FOSSIL CORALS AS ARCHIVES OF SECULAR VARIATIONS IN SEAWATER CHEMISTRY

Anne M. Gothmann

A DISSERTATION
PRESENTED TO THE FACULTY OF
PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

RECOMMENDED FOR ACCEPTANCE
BY THE DEPARTMENT OF
GEOSCIENCES
Advisor: Michael Bender

September, 2015
ABSTRACT

Records of the elemental and isotopic composition of the oceans can help elucidate the geologic controls on seawater chemistry and climate over million-year timescales. This thesis describes the development of a new fossil coral archive that can be used to reconstruct properties of seawater chemistry for the past ~200 My. It also details the application of this archive to investigate changes in seawater Mg/Ca, Sr/Ca, U/Ca, $\delta^{26}$Mg, and $\delta^{44}$Ca over the Mesozoic and Cenozoic.

Results of diagenetic tests used to validate ~60 fossil coral samples for studies of seawater paleochemistry are presented in Chapters 2 and 4. The validated samples range in age from Triassic through Recent. X-ray diffractometry, scanning electron microscopy, petrographic microscopy, cathodoluminescence microscopy, and micro-raman spectroscopy studies indicate that sample mineralogy is preserved (as aragonite). Studies of $^{87}$Sr/$^{86}$Sr, carbonate clumped isotopes, trace elements sensitive to diagenesis, He/U dating, and U isotopes are used to screen for geochemical signs of alteration.

Records of seawater chemistry inferred from validated fossil coral samples are presented in Chapters 2-4. Mg/Ca$_{\text{seawater}}$ inferred from fossil corals (Chapter 2) is low during the Mesozoic, and increases by a factor of ~5 between 80 Ma and today – compatible with existing reconstructions. The record helps improve our understanding of the timing of Mg/Ca$_{\text{seawater}}$ changes since the Triassic. Inferred Sr/Ca$_{\text{seawater}}$ (Chapter 2) varies between 8 and 13 mmol/mol since ~200 Ma, with a maximum in the Late Cretaceous. This result is consistent with reconstructions from benthic foraminifera and fossil fish teeth. A record of $\delta^{26}$Mg$_{\text{seawater}}$ from fossil corals (Chapter 3) helps distinguish between two existing records that give conflicting
results, and indicates that the fraction of Mg removed from seawater as dolomite has not changed significantly over the Cenozoic. A reconstruction of fossil coral U/Ca (Chapter 4) suggests that $[U]_{\text{seawater}}$ has increased by a factor of $\sim 2$ since the Eocene, with implications for our understanding of past seawater $[\text{CO}_3^{2-}]$ and the importance of U removal in reducing sediments. In Chapter 5, a record of $\delta^{44}\text{Ca}$ from fossil corals is presented. This record may reflect changes in coral Ca isotope discrimination through time, rather than changes in $\delta^{44}\text{Ca}_{\text{seawater}}$. 

ACKNOWLEDGEMENTS

I would like to thank the very many people who have had a profound impact on the work presented in this thesis. In addition to the advisors, postdocs, lab technicians, and graduate student peers who I’ve worked with at Princeton, I feel fortunate to have worked in the labs of many other PIs, without whom this thesis would have been far from possible.

I would be nowhere if not for my primary advisor, Michael Bender. The breadth of Michael’s scientific expertise, his tenacity, and his depth of thought have motivated me to become a better scientist each day. Mostly through example, Michael has taught me the importance of considering scientific questions with utmost care and detail before jumping to conclusions. He has also taught me the value of using precise language, and as such has helped me to become a much better scientific writer and speaker. I am not only in awe of the quality of Michael’s science; his constant support (together with an occasional golf-based metaphor) have also been indispensable in helping me navigate my way through a PhD. Whenever exciting data rolled in, I knew I could look forward to an impassioned ‘yippee’ from Michael. Whenever I presented at a conference or workshop, he was there to make sure I was comfortable and prepared. Whenever I encountered problems with data or methods, he helped me to take a step back, and took the time to think things through with me until the solution became clear. It is difficult to imagine a scientific experience where I do not have Michael as my advisor. I can only hope that his guidance over the last 5 years has become deeply enough ingrained that it continues to direct me in my future endeavors.

In addition to Michael, I am grateful to have been able to work with a legion of other supportive advisors. In particular, John Higgins has graciously welcomed me into his lab, treated me like one of his own graduate students, and has strongly influenced the way I think about
seawater chemistry, the global carbon cycle, and geochemical modeling. His willingness to help with all things – whether it be thinking through a new scientific idea, troubleshooting lab-related issues, or offering general career guidance – is truly remarkable. In addition, he has taught me to always be ‘cautiously optimistic’ in the lab, making all of my experiences with ICP-MS happy ones.

From Jess Adkins I have learned about the fun that is coral biomineralization, and more importantly, to view my data with a quantitatively critical eye. Jess (together with Yunbin Guan) helped steer me through my first experiences with analytical geochemistry as a graduate student. Jess’s generosity – from the very first year of my PhD and continuing onward – has enabled much of my thesis work.

One of the luckiest moments of my PhD was finding an important sample ID in a paper written by Jarek Stolarski. Jarek’s endless enthusiasm for science never ceases to amaze me, and I can always count on his anecdotes (delivered either in person, via email, or over Skype) as a source of laughter. Jarek’s studies of the macro- and micro-morphology of coral skeletons are works of art that have opened my eyes to the intricacies of coral biology.

Kate Dennis and Dan Schrag welcomed me into the Schrag Lab to learn carbonate clumped isotope paleothermometry. Kate’s patience, guidance (both inside and outside of lab), and keen intuition make her one of the best mentors I’ve ever had. Blair Schoene introduced me to TIMS and has helped me to hone my clean lab skillset. Blair’s meticulous approach toward labwork has, without a doubt, made me a more careful scientist. Many others have also welcomed me into their labs and have helped me learn new measurement techniques from a fundamental level: Ken Farley and Ryan McKeon helped me to learn how to make measurements of $^4$He, Noah Planavsky and Xiangli Wang helped me make U isotope
measurements, Jerry Poirier (formerly of the Princeton Imagining and Analysis Center) helped me learn how to use two different scanning electron microscopes and an X-ray diffractometer.

Wally Broecker’s work is generally an inspiration to me – as it is for so many other geochemists – but his thoughts on seawater chemistry in particular have had a large impact on my thesis. His insistence that we measure uranium in fossil corals has led to one of my favorite chapters presented here (Chapter 4).

I would also like to thank my other committee members – Danny Sigman and Adam Maloof. They have always been available to lend a helpful ear when I’ve been in need. Their comments during committee meetings, lab meetings, and practice talks over the last 5 years have been crucial in shaping my dissertation research. In addition, Satish Myneni, François Morel, and Alex Gagnon have all helped me understand important geochemical concepts, and have influenced my scientific thinking about much of the data included in this thesis. Satish has been an invaluable source of information on spectroscopy and mineralogy. François has helped me to think about metal complexation in seawater. Alex Gagnon has been a constant source of thought-provoking ideas regarding SIMS methodologies and coral biomineralization from the time when he sat in front of an SEM with Michael and me during the 1st year of my PhD.

In addition to the myriad of PIs who have welcomed me into their labs, I have had the opportunity to interact with countless postdocs, lab technicians, and graduate student peers who have made my thesis experience extraordinary. I would like to thank all of the members of the Bender and Sigman Labs at Princeton: Katye Altieri, Bonnie Chang, Elle Chimiak, Jason Cutrera, Karen Ellis, Sarah Fawcett, Paul Gauthier, Julie Granger, Mathis Hain, Kuan Huang, Bror Jönsson, Emma Kast, Sebastian Kopf, Dario Marconi, Bob Mika, Sergey Oleynik, Patrick
Of the ‘Benderites’ and ‘Sigmoids’, I would particularly like to thank Audrey, Tony and Mathis. I feel incredibly lucky to have had Audrey as a lab-mate. She is one of the most caring, steadfast, and thoughtful friends I have ever met, and these qualities also shine through in her scientific work. My experience at Princeton would not have been nearly as joyous if I did not sit back-to-back with her for four years. Tony has been an endless source of interesting discussions – whether they be about corals, geochemistry more broadly, or about the intricacies of academia. His perceptiveness is astounding, and I have learned very much from him since we’ve started as graduate students together. Mathis has been one of the most patient and giving teachers I have ever encountered. Because of Mathis, I now feel comfortable with both carbonate chemistry and MATLAB.

I am also grateful for the official (and unofficial) members of the Higgins Lab: Anne-Sofie Ahm, Alliya Akhtar, Or Bialik, Clara Blättler, Blake Dyer, Liz Lundstrom, Dani Ramos, and Sarah Jane White. Liz Lundstrom has a contagiously positive attitude and has a way of making even the most disappointing days in the lab enjoyable. Her scrupulous approach toward solving problems is something every scientist should emulate. Clara Blättler’s work is an exemplar of first-rate science. I feel fortunate to have been able to learn from her, and to take part in helping her and Liz craft the most creative birthday cakes I’ve ever seen. Like Clara, Jon Husson has been a wonderful role model throughout my time at Princeton. He is one of the best investigators of science (and other things) I’ve come across, and my favorite person to talk to about Harry Potter and Game of Thrones. Alliya Akhtar and Blake Dyer helped me learn the ins and outs of the Sercon, and I am hugely appreciative for their assistance. Dani Ramos’s Amherst
heritage should put us at odds, but my time working alongside her and Anne-Sofie Ahm in the Higgins lab has been nothing less than fantastic. I not only enjoy talking to Sarah Jane White about our struggles on the Element 2, but I am also indebted to her for her help with thinking about uranium complexation chemistry.

I am so appreciative as well for the outstanding Princeton Geosciences staff – especially Sheryl Robas, Dawn Reading, Mary Rose Russo, Doreen Sullivan, Eva Groves, and Theresa Autino. I also thank Laurel Goodell, Jessica Irving, and the students of GEO203 for providing an outstanding environment in which to be a teaching assistant.

In addition to the people at Princeton, I need to thank the remarkable graduate students and postdocs in Jess Adkins’s lab at Caltech. Andrea Burke, Sophie Hines, Guillaume Paris, Ted Present, James Rae, Adam Subhas, and Nithya Thiagarajan have made Pasadena feel like home whenever I’ve visited. Guillaume Paris helped me through my first experience in a clean lab, and both he and James Rae have contributed many helpful ideas regarding my thesis data.

I am grateful to all of the people and institutions who have contributed samples for my thesis work: Steve Cairns and Tim Coffer (Smithsonian Institution), Linda Ivany, Bill Thompson and Anne Cohen, Roger Portell (FMNH), the USGS Core Research Center, and the Paleontological Research Institution.

I would have never endeavored to undertake a PhD in Geosciences without the educators who encouraged me in high school and at Williams College. Mea Cook whetted my appetite for paleoclimate and introduced me to geoscience research. Years after graduating from college I remain amazed by her dedication to teaching and still seek her out for advice. Ronadh Cox and David Dethier also played a great role in my becoming an Earth scientist. David would
talk with me about geology over coffee in Schow Library for hours, and during that time he convinced me to double major in Geoscience. Ronadh taught me the geologic timescale, gave me my first introduction to scientific writing, and has been a supreme role model for a woman in science. Bud Wobus and Paul Karabinos have always welcomed me into the Williams Geosciences family, both during and after graduation. Susan Arrigoni and her biology class at Millburn High School made me fall in love with science.

