the record at intervals of high stress (Figure 16). Abundance of globotruncanids shoot from an average of 20% in the middle bathyal sections to 70% correlative to increased fragmentation and low magnetic susceptibility in upper Maastrichtian intervals. Other robust species such as Planoglobulina brazoensis also show anomalously high abundance correlative to peaks in other dissolution based proxies.

Tremendous increase in abundances of specialist k-strategists (globotruncanita, globotruncana, P. brazoensis) in the pre-boundary acidification interval contradicts their biological functionality (Gerta Keller and Abramovich 2009). Intervals of high stress condition are not favourable for the growth of specialist species. This contradiction can be well explained by the resistance of select foraminifera shells to dissolution damage. High fragmentation also with additional data indicating preservation bias in the planktic foraminifer record legitimize the use of fragmentation index as an authentic proxy for ocean acidification.

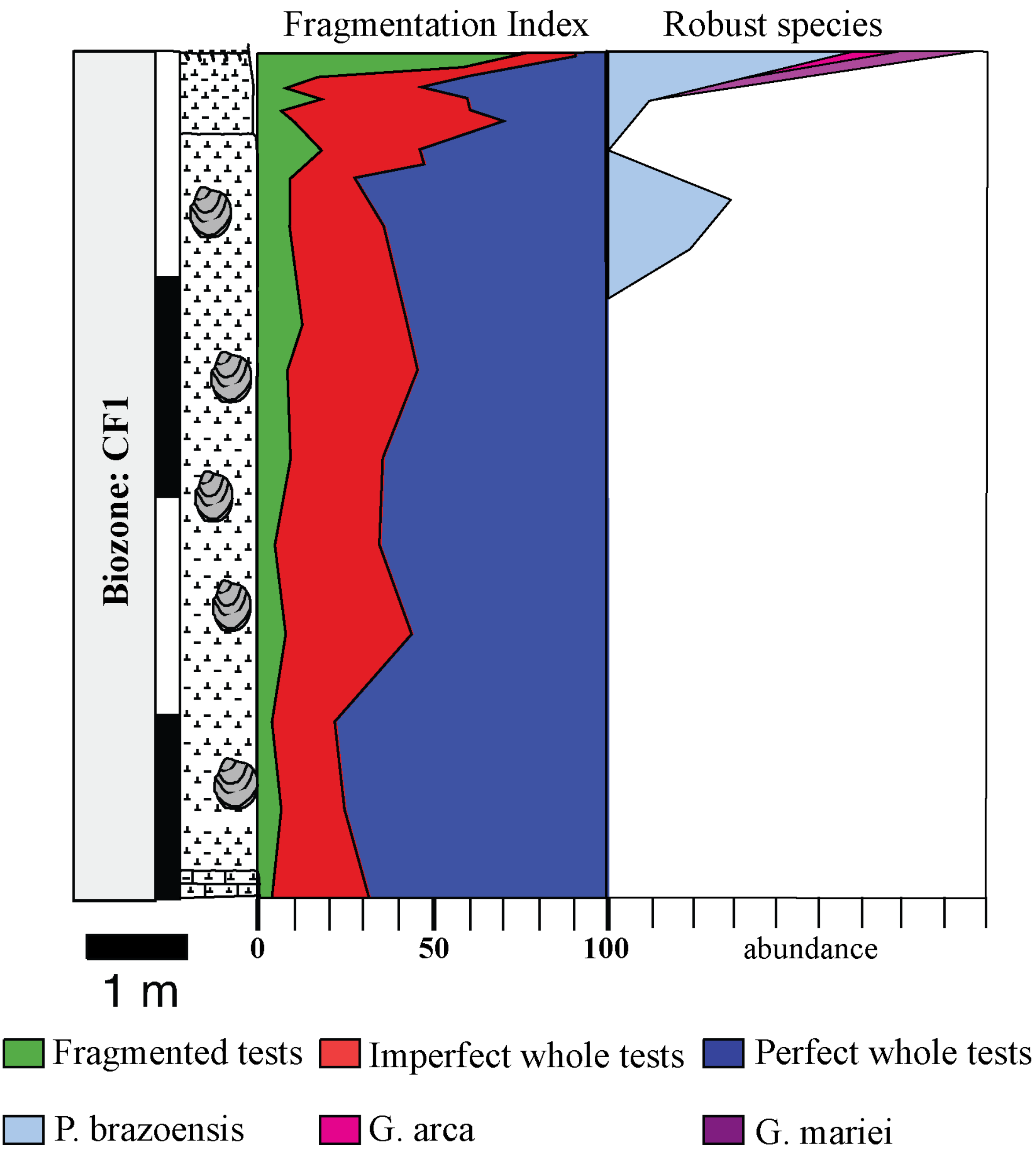

Figure 16-. Trends of Faunal data of Maastrichtian section from Bidart fits the observations and inferences deduced from the study. Enhance fragmentation due to acidification has been validated. Also, there is an enrichment of dissolution resistant morphologies.