Most importantly, I need to thank my family and friends, whose love never ceases to keep me happy both inside and outside of the lab. Thanks to my dad for always taking an interest in my work, for teaching me how to be detail-oriented, and for passing on his love of acting and musical theater – I am a better public speaker because of it. Thanks to my Mom for being the best teacher I’ve had in my life, and for inspiring me to be one too. Thanks to my brother, A.J., for always reminding me how to be lighthearted. Thanks to Jan and Leanne for always keeping me grounded. Thanks to my grandmothers, Josephine and Raye, who are the two strongest women I know and whose decisions and experiences are constant reminders to pursue my dreams. Lastly, I want to thank Jamie – my best friend: Thanks for quizzing me on generals topics, for keeping me company on trips to the lab to condition columns, for proofreading drafts of manuscripts, and for learning about so many elements on the periodic table that you were able to pick a favorite (strontium).
## Contents

Abstract ................................................................................................................................. i

Acknowledgements ............................................................................................................... iii

List of Figures ......................................................................................................................... xiv

List of Tables ......................................................................................................................... xvi

1. Introduction ...................................................................................................................... 1
   1.1 Global change in Earth’s surface environment ......................................................... 1
   1.2 The geological importance of seawater chemistry .................................................. 3
   1.3 Biogenic carbonates as archives of seawater chemistry ........................................... 8
      1.3.1 Scleractinian fossil corals ................................................................................. 9
      1.3.2 The problem of diagenesis .............................................................................. 11
      1.3.3 The problem of vital effects ............................................................................. 13
   1.4 Thesis Overview ......................................................................................................... 15

References ............................................................................................................................ 18

2. Fossil corals as archives of secular variations in seawater chemistry since the Mesozoic .............................................................................................................................. 28
   2.1 Abstract ...................................................................................................................... 28
   2.2 Introduction ................................................................................................................ 29
      2.2.1 Coral background ........................................................................................... 31
      2.2.2 Corals as recorders of seawater properties ..................................................... 33
      2.2.3 Fossil coral preservation ................................................................................ 35
2.3 Samples and Methods ................................................................. 37
  2.3.1 Sample preparation .......................................................... 37
  2.3.2 X-ray diffraction ............................................................... 38
  2.3.3 Imaging methods .............................................................. 38
  2.3.4 Secondary Ion Mass Spectrometry (SIMS) ................................... 47
  2.3.5 Clumped Isotopes ............................................................ 49
  2.3.6 Sr Isotopes .................................................................. 49
2.4 Results and Discussion ................................................................. 50
  2.4.1 Screening samples for diagenesis ........................................... 50
    2.4.1.1 X-ray Diffraction ......................................................... 51
    2.4.1.2 Microscopy ................................................................. 53
    2.4.1.3 Mn/Ca Ratios .............................................................. 55
    2.4.1.4 Trace element patterns ............................................... 60
    2.4.1.5 Carbonate clumped isotopes ...................................... 63
    2.4.1.6 Sr Isotopes ................................................................. 65
  2.4.2 Secular variations in seawater Mg/Ca ....................................... 69
  2.4.3 Secular variations in seawater Sr/Ca ....................................... 74
2.5 Conclusion ............................................................................ 76
2.6 Acknowledgements .................................................................. 76
2.7 Supplementary .......................................................................... 77
2.8 Author contributions and previous presentations of this work ............ 77

References 80
3. A Cenozoic record of Mg isotopes from fossil corals ........................................... 94

3.1 Abstract ......................................................................................................................... 94
3.2 Introduction ..................................................................................................................... 96
3.3 Methods ......................................................................................................................... 100
3.4 Results .......................................................................................................................... 102
3.5 Discussion ..................................................................................................................... 105
  3.5.1 Preservation of fossil coral $\delta^{26}$Mg................................................................. 105
  3.5.2 Absence of significant coral Mg isotope vital effects ............................................. 107
  3.5.3 Mg isotope records and their implications for controls on seawater [Mg]................................................................. 110
3.6 Conclusions .................................................................................................................. 112
3.7 Author contributions and previous presentations of this work.............................. 112
3.8 Supplementary............................................................................................................ 113

References ....................................................................................................................... 116

4. Variations in seawater uranium concentration during the Cenozoic reconstructed from well preserved aragonitic fossil corals ........................................................................... 123

4.1 Abstract ......................................................................................................................... 123
4.2 Introduction ..................................................................................................................... 124
4.3 Methods ......................................................................................................................... 126
  4.3.1 U/Ca measurements................................................................................................. 126
  4.3.2 $^4$He measurements .............................................................................................. 127
  4.3.3 Uranium isotope analyses......................................................................................... 128
4.4 Results and Discussion................................................................................................. 129
List of Figures

1.1 Phanerozoic summary of changes in climate, sea level, and ocean chemistry .................. 3
1.2 Schematic of the global carbon cycle ............................................................................ 6
1.3 Relationship between coral Sr/Ca and seawater Sr/Ca .................................................. 10
1.4 Diagenetic alteration in fossil corals ............................................................................... 13

2.1 Structure of the coral skeleton ....................................................................................... 30
2.2 Map of sample provenance .......................................................................................... 35
2.3 Characterization of diagenesis by petrographic, optical microscopy, and SEM ............ 52
2.4 Characterization of preservation by Cathodoluminescence and Raman ....................... 54
2.5 Mn/Ca as a diagenetic indicator of small-scale alteration in Cretaceous corals .......... 57
2.6 Representative plots of Sr/Ca vs. Mg/Ca for fossil corals ............................................... 59
2.7 S/Ca and Na/Ca relationships in modern coral, fossil coral, and inorganic aragonite ... 61
2.8 Carbonate clumped isotope results ............................................................................... 64
2.9 Sr isotope results ......................................................................................................... 66
2.10 Records of Mg/Ca and Sr/Ca from fossil corals ........................................................... 68
2.11 Additional representations of Mg/Ca measured in fossil corals .................................. 72

3.1 Summary of reconstructions of seawater [Mg] and [Ca] ............................................... 95
3.2 Schematic of the seawater Mg isotope mass balance ..................................................... 97
3.3 Cenozoic records of seawater Mg isotopes .................................................................. 104
3.4 Comparison of Mg/Ca ratios measured by SIMS and on bulk powders by ICP-MS .... 106
3.5 Triple isotope plot showing Mg isotope results ......................................................... 113
3.6 Results of model calculations showing the effects of a Cenozoic decrease in
dolomitization and a Cenozoic decrease in Mg uptake in clays on seawater δ²⁶Mg .......... 114

4.1 Corrected He/U ages vs. Expected stratigraphic age ..................................................... 135
4.2 Summary of fossil coral uranium isotope results .............................................................. 137
4.3 Fossil coral U/Ca and reconstructed seawater [U] vs. Geologic Age ................................ 142
4.4 Seawater [Ca] inferred from fossil coral U/Ca.................................................................. 147
4.5 Schematic of the modern seawater U mass balance ......................................................... 149
4.6 Modeled histories of seawater [U] and U isotopes............................................................. 153

5.1 Sketch of key skeletal compartments and reservoirs that play a role in coral
calcification .......................................................................................................................... 172
5.2 Records of seawater δ⁴⁴/⁴⁰Ca vs. time ............................................................................. 181
5.3 Fossil and cultured coral Ca isotope discrimination ......................................................... 190
5.4 Results of Rayleigh fractionation calculations .................................................................. 196
5.5 Schematic showing the steady-state Ca mass balance of the coral calcifying fluid..... 198
5.6 Calcification rates of cultured corals ............................................................................... 204
5.7 δ⁴⁴Ca of cultured corals vs. culture solution [Mg] ............................................................. 205

A.1 Lithium gravity column calibrations ................................................................. 222
A.2 Chromatograms showing measurements of sample conductivity from IC .......... 224
A.3 Mixing plot between LSVEC Li and blank Li ............................................................. 226
A.4 Isotopic composition of Li in pure lithium standards doped with Na ...................... 226
A.5 Increase in the intensity of the machine Li blank over an analytical session............ 228
## List of Tables

2.1 Summary of diagenetic test results ............................................................................. 39

3.1 Results of Mg isotope analyses for fossil corals ....................................................... 102

3.2 Parameters and initial conditions chosen for 1-box model of the Mg seawater balance
........................................................................................................................................ 114

4.1 Summary of sources and sinks of seawater U ............................................................. 125

4.2 Summary of U/Ca results, He/U dating experiments, and alpha ejection corrections . 132

5.1 Results of Ca isotope analyses in recent and fossil corals ........................................ 183

5.2 Results of Ca isotope analyses in bulk carbonates .................................................... 184

5.3 Results of Ca isotope analyses in cultured corals ..................................................... 191

5.4 Fossil coral identification and provenance ................................................................. 202

A.1 Results of Li isotope standard measurements ......................................................... 230
Chapter 1.

Introduction

1.1 Global change in Earth’s surface environment

For the last few decades, the concept of global change has been associated most commonly with anthropogenic climate change and its impacts on the atmosphere, hydrosphere, and biosphere. The burning of fossil fuels has caused atmospheric CO$_2$ concentrations to rise from a pre-industrial level of ~280 parts per million (ppm) to 403 ppm today (CO2now.org). This rise in atmospheric pCO$_2$ has been accompanied, since the late 19$^{th}$ century, by a 0.85 °C increase in global temperature, a 26% increase in the acidity of the surface ocean, a ~0.2 m increase in global sea level, and increased extinction rates for organisms living both on land and in the oceans (IPCC, 2014).

Since Earth’s formation 4.57 billion years ago (Connelly et al., 2012), its surface environment has also sustained significant natural changes. As indicated by the presence of microfossils in the 3.46 billion-year old Apex chert from Australia, life on Earth evolved at least that long ago (Brasier et al. 2015; Schopf et al. 1993). Free oxygen in the atmosphere, however, which is required for much of modern life to survive, was scarce until between 2.4 and 2.1 billion years ago (Lyons et al. 2014). Earth’s climate and environment have also experienced periods of intense cold. During the Neoproterozoic (1000 to 542 million years ago), there were durations of time for which ice was thought to cover the entire surface of the globe. These periods are referred to as ‘Snowball Earth’ episodes (Hoffman et al. 1998). Less extreme glaciation has occurred during the Pleistocene ice ages – during which concentrations of
atmospheric carbon dioxide and methane in the atmosphere, ocean dynamics, biology, and global temperatures have varied (Petit et al. 1999; Lüthi et al. 2008). Similar ‘ice ages’ are thought to have occurred during the Late Paleozoic – from ~350 to ~290 million years ago (Montañez and Poulsen, 2013). In the Eocene, about 50 million years ago, Earth’s climate was so warm that crocodiles lived as far north as Ellesmere Island, which is situated in the Canadian arctic just west of Greenland (Estes and Hutchinson, 1980). Around the same time, India collided with southern Asia (Bouilhol et al. 2013) after which global temperatures began to gradually cool toward the present (Zachos et al. 2001).

The observations of global change listed above, in addition to a range of others not mentioned here, beg fundamental questions about the world around us: What are the geologic processes responsible for driving observed climatic changes on Earth and how are they regulated? How do these climatic changes relate to other major changes in Earth’s surface environment, such as changes in tectonics or the chemical composition of the oceans? How does Earth’s biosphere respond to variations in environmental boundary conditions?

The research presented in this thesis aims to address parts of the abovementioned questions in the context of the last ~200 million years of Earth history, during which climate has naturally transitioned between times of relative warmth (a ‘greenhouse climate’) and relative cold (an ‘icehouse climate’) (Fig. 1.1). The mechanisms driving the shifts between ‘greenhouse’ and ‘icehouse’ are not completely understood. However, the fact that fluctuations between greenhouse and icehouse have occurred every ~100 million years or so since the beginning of the Phanerozoic (542 million years ago), points to the existence of geological forces that are able to both perturb and strongly stabilize the climate system. Importantly, in line with the questions above, the shifts between greenhouse and icehouse climate coincide with other notable
environmental changes: (1) variations in global sea levels, (2) changes in the motion and configuration of Earth’s continents, and (3) variations in the chemical composition of the oceans.

**Figure 1.1** Summary of changes in climate, sea level, ocean chemistry, and the configuration of the continents for the last 542 million years. Timing of changes in ocean chemistry coincide with changes in global climate and sea level. Data in the ocean chemistry panel come from Lowenstein et al. (2001; 2003; 2005), Horita et al. (2002), Timofeeff et al. (2006), Dickson et al. (2002; 2004), Coggon et al. (2010), Rausch et al. (2010), and Gothmann et al. (2015).

### 1.2 The geological importance of seawater chemistry

Through connections with the atmosphere, biosphere, and lithosphere, the chemical composition of the oceans integrates geological processes that control Earth’s climate and
environment. As such, knowledge of seawater chemistry and its evolution can offer valuable insight into the evolution of the Earth system through time. Seawater chemistry’s importance in the context of Earth history was noticed early on, as reflected in the following quote from a seminal paper by Rubey (1951):

My interest in this general problem [the composition of seawater] grew from a paper on which I began working a number of years ago…It soon became evident that this question ramifies almost endlessly into nearly every fundamental problem of earth history and far beyond into the foggy borderlands between other scientific disciplines.

– William W. Rubey (1951)

The origins of seawater chemistry have also been of interest to a range of earlier natural scientists including Pliny the Elder, Aristotle, and Robert Boyle (Riley, 1965).

The concentration of any element in seawater is determined by the rate of delivery of that element to the oceans relative to the rate of its removal, with processes that deliver elements to seawater referred to as sources and the processes that remove them referred to as sinks. Imbalances in this so-called “mass-balance” drive changes in the seawater concentration for that element, as shown by the first order differential equation below, where \([C]\) represents the concentration of the element of interest:

\[
\text{Change in concentration} = \frac{d[C]}{dt} = \text{sources} - \text{sinks} \quad (\text{Eqn. 1.1}),
\]

The length of time it takes for the concentration of an element to respond to such imbalances is described by the residence time of the element, which is proportional to the concentration of the element in seawater and the rate at which the element is delivered. Residence times for elements in seawater vary from a few years to 10s of millions of years (Sarmiento and Gruber, 2006). The
elements of interest for this thesis (magnesium, calcium, uranium, strontium) are elements that have residence times on the order of 1 million years.

The processes that control the abundance of most major ions in seawater (including magnesium and calcium) are also intimately connected with the geological carbon cycle, as depicted in simplified form in Figure 1.2. Carbon (C), in the form of CO$_2$, is delivered to the atmosphere from the Deep Earth by volcanism. This carbon dioxide then reacts with water molecules in the atmosphere, where it forms carbonic acid, and is precipitated out as rain:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \text{(aq)}$$  \hspace{1cm} (Eqn. 1.2)

The subsequent reaction of carbonic acid and carbonate and silicate rocks on the continents, results in the production of ions including magnesium (Mg), calcium (Ca), and potassium (K). These ions, together with carbon, are eventually delivered to seawater by rivers (Eqn. 1.3 and 1.4):

*Silicate weathering:* \hspace{1cm} $\text{H}_2\text{CO}_3\text{(aq)} + \text{CaSiO}_3\text{(s)} \rightarrow \text{Ca}^{2+}\text{(aq)} + \text{HCO}_3^-\text{(aq)} + \text{HSiO}_3^-\text{(aq)} \rightarrow$

$$\text{CaCO}_3\text{(s)} + \text{H}_2\text{SiO}_3\text{(aq)}$$ \hspace{1cm} (Eqn. 1.3)

*Carbonate weathering:* \hspace{1cm} $\text{H}_2\text{CO}_3\text{(aq)} + \text{CaCO}_3\text{(s)} \rightarrow \text{Ca}^{2+}\text{(aq)} + 2\text{HCO}_3^-\text{(aq)} \rightarrow$

$$\text{CaCO}_3\text{(s)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$$ \hspace{1cm} (Eqn. 1.4)

In Eqn. 1.3, the mineral wollastonite (CaSiO$_3$) represents a typical silicate mineral, but other elements including Mg, Al, K, etc. also comprise most silicate rocks. After delivery to the oceans, carbon is eventually removed by deposition as calcium carbonate (CaCO$_3$; see the
right side of Eqns 1.3 and 1.4) or organic matter. The accompanying delivery of Mg, Ca, Al, and K is eventually balanced by the formation of carbonate minerals and clays in seawater. These minerals are deposited on the ocean floor, on continental margins, and are formed through alteration of basaltic ocean crust.

Figure 1.2 Simplified schematic of the global carbon cycle. Sources of carbon to the ocean-atmosphere system are represented by red arrows. Carbon is removed by the deposition of calcium carbonate and burial of organic matter in sediments, as shown by dark blue arrows. The figure is based on Paul Hoffmann’s schematic of the global carbon cycle (www.snowballearth.org).

Notice that in the silicate weathering equation (Eqn. 1.4), the carbon term (actually carbonic acid) on the left side is absent from the products (on the right). In the carbonate weathering equation (Eqn. 1.3), the carbon dioxide term exists on both sides. Thus, it is only the
weathering of silicate rocks that serves to transfer carbon dioxide out of the atmosphere and ocean. Because of its ability to act as a net sink for atmospheric carbon dioxide, silicate weathering is one of the key stabilizers of Earth’s climate system (Walker, 1981). This stabilization is referred to as a negative ‘feedback’, and is thought to operate through a link to temperature as follows: The more carbon dioxide in the atmosphere, the higher global temperatures become; increased temperatures then cause the rates of silicate weathering to increase, stripping CO$_2$ out of the atmosphere more efficiently and opposing the initial CO$_2$ perturbation. The silicate weathering feedback operates on long timescales – on the order of $10^5$ - $10^6$ years.

The same geologic processes that regulate the cycling of carbon and the concentration of elements such as Mg and Ca in seawater can also act to alter the isotopic composition of elements in seawater. Because isotope fractionations can occur as a result of certain geological processes (e.g., silicate weathering and mineral precipitation from seawater), histories of the isotopic composition of seawater can also provide insight into the importance of those geological processes through time. For example, fractionation of Mg isotopes occurs during the formation of carbonate rocks in seawater; fractionation of lithium (Li) isotopes occurs during the weathering of silicate rocks and the formation of clays; fractionation of C isotopes occurs during biological incorporation of carbon into biomass (Higgins and Schrag, 2010; Huh et al. 2001; Pistiner and Henderson, 2003; O’Leary, 1981). As a side note, the isotopes of Mg and Li represent ‘non-traditional’ stable isotope systems – measurements of which have only been facilitated in the last decade or two, enabled by innovations in mass spectrometry. Three non-traditional stable isotope systems will be explored in this thesis: (1) the isotopes of Mg, (2) the isotopes of Ca, and (3) the isotopes of uranium (U).
1.3 Biogenic carbonates as archives of seawater chemistry

The previous two sections have been devoted to explaining the importance of global change over Earth’s history, and the relevance of understanding the evolution of seawater composition through time. But how do we access past changes in seawater composition if we cannot directly measure the composition of ancient oceans? Most evidence for past changes in Earth’s environment comes indirectly from proxies. Proxies are physical or chemical parameters that, through calibration, are known to correlate with some environmental or climatic parameter of interest. For example, scientists have found a relationship between temperature and the Mg to Ca ratio in the shells of marine organisms called foraminifera (Chave, 1954; Savin and Douglas, 1973). This relationship has been used to reconstruct seawater temperature throughout the Cenozoic – the last 60 million years of Earth history (Lear et al. 2000; Billups and Schrag, 2002). The Mg/Ca-temperature proxy has been calibrated via experiments where the foraminifera are reared in seawater solutions of varying temperature, and the shells grown during the experiments are chemically analyzed (Nürnberg et al. 1996; Lea et al. 1999). The proxy has also been calibrated via core-top comparisons (Elderfield and Ganssen, 2000).

Multiple different proxy-archives have been used to reconstruct past changes in the chemical composition of seawater. Examples include the composition of fluid inclusions trapped in evaporite minerals (e.g. Zimmermann, 2000; Lowenstein et al. 2001; Paris et al. 2010), carbonate minerals formed in altered oceanic crust (Coggon et al. 2010; Rausch et al. 2013), altered silicate rocks of the oceanic crust (Coogan, 2009), and biogenic carbonates and phosphates (i.e. shells, skeletons, or teeth formed by marine organisms; Veizer et al. 1999; Lear et al. 2003; Balter et al., 2011; Dickson 2002; 2004; Ivany et al. 2004; Griffiths et al. 2012; Evans et al. 2013). Scleractinian corals, which form biologically precipitated skeletons composed
CHAPTER 1. INTRODUCTION

of aragonite (the orthorhombic form of calcium carbonate) are the archives focused on in this thesis.

1.3.1 Scleractinian fossil corals

Scleractinian corals first appear in the rock record during the Triassic, and as such, fossil coral skeletons have the potential to be used as archives of paleoenvironmental changes occurring over the last ~200 million years. Coral habitats range from the warm surface ocean to the cold deep ocean (Stanley and Cairns, 1988; Stanley, 2003; Robinson et al. 2014). They can either exist in solitary form (typically without symbionts), or as colonial organisms (typically alongside dinoflagellate symbionts) – the latter forming coral reefs (Stanley, 2003; Schuhmacher and Zibrowius, 1985).

Because of their global distribution, scleractinian corals (both surface-dwelling and deep-sea) are valuable archives of paleoenvironmental change. The fact that it is possible to date the age of coral skeletons (by counting growth bands as for tree-rings, or by geochemical methods) makes them of additional interest (Bender, 1973; Thompson et al. 2003; Robinson et al. 2006). Scleractinian corals have been used as proxies of a variety of different environmental parameters. For example, as early as the 1970s, their oxygen isotope compositions and strontium (Sr) to Ca ratios have been of interest as proxies for past changes in ocean temperature (Weber and Woodhead, 1972; Weber, 1973).
Chapter 1. Introduction

Figure 1.3 The Sr/Ca of corals is linearly related to the Sr/Ca of the seawater in which they are grown. Plotted data are from a study conducted by Swart (1981) in which he grew different species of coral in solutions with varying Sr/Ca ratios, and analyzed the composition of the newly grown skeletons.