Conclusions

Experiments confirm two generalised observations of Cretaceous planktic foraminifera : (i) planktic foraminifera tests are susceptible to enhanced fragmentation during intervals of palaeocean acidification , (ii) some morphotypes of Cretaceous planktic foraminifera are more resistant to fragmentation (taphonomic damage) compared to others. Thesis study also attempts to provide theoretical basis (fragility Index) that explains the nature of the results.

Results from experimentation reveal that acidic (low pH) conditions in the ocean render planktic foraminifera tests more prone to fragmentation. The study also reveals globotruncanids to be the most dissolution resistant morphotype in contrast with heterohelicids being experimentally confirmed as the most fragile morphotypes.

Fragility Index quantified for Maastrichtian foraminifera morphotypes are in full agreement to the experimental results. Low fragility Index of globotruncanids is in agreement with its correspondingly low Fragmentation Index values. Similarly, high fragility Index of heterohelicids (biserials) is in complete agreement with its high Fragmentation Index.

All the results obtained from this study suggest that interval of low palaeocean pH should exhibit very high fragmentation of fossil planktic foraminifera and anomalous increase in abundance of most robust species. Generalisations from experiments accurately fit into faunal data sets of Late-Cretaceous sections (Bidart). Therefore, validation of fragmentation Index and preservation bias in Maastrichtian assemblage, as a proxy for ocean acidification, strengthens the connection between Deccan Volcanism and end-Cretaceous ocean acidification interval.

Bibliography

Abramovich, Sigal, and Gerta Keller. 2002. “High Stress Late Maastrichtian Paleoenvironment : Inference from Planktonic Foraminifera in Tunisia.” 178.

Alvarez, L W, W Alvarez, F Asaro, and H V Michel. 1980. “Extraterrestrial Cause for the Cretaceous-Tertiary Extinction - Experimental Results and Theoretical Interpretation.” *Science* 208(4448): 1095–1108.

Berger, H, and David J W Piper. 1972. “DIFFERENTIAL.” 17(March).

Berger, Wolfgang H. 1968. “PLANKTONIC FORAMINIFERA: SELECTIVE SOLUTION AND THE LYSOCLINE.” *Marine Geology* 8(1970): 111–38.

Bohor, Bruce F. 1990. “Shock Induced Microdeformations in Quartz and Other Mineralogical Indications of an Impact Event at the Cretaceous-Tertiary Boundary.” 171: 359–72.

Bond, David P.G., and Paul B. Wignall. 2010. “Pyrite Framboid Study of Marine Permian-Triassic Boundary Sections: A Complex Anoxic Event and Its Relationship to Contemporaneous Mass Extinction.” *Bulletin of the Geological Society of America* 122(7–8): 1265–79.

Bond, David P G, and Stephen E Grasby. 2017. “On the Causes of Mass Extinctions.” *Palaeogeography, Palaeoclimatology, Palaeoecology* 478: 3–29. http://dx.doi.org/10.1016/j.palaeo.2016.11.005.

Bond, David P G, and Paul B Wignall. 2014. “Large Igneous Provinces and Mass Extinctions: An Update.” In , 29–55.

Boynton, William V. et al. 2002. “Chicxulub Crater: A Possible Cretaceous/Tertiary Boundary Impact Crater on the Yucatán Peninsula, Mexico.” *Geology* 19(9): 867.

Chenet, Anne-lise. 2008. “Determination of Rapid Deccan Eruptions across the Cretaceous-Tertiary Boundary Using Paleomagnetic Secular Variation : Results from a 1200-m-Thick Section in the Mahabaleshwar Escarpment.” 113.