It has also been observed that corals do not discriminate against the uptake of some trace elements in seawater (e.g., U, Sr). Broecker et al. (2013) called corals ‘sloppy chemists’ in describing this tendency. Pioneering work by Swart (1981) and Swart and Hubbard (1982), in which corals were cultured in seawater solutions with varying elemental compositions, suggested that Sr, Mg, and U in corals may be taken up into the coral skeleton in proportion to their abundance in seawater (e.g., Fig. 1.3). This behavior makes corals prime candidates for reconstructing past seawater chemistry.
1.3.2 The problem of diagenesis

Diagenesis can be defined as the transformation of the physical and chemical properties of a mineral over time, after its deposition, due to interactions with the surrounding environment. These transformations are critical to avoid in materials used as archives of paleoenvironmental change because diagenesis can mask true paleoenvironmental signatures and lead to inaccuracies in reconstructions of past environments (Kinsman, 1969; Brand and Veizer, 1980). As such, it is important to carefully test any archive used for paleoenvironmental reconstruction (including fossil corals) for the presence of diagenesis. Because the mineral aragonite is metastable at Earth’s surface, fossil coral skeletons are particularly susceptible to diagenetic alteration.

Diagenesis can occur via dissolution of the original mineral phase, and reprecipitation of another (e.g., for the case of aragonitic corals – primary aragonite is usually replaced with calcite). Sometimes this dissolution results from interaction with thin films of water percolating along grain boundaries, leading to the general preservation of some crystalline textures even after alteration. Alternatively, dissolution can occur via interaction with larger pools of fluid, leading to the development of coarser and chalkier alteration fabrics (Fig. 1.4; Brand and Veizer, 1980; Pingitore, 1976). Carbonate minerals can also be physically bored by other marine organisms, which encourages the growth of diagenetic cements in the resulting pore space (Northdurft and Webb, 2009).

From a geochemical standpoint, there are two main factors that determine the composition of a diagenetic phase. First is the mineralogy. Because the partitioning of trace elements and isotopes into different minerals varies, diagenetic replacement of one mineral form by another can lead to substantial changes in chemical composition. As stated above, for the case
of corals, aragonite is usually replaced by calcite, which leads to decreases in the Sr concentration of the skeleton and increases in the Mg concentration (Pingitore, 1978; Brand and Veizer, 1980; Allison et al. 2007; Cochran et al. 2010; Griffiths et al. 2012). Techniques such as X-ray diffractometry (XRD), Raman spectroscopy, Scanning Electron Microscopy (SEM) imaging, and Electron Backscatter Diffraction (EBSD) can be successfully used to screen for such mineralogical changes (Cusack et al. 2008; Bar-Matthews et al. 1993; Stolarski and Mazur, 2005; Frankowiak et al. 2013; Gothmann et al. 2015). For sediments that undergo no change in mineralogy during alteration, diagenesis can be more difficult to detect.

A second factor is the geochemical composition of the diagenetic fluid, which can include seawater, meteoric water, and pore water. The chemical composition of the alteration product will reflect the composition of the fluid by which it was altered. As a result, studies of trace element and isotope patterns can also be useful for recognizing diagenesis. For example, many reducing diagenetic fluids are enriched in manganese, which cause this element to be enriched in altered carbonates (Mucci, 1988, Brand and Veizer, 1980).
**Figure 1.4** Diagenetic alteration in coral skeletons. (a) Transmitted light microscope image of a diagenetically altered Triassic-age fossil coral. Light grey/brown regions correspond to the coral skeleton. Dissolution pits are present within the coral skeleton. Secondary minerals (reddish-brown in color) can be seen growing on the outer edges of the skeleton and also within the skeleton. (b) Scanning electron microscope image of an altered Cretaceous age coral. The entire skeleton (originally aragonite) has been replaced by calcite. Blocky crystal shapes characteristic of calcite are present.

**1.3.3 The problem of vital effects**

‘Vital effects’ can be broadly defined as deviations in the chemical composition of biologically precipitated minerals away from the composition expected for the inorganic mineral form (e.g., aragonite precipitated by coral vs. aragonite cements precipitated from seawater). The vital effect was first recognized by Epstein (1951), who noted that the oxygen isotope composition of *biominerals*, including the skeletons of corals and echinoderms, seemed to be deposited out of equilibrium with the seawater in which they were grown.
Chapter 1. Introduction

Vital effects can manifest both as deviations in the fine-scale chemical composition of the biomineral and in the bulk composition (Weber and Woodhead, 1972; Meibom, 2004; Cohen et al. 2006; Bentov and Erez, 2006; Gagnon et al. 2007; Tambutté et al. 2011). Problematically, the magnitude of these deviations can differ substantially between species, with implications for the faithfulness of records derived from multi-species archives (Bentov and Erez, 2006; Weiner and Dove, 2003). Historically, there have been two main approaches taken to deal with the presence of vital effects in biologically precipitated minerals: (1) avoid using taxa for which vital effects are present as paleoenvironmental archives, or (2) calibrate offsets in vital effects for modern species, and assume that they stay constant through time. When extending paleoenvironmental records back millions of years, researchers also encounter the problem of evolution and extinction. Going back in time, modern species eventually disappear from the sedimentary record. Likewise, ancient species that have gone extinct cannot be directly calibrated. This issue is typically accounted for by linking together data from different species and, where data overlap, applying an offset between the extant species (for which a calibration exists) and an extinct species (for which a calibration does not).

It is clear that vital effects have the potential to significantly limit the development of robust paleorecords. However, ongoing studies of the mechanisms by which organisms form mineralized skeletons or shells – termed biomineralization – can help provide new insight into the origin of vital effects. Such work may eventually help distinguish between vital effect signatures in the sedimentary record, and environmental ones. For the case of corals, many important studies have been performed over the last decade that have improved our current understanding of biomineralization mechanisms (McConnaughey, 1989; Adkins et al. 2003; Cohen et al. 2006; Erez and Braun, 2007; Gagnon et al. 2007; Gaetani et al. 2011; Gagnon et al.
2013). If accurate models of biomineralization can be developed, these models may be able to predict how geochemical signatures of vital effects respond to variations in environmental boundary conditions (Weiner and Dove, 2003; Cohen and Gaetani, 2010).

Finally, it is important to note that biominerals are not the only archives with complicating factors like vital effects; inorganic paleoenvironmental archives have their own, separate limitations. For example, carbonates precipitated in altered oceanic basalt, which have been used to estimate the Mg to Ca ratio of past seawater, are formed from hydrothermal fluids that are geochemically distinct from seawater due to interaction with basalt. As a result, the magnitude of this interaction must be accurately accounted for in order to successfully reconstruct the Mg to Ca ratio of seawater (Coggon et al. 2010; Rausch et al. 2013). Similarly, reconstructions of seawater Ca concentrations and sulfate ($SO_4^{2-}$) concentrations from fluid inclusions in halite rest on assumptions made about the concentration product of $Ca^{2+}$ and $SO_4^{2-}$ in seawater and its constancy through time. These assumptions lead to large uncertainties in the reconstructed concentrations of both ions (Lowenstein et al. 2003; Brennan et al. 2013).

1.4 Thesis Overview

The introduction thus far has consisted of three main parts: (1) a discussion of the importance of understanding global environmental change (Section 1.1), (2) a summary of the significance of the chemical composition of the oceans in the context of paleoenvironmental change and the carbon cycle (Section 1.2), and (3) an explanation of how records of ancient seawater chemistry are assembled from different geological materials, with a focus on the subjects of this thesis – scleractinian corals (Section 1.3). These three sections provide an
overview of concepts fundamental to Chapters 2-5, each of which focuses on the fossil coral-derived reconstruction of different elemental or isotopic parameters.

In Chapter 2, the fossil coral samples that will be the focus of the rest of this thesis are presented. First, the provenance of these samples is outlined, and the microscopic and geochemical testing that was used to screen the samples for diagenesis is also detailed. Then, from measurements of Mg/Ca and Sr/Ca ratios in the fossil coral skeletons, we reconstruct records of seawater Mg/Ca and Sr/Ca since the Mesozoic (~200 million years ago). Finally, coral-based records of seawater Mg/Ca and Sr/Ca are compared with previously published records.

Chapter 3 presents a record of seawater $\delta^{26}$Mg from the same set of fossil corals, with a goal of shedding further light on the mechanisms driving variations in seawater Mg/Ca over the last 200 million years. Importantly, the record presented from corals also helps distinguish between two existing records of the Mg isotope composition of Cenozoic seawater, which give conflicting results.

Chapter 4 shifts focus to the geochemistry of U in fossil corals. Broecker (1971; 2013) suggested that the U/Ca composition of well preserved fossil corals may reflect variations in seawater carbonate ion concentrations. We measure U/Ca in Cenozoic-age fossil coral samples and explore this possibility in light of our results. This chapter also investigates the implications of our U/Ca record for understanding changes in U removal in reducing sediments through time. Measurements of $^4$He in fossil corals, together with U isotope data, help to further constrain the preservation of fossil coral samples.

Chapter 5 centers on the Ca isotopic composition of coral skeletons, and details a case where the composition of corals does not seem to reflect the composition of seawater. Instead,
changes in coral Ca isotopes through time may reflect the presence of ‘vital effects’. Possible origins of these vital effects are explored.

Together, these chapters present new information about how and why seawater chemistry has evolved through time. They also illuminate the importance of recognizing diagenetic alteration and the presence of vital effects in archives utilized for paleoenvironmental study. It goes without saying that much additional work is needed to fully answer the questions posed at the beginning of this introduction. However, the samples described as part of this work are available to measure for additional seawater properties, and their study will hopefully continue to shed light on the geological controls on climate and seawater chemistry over the last 200 million years.
CHAPTER 1. INTRODUCTION

References


CHAPTER 1. INTRODUCTION


Solving the mystery of the vital effect. *European Mineralogical Union Notes in Mineralogy* 11, 377-397.


Evans, D., Müller, R., Oron, S., and Renema, W. 2013. Eocene seasonality and seawater alkaline
CHAPTER 1. INTRODUCTION


Chapter 1. Introduction


CHAPTER 1. INTRODUCTION


Chapter 2. Fossil corals as an archive of secular variations in seawater chemistry since the Mesozoic

2.1 Abstract

Numerous archives suggest that the major ion and isotopic composition of seawater has changed in parallel with large variations in geologic processes and Earth’s climate. However, our understanding of the mechanisms driving secular changes in seawater chemistry on geologic timescales is limited by the resolution of data in time, large uncertainties in seawater chemistry reconstructions, and ambiguities introduced by sample diagenesis. We validated the preservation of a suite of ~60 unrecrystallized aragonitic fossil scleractinian corals, ranging in age from Triassic through Recent, for use as new archives of past seawater chemistry. Optical and secondary electron microscopy (SEM) studies reveal that fossil coral crystal fabrics are similar to those of modern coralline aragonite. X-ray diffractometry (XRD), cathodoluminescence microscopy (CL), and Raman studies confirm that these specimens contain little to no secondary calcite. In order to screen for geochemical changes indicative of alteration, we measured $^{87}$Sr/$^{86}$Sr ratios, clumped isotopes, and trace element ratios sensitive to diagenesis (e.g., Mn/Ca). We retain samples when these tests either fail to identify any diagenetic modifications, or identify specific domains free of detectable alteration.

Using the validated fossil coral archive we reconstruct seawater Mg/Ca and Sr/Ca ratios, measured by Secondary Ion Mass Spectrometry (SIMS), back to ~230 Ma. The effects of
temperature on coral trace element incorporation cannot explain the trends observed in our fossil coral Mg/Ca and Sr/Ca data. In agreement with independent records, seawater Mg/Ca molar ratios inferred from corals are low (Mg/Ca ~ 1) during the Cretaceous and Jurassic, and increase between the Early Cenozoic and present (Mg/Ca = 5.2). Seawater Sr/Ca ratios from corals vary systematically between ~8 and 13 mmol/mol since 230 Ma, with maximum values in the Cretaceous and Paleogene. The coral Sr/Ca record disagrees with records from hydrothermal CaCO$_3$ veins, but is similar to those reconstructed from other biogenic carbonates, especially benthic foraminifera. The agreement between corals and other archives, for both Sr/Ca and Mg/Ca ratios, further validates our records. In return, fossil coral records improve our understanding of past variations in seawater Mg/Ca and Sr/Ca.

2.2 Introduction

There have been large changes in the major ion concentration and isotopic composition of seawater since the Neoproterozoic as indicated from studies of the mineralogy and geochemistry of marine evaporites, barites and both inorganic and biogenic carbonates (Sandberg, 1983; Hardie, 1996, 2003; Paytan et al., 1998, 2004; Lowenstein et al., 2001, 2003, 2005; Horita et al. 2002; Dickson, 2002, 2004; Ries, 2004; Timofeeff et al., 2006; Porter, 2010; Zhuravlev and Wood, 2008; McArthur et al., 2001; Coggon et al., 2010; Farkaš et al., 2007; Blättler et al., 2012; Misra and Froelich, 2012). An important finding of these studies is that the Mg/Ca ratio of seawater has varied by up to a factor of 5 throughout the Phanerozoic. Times of higher Mg/Ca ratios (‘aragonite seas’) are coeval with times corresponding to greater deposition of inorganic aragonite cements, sea-level lowstands, and “icehouse” climates. Times of lower
Mg/Ca ratios (‘calcite seas’) are coeval with times corresponding to greater deposition of calcite cements, sea-level highstands, and “greenhouse” climates (Sandberg, 1983; Hardie, 1996; Lowenstein et al., 2001). These results suggest a fundamental link between seawater chemistry, carbonate mineralogy and Earth's climate state.

**Figure 2.1** Coral skeletal structure. (a) Sketch of Desmophyllum dianthus, a deep-sea coral, showing the arrangement of the thecal wall and septa. Samples are sectioned in the transverse plane, perpendicular to the vertical axis of the coral calyx. The scale bar indicates the typical size of solitary corals that are part of our sample set. (b) Sketch showing the sectioning of a coral septum, and (c) a thin section image of the coral septum, taken with a petrographic microscope. COCs, also called ‘rapid accretion deposits’ (Stolarski, 2003), are oriented parallel to the coral septum and appear opaque and dark in color. Coral ‘fibers’, or ‘thickening deposits’ (Stolarski, 2003), radiate outward from the COCs.
A thorough understanding of the geologic and geochemical processes driving this link has yet to be achieved, but would provide valuable insight into the interaction between major domains in the Earth system. Existing records of paleo-seawater chemistry, while pioneering and profoundly important, are limited by the resolution of data in time, uncertainties introduced by assumptions invoked in the reconstructions, or ambiguities introduced by sample diagenesis. In order to supplement existing studies of past seawater chemistry, we assembled a new archive of ~60 exceptionally well preserved fossil corals, documented their preservation for seawater paleochemistry studies, and used these samples to reconstruct past seawater Mg/Ca and Sr/Ca ratios back to ~230 Ma.

2.2.1 Coral background

Paleontological evidence and phylogenetic analyses suggest that aragonitic scleractinian corals evolved during the Early Paleozoic (Stanley, 2003; Stolarski et al., 2011), and scleractinian corals first appeared in the rock record in the Middle to Late Triassic. Consequently, corals have the potential to yield a ~230 Myr record of seawater chemistry spanning a full “cycle” of aragonite and calcite seas (Sandberg, 1983; Hardie, 1996). This feature, along with the observation that corals generally incorporate many trace elements in proportions that are related to their abundance in seawater (Cohen and McConnaughey, 2003; de Villiers et al, 1994; Lea et al., 1989) make corals attractive subjects for paleochemistry studies. Aragonitic scleractinian corals can either grow as large colonies that may form reefs (often harboring dinoflagellate symbionts called zooxanthellae) or as solitary organisms (most
frequently without zooxanthellae). Their habitats range from the warm, supersaturated surface ocean to the cold deep ocean.

A sketch of a hand sample and a thin section of a solitary coral, here modeled after the deep sea coral *Desmophyllum dianthus*, is shown in Fig. 2.1. The coral skeleton (or corallum) consists of a cup-like structure (calyx), which hosts the coral animal (polyp). The calyx is made up of an outer wall called the ‘theca’ and radially oriented plates called ‘septa’, which provide further structure.

Two aragonite crystal morphologies exist within the skeleton, which are also distinguishable by their geochemistry. Centers of Calcification (COCs), also called ‘Rapid Accretion Deposits’ (Stolarski, 2003), appear to run down the middle of coral septa and thecal wall when corals are viewed in cross section (Fig. 2.1). COCs may represent the zone where skeletal growth and CaCO₃ precipitation is initiated (Bryan and Hill, 1941; Cuif and Dauphin, 1998). Alternatively, COCs may be formed simultaneously with the rest of the growing skeleton but with higher extension rates (Stolarski 2003; Brahmi et al., 2012). It has been suggested that the extension rate of the COCs and the possible influence of an amorphous calcium carbonate precursor phase also may lead to greater incorporation of organics or trace elements in this region (Cuif et al., 2003; Meibom et al., 2004, 2007; Sinclair et al., 2006). For the reasons described above, COCs are particularly susceptible to diagenetic alteration and recrystallization.

Coral ‘fibers’, also called ‘Thickening Deposits’ (Stolarski, 2003), exist as acicular needles extending out from the COCs and account for most of the mass of the coral skeleton (Perrin, 2003; Cuif and Dauphin, 1998; Tambutté et al., 2011). Typically, the fibers grow at slower rates than the COCs and are characterized by a different trace element composition (Meibom et al., 2004; Gagnon et al., 2007). Identifying these crystal morphologies, accounting for their distinct
Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry since the Mesozoic

Chemistries, and studying their relative preservation is important for reconstructing environmental signals (Gagnon et al., 2007; Meibom et al., 2008).

If corals are to be utilized as archives of past seawater chemistry, two requirements must be fulfilled. First, there must be a quantifiable relationship between the property of interest (e.g., Mg/Ca) measured in the coral, and that property in seawater. Second, fossil corals must be preserved such that they retain their original geochemical composition. For our purposes, it is not essential that a specimen be entirely composed of pristine biogenic aragonite. This condition is rarely, if ever, met (Allison et al., 2007; Griffiths et al., 2013). For example, secondary aragonite overgrowths have been found in a modern coral as young as 40 years old, and secondary calcite cements have been found in fossil corals that lived less than one thousand years ago (Sayani et al., 2011). Instead, we require that either (1) the main coral skeleton retains its primary mineralogy, crystal habit, and geochemistry regardless of whether secondary overgrowths are present, and/or (2) that corals possess domains of pristine aragonite that are large enough to sample for our studies.

2.2.2 Corals as recorders of seawater properties

There is a strong foundation for reconstructing seawater Sr/Ca from corals, and some evidence that corals should accurately record past seawater Mg/Ca as well. Coral Sr/Ca ratios are higher than the seawater Sr/Ca ratio by only 15-20%, consistent with the inorganic aragonite partition coefficient: Sr/Ca_{aragonite}/Sr/Ca_{solution} = 1.15 (Gaetani and Cohen, 2006). In a pioneering study, Swart (1981) grew corals in solutions with varying Sr/Ca compositions and found that the Sr/Ca ratios measured in the newly grown skeletons increased linearly with the Sr/Ca ratio of the growth solutions, suggesting that coral Sr/Ca is dependent on seawater Sr/Ca. They also found
that Sr/Ca depended on Mg/Ca – a result that remains to be verified. The coral Sr/Ca temperature dependence is small as well; for every 1°C increase in temperature there is only a 1% decrease in Sr/Ca, indicating that temperature should not significantly bias seawater Sr/Ca reconstructions (Beck et al., 1992; de Villiers et al., 1994; Marshall and McCulloch, 2002; Corrège et al., 2006; Gagan et al., 2012). In addition, while Sr/Ca ratios have been shown to vary over scales of microns and tens of microns within the coral skeleton (Meibom et al., 2004; Gagnon et al., 2007), indicating the presence of ‘vital effects’, bulk coral Sr/Ca ratios are less variable. For example, modern surface corals living in waters between 20 and 30°C give Sr/Ca ratios ranging between 8.8 and 9.5 mmol/mol (Beck et al., 1992; de Villiers et al., 1994; McCulloch et al., 1999), suggesting that it should be possible to resolve changes in the seawater Sr/Ca ratio that are ~1 mmol/mol or greater. These observations show that seawater Sr/Ca likely is the dominant control on the Sr/Ca ratio of the coral skeleton, and that corals are prime candidates for reconstructing past seawater Sr/Ca.

Some empirical evidence also suggests that coral Mg/Ca scales with the seawater ratio. Ries et al. (2006), working with a small dataset, found that the Mg/Ca composition of coral aragonite grown in culture solutions with different Mg/Ca ratios was positively correlated with the Mg/Ca ratio of the growth solution. Likewise, Lorens and Bender (1980) found a linear dependence between Mg/Ca in mussel aragonite and the Mg/Ca of the water in which it was grown. Finally, as we show below, the Mg/Ca ratios of fossil corals measured in this study track past seawater Mg/Ca ratios as inferred from other archives.

On the other hand, it is unclear whether Mg substitutes into the aragonite crystal lattice, or whether it exists primarily in either organic or disordered inorganic compounds (Finch and Allison, 2008). Observations that Mg/Ca ratios in modern coral fibers (excluding COCs)
vary by about a factor of 3 on length scales \( \leq 1 \, \mu m \) also highlight that fine scale variations in Mg/Ca depend on vital effects that remain to be understood (Meibom et al., 2004; 2008). SIMS analyses (spot diameter \( \sim 30 \, \mu m \)), which we use here to measure element/Ca ratios, serve to average out this considerable variability at the \( \leq 1 \, \mu m \) scale and are thus well-suited for our purpose. In this study, we assume a linear dependence of the Mg/Ca ratio of corals on seawater Mg/Ca. This assumption will be reassessed as coral chemistry is better understood.