Chenet, Anne-lise, and Vincent Courtillot. 2009. “Determination of Rapid Deccan Eruptions across the Cretaceous- Tertiary Boundary Using Paleomagnetic Secular Variation : 2 .

Constraints from Analysis of Eight New Sections and Synthesis for a 3500-m-Thick Composite Section.” 114: 1–38.

Courtillot, Vincent E., and Paul R. Renne. 2003. “On the Ages of Flood Basalt Events.” *Comptes Rendus - Geoscience* 335(1): 113–40.

Doney, Scott C., Victoria J. Fabry, Richard A. Feely, and Joan A. Kleypas. 2008. “ Ocean Acidification: The Other CO 2 Problem .” *Annual Review of Marine Science* 1(1): 169–92.

Font, Eric et al. 2016. “Mercury Anomaly , Deccan Volcanism , and the End-Cretaceous Mass Extinction.” 44(2): 171–74.

Font, Eric, Thierry Adatte, Mariana Andrade, et al. 2018. “Deccan Volcanism Induced High-Stress Environment during the Cretaceous–Paleogene Transition at Zumaia, Spain: Evidence from Magnetic, Mineralogical and Biostratigraphic Records.” *Earth and Planetary Science Letters* 484: 53–66. https://doi.org/10.1016/j.epsl.2017.11.055.

Font, Eric, Thierry Adatte, Gerta Keller, et al. 2018. “The Global Imprint of Deccan Volcanism in the Sedimentary Record across the End-Cretaceous Mass Extinction.” 20: 50019.

Font, Eric, Gerta Keller, and Cristina Veiga-pires. 2014. “Atmospheric Halogen and Acid Rains during the Main Phase of Deccan Eruptions : Magnetic and Mineral Evidence.” 2505(18): 353–68.

Gómez, Juan J., and Antonio Goy. 2011. “Warming-Driven Mass Extinction in the Early Toarcian (Early Jurassic) of Northern and Central Spain. Correlation with Other Time-Equivalent European Sections.” *Palaeogeography, Palaeoclimatology, Palaeoecology* 306(3–4): 176–95. http://dx.doi.org/10.1016/j.palaeo.2011.04.018.

Good, Norman E et al. 1966. “Ion For.” (2): 467–77.

Hautmann, Michael. 2004. “Effect of End-Triassic CO2 Maximum on Carbonate Sedimentation and Marine Mass Extinction.” *Facies* 50(2): 257–61.

Hildebrand, Alan R et al. 1991. “Geology Chicxulub Crater : A Possible Cretaceous / Tertiary Boundary Impact Crater on The.” (May 2009).

Honisch, B. et al. 2012. “The Geological Record of Ocean Acidification.” *Science* 335(6072):

1058–63.

Joachimski, M. M. et al. 2009. “Devonian Climate and Reef Evolution: Insights from Oxygen Isotopes in Apatite.” *Earth and Planetary Science Letters* 284(3–4): 599–609. http://dx.doi.org/10.1016/j.epsl.2009.05.028.

Keller, G. et al. 2008. “Main Deccan Volcanism Phase Ends near the K–T Boundary: Evidence from the Krishna–Godavari Basin, SE India.” *Earth and Planetary Science Letters* 268(3–4): 293–311.

Keller, G. et. al. 2011. “Deccan Volcanism Linked to the Cretaceous-Tertiary Boundary Mass Extinction: New Evidence from ONGC Wells in the Krishna-Godavari Basin.” *Journal of the Geological Society of India* 78(5): 399–428.

Keller, G., W. Stinnesbeck, T. Adatte, and D. Stüben. 2003. “Multiple Impacts across the Cretaceous-Tertiary Boundary.” *Earth-Science Reviews* 62(3–4): 327–63.

Keller, Gerta et al. 2007. “Chicxulub Impact Predates K-T Boundary: New Evidence from Brazos, Texas.” *Earth and Planetary Science Letters* 255(3–4): 339–56.

Keller, Gerta et al. 2010. “More Evidence That the Chicxulub Impact Predates the K/T Mass Extinction.” *Meteoritics & Planetary Science* 39(7): 1127–44.

Keller, Gerta, and Sigal Abramovich. 2009. “Lilliput Effect in Late Maastrichtian Planktic Foraminifera: Response to Environmental Stress.” *Palaeogeography, Palaeoclimatology, Palaeoecology* 284(1–2): 47–62. http://dx.doi.org/10.1016/j.palaeo.2009.08.029.