### 2.2.3 Fossil coral preservation

Scleractinian corals build skeletons of aragonite, a metastable polymorph of \( CaCO_3 \). Most fossil corals undergo recrystallization to calcite, during which elements and isotopes can be exchanged, altering the geochemistry of the skeleton and rendering the fossils unsuitable for paleochemical study (Pingitore, 1976; Brand and Veizer, 1980). However, it is possible to find specimens as old as Triassic in age that retain their original aragonitic mineralogy (Bender, 1973; Sorauf, 1999; Ivany et al., 2004; Stolarski and Mazur, 2005; Stanley and Swart, 1995; Mertz-Kraus et al., 2009; Getty et al., 2001; Denniston et al., 2008; Griffiths et al., 2013). Indeed, preservation of coral aragonite may be more straightforward to assess than preservation of calcite because the very survival of aragonite suggests that a specimen is unaltered. Stolarski et al. (2007) also recently identified a set of Cretaceous-age scleractinian corals composed of primary calcite and suggested that these corals may have produced calcitic skeletons as a result of the low Mg/Ca ratio of the Cretaceous ocean. In this study, we focus only on aragonitic corals.
Figure 2.2 (a) World physical map showing locations from which samples were collected (see also Table 2.1) and enlarged maps of (b) Europe and (c) North America. Maps taken from ArcGIS (Source: US National Park Service; Esri, DeLorme).

While many previous workers have used petrographic and mineralogical techniques to assess coral preservation, geochemical tools have also been employed (Bender, 1973; Allison et al., 2007; Griffiths et al., 2013). For example, Bender (1973) identified ~45 well preserved Cenozoic corals and dated them by U-Th/He. The aragonitic fossil coral skeletons did retain most of their radiogenic He suggesting good preservation. By pairing petrographic and mineralogical tools with geochemical means of assessing preservation, we show that it is possible to identify fossil coral specimens that can be used to reconstruct original environmental properties, and we construct ~230 My records of seawater Sr/Ca and Mg/Ca ratios that
supplement previous studies. Our validations also yield a set of specimens that can be used by others to study additional properties of seawater.

2.3 Samples and Methods

Fig. 2.2 illustrates the range of geologic localities from which samples were collected, and Table 2.1 lists the diagenetic tests performed on each specimen to validate their preservation. A complete summary of ages, locations, loaning institutions, and classifications of fossil coral specimens that we deem fit for use in paleochemistry reconstructions is given in the Supplementary S1. Supplementary S2 gives a list of additional specimens that were examined, but which did not pass our diagenetic tests.

2.3.1 Sample preparation

The majority of samples were prepared at Princeton University for chemical analysis. In preparation for optical microscopy, SEM examination, and trace element analysis by SIMS, thick sections approximately 1 cm in width were cut from each hand sample in the transverse plane perpendicular to the coral septa. Sections were ultrasonicated in deionized water for 20 minutes (3x). Thin sections were prepared either by Applied Petrographic Services, Inc. or at the Institute of Paleobiology in Warsaw, Poland as described in Stolarski and Mazur (2005). Prior to SIMS analysis, thin sections were carbon-coated at the GPS Division Analytical Facility at the California Institute of Technology.

For clumped isotope and Sr isotope analyses, ~50 mg pieces of coral were chipped from hand samples, cleaned as described above, and powdered using a mortar and pestle. In the
case of older specimens with coexisting sparry calcite infill, powders were drilled using a Dremel tool from fresh-cut surfaces of hand samples and/or thick sections. In many cases, we could not avoid secondary cements in these samples and we quantify the amount of secondary calcite in powders using XRD. Good clumped isotope and Sr isotope results for these mixed powders validate the samples for SIMS measurements. However, we note that bulk measurements of geochemical properties in these samples will contain a diagenetic component.

2.3.2 X-ray diffraction

Thin sections and aliquots of powder samples used for bulk geochemistry were examined for the presence of aragonite and calcite using a Bruker D8 Discover XRD at Princeton University. Specimens that gave XRD patterns with both aragonite and calcite peaks required further investigation by SEM and optical microscopy to determine if there were domains of well preserved material appropriate for our study (Table 2.1, Supplementary S3, S4).

2.3.3 Imaging methods

Polished thin sections were studied with a Leica DMLP microscope (Princeton University) and a Nikon Eclipse 80i microscope fitted with a DS-5Mc cooled camera head (Institute of Paleobiology, Warsaw) to look for textures indicative of alteration. Observations were performed in transmitted, polarized, and reflected light. Regions that were determined to be best preserved were imaged in reflected light using a Zeiss Discovery V12 microscope (Princeton University Imaging and Analysis Center) to provide a map for sampling during SIMS analysis.
Table 2.1 Summary of diagenetic tests performed on samples that we find to be well preserved enough to reconstruct seawater Mg/Ca and Sr/Ca. ‘-’ = test performed and passed, ‘X’ = test performed and not passed, ‘ND’ = test not performed. ‘AC’ = acicular texture; ‘I’ = indurated with calcite or sediment; ‘SA’ = secondary aragonite overgrowth; ‘D’ = COC dissolution; ‘M’ = mud infilling; ‘A’ = aragonite; ‘C’ = calcite; ‘S’ = silicates. (*) Represents samples that are unsuitable for bulk analysis. Bold-faced samples correspond to those which failed one of our diagenetic tests, but which may still be suitable for study by microanalysis.
### Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry Since the Mesozoic

| Pl6  | 0.1 | Barbados | Caloosahatchee Fm., Florida (26.0° N, 81.7° W) | ND | AC | ND | ND | A | ND | ND | ND | 0.2 | 4.45 | 8.71 |
|------|-----|----------|-------------------------------------------|----|----|----|----|---|----|----|----|----|-----|-----|-----|
| Pl7  | 2.3 |          | Waccamaw Fm., North Carolina (33.9°N, 78.8° W) | ND | AC | ND | ND | A | <1% | 2.3 | ND | 0.5 | 2.99 | 9.00 |
| Pl8  | 2.2 |          | Limon Group, Moin Fm., Costa Rica. (10.0°N, 83.1° W) | ND | AC | ND | ND | A | <1% | 2.2 | ND | 4.9 | 3.11 | 9.32 |
| Pl9  | 2.2 |          | Gurabo Fm., Dominican Republic (19.5° N, 70.7° W) | ND | AC | ND | ND | A | ND | ND | ND | 2.3 | 2.23 | 9.70 |
| Pl11 | 3.5 |          | Tamiami Fm., Pinecrest Beds, Florida (26.9° N, 82.0° W) | ND | AC | ND | ND | A | ND | ND | 32 | 1.0 | 2.97 | 9.04 |
| Pl12*| 3.8 |          | Yorktown Fm., Virginia (37.2° N, 76.9° W) | ND | AC | ND | ND | A | 2% calcite | 3.8 | ND | 0.6 | 3.74 | 8.82 |
| Pl13 | 2.3 |          | Chipola Fm., Florida (30.4° N, 85.0° W) | ND | AC | ND | ND | A | <1% | 2.3 | 24 | 2.9 | 2.29 | 9.79 |
| Mi1  | 18.0|          | - | AC | ND | - | A | <1% | 18.0 | 22 | 1.7 | 2.09 | 10.76 |
### Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry Since the Mesozoic

| Mi2 | 17.8 | Chipola Fm., Florida (30.4° N, 85.0° W) | - | AC; SA | ND | - | A | <1% | 17.8 | 21 | 0.7 | 2.61 | 10.44 |
| Mi3 | 18.2 | Chipola Fm., Florida (30.4° N, 85.0° W) | - | AC | ND | - | A | <1% | 18.2 | 27 | 1.4 | 1.67 | 10.21 |
| Mi4 | 18.0 | Enewetak Atoll, Marshalls Islands (11.6° N, 162.3° E) | ND | AC; M | ND | ND | A | ND | ND | ND | 1.6 | 3.09 | 9.08 |
| Mi5 | 18.0 | Enewetak Atoll, Marshalls Islands (11.6° N, 162.3° E) | ND | AC | ND | ND | A | ND | ND | ND | 0.3 | 3.56 | 8.81 |
| Mi6 | 5.4 | Dominican Republic (19.5° N, 70.7° W) | ND | AC | ND | ND | A | <1% | 5.4 | 32 | 0.5 | 3.95 | 8.40 |
| Mi7 | 14.0 | Holy Cross Mountains, Korytnica Basin, Poland (50.6° N, 20.5° E) | ND | AC | ND | ND | A | <1% | 14.0 | ND | 0.4 | 2.16 | 10.11 |
| Mi8 | 14.0 | Florida | ND | AC; M | ND | ND | A | ND | ND | 29 | 1.8 | 1.68 | 10.29 |
| Mi9* | 7.4 | Enewetak Atoll, (11.6°N, 162.3°E) | ND | AC; M | ND | ND | A | 4% calcite | 7.4 | ND | 0.3 | 3.77 | 8.50 |
| Mi10 | 8.0 | Enewetak Atoll, (11.6°N, 162.3°E) | ND | AC; SA | ND | ND | A | ND | ND | ND | 0.8 | 3.41 | 8.77 |
### Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry Since the Mesozoic

<table>
<thead>
<tr>
<th>Mi</th>
<th>Year</th>
<th>Site Details</th>
<th>Calculations</th>
<th>Calcium Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mi11</td>
<td>9.3</td>
<td>Enewetak Atoll, Marshalls Islands. (11.6°N, 162.3°E)</td>
<td>ND AC ND ND A</td>
<td>0.3 3.48 8.63</td>
</tr>
<tr>
<td>Mi12</td>
<td>10.0</td>
<td>Enewetak Atoll, Marshalls Islands. (11.6°N, 162.3°E)</td>
<td>ND AC; SA ND ND A</td>
<td>0.1 4.06 8.57</td>
</tr>
<tr>
<td>Mi13</td>
<td>9.4</td>
<td>Enewetak Atoll, Marshalls Islands. (11.6°N, 162.3°E)</td>
<td>- AC; SA; M ND ND A</td>
<td>1% calcite 9.4 ND 0.1 2.49 8.95</td>
</tr>
<tr>
<td>Mi14</td>
<td>11.0</td>
<td>Enewetak Atoll, Marshalls Islands. (11.6°N, 162.3°E)</td>
<td>- AC; SA; M ND ND A</td>
<td>1% calcite 11.0 ND 0.1 2.61 9.57</td>
</tr>
<tr>
<td>Mi15</td>
<td>11.9</td>
<td>Enewetak Atoll, Marshalls Islands. (11.6°N, 162.3°E)</td>
<td>- AC; SA; M ND ND A</td>
<td>0.1 3.81 8.59</td>
</tr>
<tr>
<td>Mi16</td>
<td>10.5</td>
<td>Enewetak Atoll, Marshalls Islands. (11.6°N, 162.3°E)</td>
<td>ND AC ND ND A</td>
<td>1% calcite 10.5 ND 0.5 2.98 8.76</td>
</tr>
<tr>
<td>Mi17</td>
<td>12.3</td>
<td>Enewetak Atoll, Marshalls Islands. (11.6°N, 162.3°E)</td>
<td>- AC; SA ND ND A</td>
<td>0.5 3.75 8.87</td>
</tr>
<tr>
<td>Mi18</td>
<td>15.3</td>
<td>Enewetak Atoll, Marshalls Islands. (11.6°N, 162.3°E)</td>
<td>ND AC; SA ND ND A</td>
<td>0.5 3.40 9.12</td>
</tr>
</tbody>
</table>
## Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry Since the Mesozoic

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcite Content</th>
<th>Location Details</th>
<th>Percentage of Calcite</th>
<th>Latitude</th>
<th>Longitude</th>
<th>pH Value</th>
<th>pCO2 (μatm)</th>
<th>pO2 (μatm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ol1*</td>
<td>6%</td>
<td>Aquitane, France (43.8°N, 1.1°W)</td>
<td>23.7</td>
<td>43.8°N</td>
<td>1.1°W</td>
<td>1.5</td>
<td>1.25</td>
<td>11.10</td>
</tr>
<tr>
<td>Ol2</td>
<td>&lt;1%</td>
<td>Mississippi</td>
<td>37.7</td>
<td>37.7</td>
<td>ND</td>
<td>30</td>
<td>3.5</td>
<td>1.63</td>
</tr>
<tr>
<td>Ol3</td>
<td>&lt;1%</td>
<td>Byram Fm., Mississippi (32.0°N, 89.4°W)</td>
<td>31.8</td>
<td>31.8</td>
<td>ND</td>
<td>ND</td>
<td>1.6</td>
<td>1.68</td>
</tr>
<tr>
<td>Ol4</td>
<td>&lt;1%</td>
<td>Byram Fm., Mississippi (32.0°N, 89.4°W)</td>
<td>32.4</td>
<td>32.4</td>
<td>ND</td>
<td>ND</td>
<td>2.3</td>
<td>1.73</td>
</tr>
<tr>
<td>Ol5</td>
<td>&lt;1%</td>
<td>Byram Fm., Mississippi (32.0°N, 89.4°W)</td>
<td>32.6</td>
<td>32.6</td>
<td>ND</td>
<td>ND</td>
<td>3.2</td>
<td>3.03</td>
</tr>
<tr>
<td>Ol6</td>
<td>&lt;1%</td>
<td>Byram Fm., Mississippi (32.0°N, 89.4°W)</td>
<td>30.0</td>
<td>30.0</td>
<td>ND</td>
<td>ND</td>
<td>2.3</td>
<td>1.92</td>
</tr>
<tr>
<td>E1</td>
<td>&lt;1%</td>
<td>Gosport Sand Fm., Alabama (31.5°N, 87.9°W)</td>
<td>39.2</td>
<td>39.2</td>
<td>ND</td>
<td>ND</td>
<td>1.7</td>
<td>1.49</td>
</tr>
<tr>
<td>E2</td>
<td>&lt;1%</td>
<td>Siemien, Poland (51.2°N, 22.6°E)</td>
<td>38.6</td>
<td>38.6</td>
<td>ND</td>
<td>ND</td>
<td>1.2</td>
<td>1.16</td>
</tr>
</tbody>
</table>
## Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry since the Mesozoic

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca (%)</th>
<th>Location</th>
<th>Minerals</th>
<th>Calcite (%)</th>
<th>Mg (%)</th>
<th>Al (%)</th>
<th>Si (%)</th>
<th>Ca/Si</th>
<th>Mg/Ca</th>
<th>Al/Ca</th>
<th>F</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>E3</td>
<td>41.0</td>
<td>Mississippi</td>
<td>ND AC ND ND A &lt;1%</td>
<td>41.0</td>
<td>23</td>
<td>2.3</td>
<td>1.38</td>
<td>10.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E4</td>
<td>46.7</td>
<td>Alabama</td>
<td>ND AC ND ND A &lt;1%</td>
<td>46.7</td>
<td>30</td>
<td>2.3</td>
<td>1.35</td>
<td>10.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E5</td>
<td>39.3</td>
<td>France</td>
<td>ND AC ND - A+C 1% calcite</td>
<td>39.3</td>
<td>34</td>
<td>0.4</td>
<td>1.84</td>
<td>9.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E6</td>
<td>34.6</td>
<td>Ukraine</td>
<td>ND AC ND ND A &lt;1%</td>
<td>34.6</td>
<td>30</td>
<td>4.9</td>
<td>1.21</td>
<td>11.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E7*</td>
<td>48.9</td>
<td>Austria</td>
<td>- AC; I ND - A+C 35% calcite</td>
<td>48.9</td>
<td>40</td>
<td>1.6</td>
<td>1.57</td>
<td>9.97</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E8</td>
<td>36.9</td>
<td>Moodys Branch Fm., Louisiana (31.5° N, 87.8° W)</td>
<td>ND AC ND ND A &lt;1%</td>
<td>36.9</td>
<td>27</td>
<td>4.1</td>
<td>1.29</td>
<td>10.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pa1</td>
<td>61.0</td>
<td>Monrow Co., North Dakota</td>
<td>ND AC ND ND A ND ND 33</td>
<td>6.9</td>
<td>1.43</td>
<td>10.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pa2*</td>
<td>57.5</td>
<td>Babica Clays, Poland (49.9° N, 21.9° E)</td>
<td>- AC; D ND - A+S &gt;1% silicates</td>
<td>32.8</td>
<td>ND</td>
<td>1.6</td>
<td>1.31</td>
<td>11.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pa3</td>
<td>60.1</td>
<td>Wills Point Fm., Texas (30.3° N, 97.7° W)</td>
<td>ND AC ND ND A &lt;1%</td>
<td>60.1</td>
<td>31</td>
<td>3.5</td>
<td>1.47</td>
<td>10.92</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pa4</td>
<td>63.0</td>
<td>Sobral Fm., Seymour Island, Antarctica (64.3° S, 56.8° W)</td>
<td>- AC; D ND ND A ND ND ND 6.9</td>
<td>1.57</td>
<td>11.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K1*</td>
<td>71.4</td>
<td>Pierre Shales, Black Hills, SD. (45.1° N, 100.9° W)</td>
<td>- AC; I - - A+C+S 18% calcite</td>
<td>71.4</td>
<td>ND</td>
<td>5.1</td>
<td>0.91</td>
<td>13.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry Since the Mesozoic

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Reference Location</th>
<th>Percentage of Calcite</th>
<th>Calcite</th>
<th>Mg</th>
<th>Mg/Ca Ratio</th>
<th>Ca/Cr Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>K2*</td>
<td>Gosau, Austria</td>
<td>15%</td>
<td>86.7</td>
<td>33</td>
<td>1.2</td>
<td>0.92</td>
</tr>
<tr>
<td>K3*</td>
<td>Gosau, Austria</td>
<td>5%</td>
<td>85.8</td>
<td>35</td>
<td>1.3</td>
<td>0.47</td>
</tr>
<tr>
<td>K4*</td>
<td>Gosau, Austria</td>
<td>70%</td>
<td>84.4</td>
<td>ND</td>
<td>0.3</td>
<td>0.88</td>
</tr>
<tr>
<td>J1</td>
<td>Ostromice, Poland</td>
<td>1%</td>
<td>160.3</td>
<td>9</td>
<td>6.0</td>
<td>0.95</td>
</tr>
<tr>
<td>J2*</td>
<td>Ostromice, Poland</td>
<td>5%</td>
<td>158.8</td>
<td>ND</td>
<td>2.7</td>
<td>0.72</td>
</tr>
<tr>
<td>J3</td>
<td>Lukow, Poland</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>3.9</td>
<td>0.94</td>
</tr>
<tr>
<td>J4</td>
<td>Hohenferchesar, Germany</td>
<td>ND</td>
<td>AC; SA</td>
<td>ND</td>
<td>&lt;1%</td>
<td>161.5</td>
</tr>
<tr>
<td>Tr1*</td>
<td>Zlambach Fm., Austria</td>
<td>40%</td>
<td>206.4</td>
<td>ND</td>
<td>6.2</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Gosau, Austria (47.6° N, 13.5° E)

Ostromice, Poland (53.8° N, 14.8° E)

Lukow, Poland (51.9° N, 22.4° E)

Hohenferchesar, Germany

Zlambach Fm., Austria (47.6° N, 13.7° E)
## Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry Since the Mesozoic

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age</th>
<th>Location</th>
<th>Lat/Long</th>
<th>Type</th>
<th>Calcite</th>
<th>CaCO₃</th>
<th>Mg</th>
<th>Sr</th>
<th>**</th>
<th>**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tr2*</td>
<td>220</td>
<td>Zlambach Fm., Austria (47.6° N, 13.7° E)</td>
<td>-</td>
<td>AC; I; D</td>
<td>ND</td>
<td>ND</td>
<td>A+C</td>
<td>75% calcite</td>
<td>200.9</td>
<td>ND</td>
</tr>
<tr>
<td>Tr3*</td>
<td>220</td>
<td>Alakir Cay, Turkey (36.6° N, 30.3° E)</td>
<td>-</td>
<td>AC; I; D</td>
<td>ND</td>
<td>-</td>
<td>A+C</td>
<td>37% calcite</td>
<td>210.7</td>
<td>38</td>
</tr>
<tr>
<td>Tr4*</td>
<td>230</td>
<td>Alpe di Specie, Dolomites (46.6° N, 12.2° E)</td>
<td>-</td>
<td>AC; I; D</td>
<td>ND</td>
<td>-</td>
<td>A+C</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Tr5*</td>
<td>230</td>
<td>Alpe di Specie, Dolomites (46.6° N, 12.2° E)</td>
<td>-</td>
<td>AC; I; D</td>
<td>ND</td>
<td>-</td>
<td>A+C</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

*Sample unsuitable for bulk analysis
An FEI Quanta FEG Environmental-SEM (E-SEM) at the Princeton Imaging and Analysis Center was used to examine a subset of thin sections, concentrating specifically on those thin sections containing a mixture of aragonite and calcite as indicated by XRD. E-SEM analyses were conducted using both Secondary Electron (SE) and Backscattered Electron (BSE) modes, and were used to identify regions that exhibit the best preserved crystal morphologies.

A subset of specimens was also imaged by cathodoluminescence microscopy (CL) and Raman confocal microscopy as described in Frankowiak et al. (2013) to achieve a better spatial understanding of calcite and aragonite distributions in samples for which both polymorphs were present.

### 2.3.4 Secondary Ion Mass Spectrometry (SIMS)

Trace element ratios were measured using a Cameca ims 7f-GEO at the California Institute of Technology Microanalysis Center. A negative oxygen ion (O⁻) beam with a 25 µm raster size and a 15 nA beam current was used to pre-sputter the sample surface for 240 seconds at each analysis point. Subsequently, a 2 µm raster O⁻ beam with 5 nA beam current was used to sputter ions from the sample for data acquisition. At each spot, 15 cycles were measured for $^{23}$Na (1s/cycle counting time, $\sim$700,000 cps), $^{24}$Mg (1s/cycle counting time, $\sim$7,000 cps), $^{32}$S (6s/cycle counting time, $\sim$200 cps), $^{42}$Ca (1s/cycle counting time, $\sim$100,000 cps), $^{88}$Sr (1s/cycle counting time, 180,000 cps). $^{55}$Mn (10s/cycle counting time) count rates were low ($\sim$3 cps) in pristine samples, but up to $\sim$1,000 cps where recrystallization was significant. The total analysis time for all 15 cycles (including pre-sputtering time and measurements of other isotopes not listed here) was 10 minutes. For each fossil coral thin section, at least one transect of approximately 10 sampling points was measured across the coral septa. In most cases at least 3 transects were
measured. Achieved precision for individual coral SIMS spot data for Mg/Ca, Sr/Ca, Na/Ca, and S/Ca are <3% (2σ S.E.). Precision for Mn/Ca ranges from <2 to 25% (2σ S.E.) where recrystallization is significant.