Kring, David A. 2007. “The Chicxulub Impact Event and Its Environmental Consequences at the Cretaceous-Tertiary Boundary.” *Palaeogeography, Palaeoclimatology, Palaeoecology* 255(1–2): 4–21.

L., Fok Pun. 1982. “Settling Velocity of Planktic Foraminifera.”

Li, Chao et al. 2016. “Two Pulses of Oceanic Environmental Disturbance during the Permian–Triassic Boundary Crisis.” *Earth and Planetary Science Letters* 443: 139–52. http://dx.doi.org/10.1016/j.epsl.2016.03.030.

Li, Liangquan, and Gerta Keller. 1998. “Maastrichtian Climate , Productivity and Fauna1 Turnovers in Planktic Foraminifera in South Atlantic DSDP Sites 525A and 21.” 33: 55–

86.

Montanari, A. et al. 1983. “Spheroids at the Cretaceous-Tertiary Boundary Are Altered Impact Droplets of Basaltic Composition.” *Geology* 11(11): 668–71.

Nguyen, Thi Minh Phuong, Maria Rose Petrizzo, and Robert P Speijer. 2009. “Experimental Dissolution of a Fossil Foraminiferal Assemblage (Paleocene-Eocene Thermal Maximum, Dababiya, Egypt): Implications for Paleoenvironmental Reconstructions.” *Marine Micropaleontology* 73(3–4): 241–58. http://dx.doi.org/10.1016/j.marmicro.2009.10.005.

Payne, Jonathan L., and Lee R. Kump. 2007. “Evidence for Recurrent Early Triassic Massive Volcanism from Quantitative Interpretation of Carbon Isotope Fluctuations.” *Earth and Planetary Science Letters* 256(1–2): 264–77.

Punekar, Jahnavi et al. 2015. “A Multi-Proxy Approach to Decode the End-Cretaceous Mass Extinction.” *Palaeogeography, Palaeoclimatology, Palaeoecology* 441: 116–36. http://dx.doi.org/10.1016/j.palaeo.2015.08.025.

Punekar, Jahnavi, Paula Mateo, and Gerta Keller. 2014. “Effects of Deccan Volcanism on Paleoenvironment and Planktic Foraminifera: A Global Survey.” In , 91–116.

Sarmeinto, J. L., and N. Gruber. 2006. *Ocean Biogeochemical Dynamics*. Princeton University Press.

Schoene, Blair et al. 2015. “U-Pb Geochronology of the Deccan Traps and Relation to the End-Cretaceous Mass Extinction.” *Science* 347(6218): 182–84. http://www.sciencemag.org/cgi/doi/10.1126/science.aaa0118%5Cnpapers2://publication/doi/10.1126/science.aaa0118.

Schoene, Blair et. al. 2019. “U-Pb Constraints on Pulsed Eruption of the Deccan Traps across the End-Cretaceous Mass Extinction.” *Science* 363(6429): 862–66. http://www.sciencemag.org/lookup/doi/10.1126/science.aau2422.

Thibodeau, Alyson M. et al. 2016. “Mercury Anomalies and the Timing of Biotic Recovery Following the End-Triassic Mass Extinction.” *Nature Communications* 7(1): 1–8. http://dx.doi.org/10.1038/ncomms11147.

Toon, Owen B. et al. 2004. “Environmental Perturbations Caused by the Impacts of Asteroids and Comets.” *Reviews of Geophysics* 35(1): 41–78.

Veron, J. E.N. 2008. “Mass Extinctions and Ocean Acidification: Biological Constraints on Geological Dilemmas.” *Coral Reefs* 27(3): 459–72.

Wignall, P. B. 2001. “Large Igneous Provinces and Mass Extinctions.” *Earth Science Reviews* 53(1–2): 1–33.

Wignall, P. B. et. al. 2012. “Lethally Hot Temperatures During the Early Triassic Greenhouse.” *Science* 338(6105): 366–70.

Wignall, Paul B. et al. 2016. “Ultra-Shallow-Marine Anoxia in an Early Triassic Shallow-Marine Clastic Ramp (Spitsbergen) and the Suppression of Benthic Radiation.” *Geological Magazine* 153(2): 316–31.

Zeebe, Richard E. 2012. “History of Seawater Carbonate Chemistry , Atmospheric CO 2 , and Ocean Acidification.”