Raw data were referenced to the carbonatite standard, OKA-II, which has been found to be an accurate standard for Sr/Ca and Mg/Ca ratios for carbonate samples of unknown composition (Gabitov et al., 2013). During the course of an analytical session lasting 1 week, OKA-II was measured between 10 and 15 times. Following Gabitov et al. (2013), samples were only referenced to standard data acquired from within the sections of OKA-II that are homogeneous with respect to Mg/Ca and Sr/Ca. Measured element/Ca intensity ratios for Mg/Ca and Sr/Ca measurements in OKA-II across two years of analytical sessions are 0.163 ± 3% and 2.45 ± 2%, respectively (1σ S.D.). Measured values for Mn/Ca, Na/Ca, and S/Ca in OKA-II are 0.065 ± 3%, 0.378 ± 7 %, and 1.3×10^{-5} ± 45% (1σ S.D.) respectively. The large uncertainty in S/Ca is due to extremely low S concentrations in OKA-II and the resulting very low count rates. Precision (reproducibility) of S count rates was good in our fossil corals. Relative S/Ca ratios are robust but absolute ratios are highly uncertain. Sr/Ca and Mg/Ca elemental ratios were measured in grain matched samples of OKA-II by ID-ICP-MS (Gabitov et al., 2013), and Mn/Ca and Na/Ca ratios in OKA-II were measured using a ThermoFinnigan Element2 ICP-MS at Princeton University. S/Ca ratios in OKA-II were measured by Ion Chromatography at the California Institute of Technology as described in Paris et al. (2013).

Following SIMS analysis, each thin section was studied a second time with a petrographic microscope to determine the placement of SIMS pits. Data from SIMS pits that apparently sampled epoxy, calcite infilling, COCs, or secondary aragonite overgrowths (instead of coral skeleton) were excluded from reconstructions of seawater Sr/Ca and Mg/Ca. The full
data set from SIMS measurements, including SIMS data from spots that sampled epoxy or secondary materials, is presented in the supplementary materials (Supplementary S5, S6).

### 2.3.5 Clumped Isotopes

A representative subset of 27 fossil coral specimens was analyzed for carbonate clumped isotope paleotemperatures to test for burial diagenesis (Eiler, 2007; Dennis and Schrag, 2010; Huntington et al. 2011; Passey and Henkes, 2012). With the exception of one coral that we determined to be poorly preserved, R10 (see Supplementary S2), between 2 and 5 replicate measurements were made for each sample (Supplementary S7). Analyses were performed at Harvard University, following the procedure of Dennis and Schrag (2010), with the data presented in the absolute reference frame as described in Dennis et al. (2011). Improbably high clumped isotope temperatures (> 40°C) measured on a small number of samples are suggestive of alteration in a high temperature environment.

### 2.3.6 Sr Isotopes

Approximately 70% of the fossil corals analyzed by SIMS were also measured for Sr-isotopes (Supplementary S8). Powders of coral skeleton were dissolved in 1N HNO₃, and unspiked Sr²⁺ was isolated by ion exchange chromatography with an Eichrom Sr-spec resin. Dried separates of Sr samples were re-dissolved in 2 μL of 0.1 M H₃PO₄. The dissolved samples were then combined with a 2:1-part Ta-gel and 1 M H₃PO₄ mixture and loaded onto outgassed Re filaments. Sample load sizes were approximately 400 ng Sr.

$^{87}$Sr/$^{86}$Sr ratios were measured on an IsotopX PhoeniX62 Thermal Ionization Mass Spectrometer at Princeton University. Measurements were made using a 3-sequence dynamic
routine, where mass-87 was measured in the Axial, H1, and H2 cups, and masses-84, 85, 86, and 88 were measured in sequentially adjacent cups. Data were collected in 15 blocks of 12 cycles each. Filaments were warmed to 1 A in 30 minutes and ramped up to 2.8-3.2 A to achieve a beam intensity of 3-5 V for $^{88}$Sr and a filament temperature of $\sim$1350 °C. The Sr isotope standard NBS SRM 987 ($^{87}$Sr/$^{86}$Sr = 0.710248) was measured as a reference throughout the period of our analytical sessions and gave an average value of $^{87}$Sr/$^{86}$Sr = 0.710243 ± 0.000004 (2σ S.D.) (n=12). A modern coral standard, with an isotopic composition identical to that of modern seawater $^{87}$Sr/$^{86}$Sr = 0.70918 (Faure and Mensing, 2005), was passed through the entire chemical procedure with each group of samples, and exhibited a long term average composition of $^{87}$Sr/$^{86}$Sr = 0.709170 ± 0.000014 (2σ S.D.) (n=6).

### 2.4 Results and Discussion:

#### 2.4.1 Screening samples for diagenesis

Samples must meet the following criteria in order to be considered well preserved:

1. visual inspection of hand samples must indicate good preservation of coral morphology,
2. XRD must indicate specimens are preserved as aragonite (except in cases where corals are visibly infilled with cement),
3. optical microscopy and SEM must show preservation of crystal ultrastructure,
4. Raman spectroscopy must suggest the absence of calcite within the coral skeleton,
5. results of SIMS and CL studies must indicate low Mn concentrations within the skeleton,
6. trace element patterns found in most fossil corals must agree with those observed in most modern corals,
7. carbonate clumped isotope temperatures must be below 40°C, and
8. [Continue reading...](#)
stratigraphic age inferred from the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio must agree with independently determined stratigraphic age. All of these criteria contribute valuable insight into fossil coral preservation.

We investigated 99 samples in total using at least one of the tests above, 63 of which were determined to be well preserved for our purposes (Table 2.1, Supplementary S1, S2). Of those 63, two samples failed one of our diagenetic tests (the clumped isotope test and Sr isotope test, respectively) but passed all other tests for diagenesis. Because both of these samples are infilled with calcite or sediment, and because the clumped isotope and Sr isotope tests were performed on bulk powders containing (for these samples) a mixture of coral and infilling, we conclude that they still are likely to be suitable for microanalysis but are not well enough preserved to use for bulk geochemistry.

2.4.1.1 X-Ray Diffraction

We measured 15 thin section samples (out of the 63 samples determined to be well preserved) with both aragonite and calcite XRD peaks (Table 2.1). Three samples (Pl1, Pa2, K1) also showed peaks corresponding to silicate minerals. All of these thin sections contained visible sediment or calcite infilling when examined using a petrographic microscope, as in Fig. 2.3a. The presence of indurated calcite cement or sediment in Mesozoic and Early Cenozoic samples is common; of the 18 fossil corals older than $\sim$50 Ma that we determined to be well-preserved, 13 are characterized by infilling of the coral skeleton with secondary calcite spar as in Fig. 2.3a. In contrast, only 2 of the 46 specimens younger than $\sim$50 Ma that we determined to be well preserved are infilled, although carbonate muds are present in some specimens and secondary aragonite is also sometimes visible as protruding needles (Fig. 2.3b). Small percentages of calcite were also quantified in drilled powder samples used for bulk geochemical analyses. The presence
of calcite in these samples may be related to partial recrystallization of the COCs or the presence of carbonate muds. These samples (marked with asterisks in Table 2.1) may not be suitable for bulk geochemistry.

Figure 2.3 Characterization of diagenesis in fossil scleractinian corals by petrographic, optical microscopy, and SEM (a-f). (a) Petrographic thin section image (crossed-polars) of Upper Cretaceous coral, K4. Crystals within the primary aragonite coral septum exhibit an acicular habit, typical of coralline aragonite. The space around the coral septum is infilled with calcite cement. (b) Petrographic thin section image (crossed-polars) of Middle Miocene coral, Mi14. Acicular habit exhibited both within the primary coral skeleton, and by secondary aragonite outgrowths. Spaces are visible between needles of secondary aragonite, distinguishing them from primary material. Black regions show pore space. (c) Thin section image (transmitted light) of Upper Jurassic coral, J2,
showing both well preserved aragonite and dissolution and alteration of the COCs as evident by discoloration and texture. COCs are avoidable by using microanalysis techniques to sample. (d) Petrographic thin section image (crossed-polars) of Cretaceous coral, R2, exhibiting significant recrystallization of the skeleton. This specimen was rejected from our well preserved sample set. (e) SEM image of recrystallized sample, R16 showing blocky euhedral textures. (f) SEM image of sample R6, showing dissolution and ‘fibrous micropores’ as in Bar Matthews et al. (1993).

2.4.1.2 Microscopy

To better quantify the spatial distribution of aragonite and secondary minerals in infilled samples, we studied our samples using petrographic microscopy, Raman microscopy, SEM, and CL. Petrographic microscopy and SEM are used to identify textures typical of either primary aragonite or secondary calcite, that may suggest the absence or presence of alteration, respectively (see Fig. 2.3, Supplementary S3). In well preserved samples (e.g. Fig. 2.3a-c) the acicular habit typical of primary coralline aragonite is visible within the skeleton, suggesting good preservation of aragonite fibers. Poorly preserved specimens are often characterized by the presence of a transparent, nongranular texture within the area of the COC when viewed by optical microscopy and blocky textures extending into the fibers (Fig. 2.3d). As the COCs become more pervasively altered, these zones take on the appearance and texture of calcite spar (Fig. 2.3d,e). In specimens for which dissolution and recrystallization are limited to the COCs, it is possible to avoid these zones when choosing targets for SIMS spots (e.g. Fig. 2.3c). Other textural features that we used as exclusion criteria include dissolution pits, ‘fibrous micropores’
Figure 2.4 Characterization of preservation by Cathodoluminescence and Raman. (a) Thin section image (transmitted light) of Upper Cretaceous coral, K1. Yellow circles represent the locations of SIMS analysis spots. (b) CL image of the same region shown in (a) for Cretaceous coral, K1. Regions of red luminescence correspond to regions composed of calcite (mainly sediment). Red luminescence is absent within the coral skeleton, suggesting it is composed of aragonite and indicating that the regions analyzed were not affected by diagenesis. (c) Thin section image (transmitted light) of Cretaceous coral, K2. Yellow circles represent the locations of SIMS analysis spots. (d) Raman map of aragonite distribution for the sample shown in (c). Areas shown in green correspond to aragonite-rich zones. (e) Raman map of calcite distribution for the same sample shown in (c). Areas shown in red correspond to calcite-rich zones.
(Bar-Matthews et al., 1993; Fig. 2.3f), and evidence of micro-boring (Webb et al., 2009; Nothdurft and Webb, 2009) (see samples R5-R8, Supplementary S2; S3). While petrographic microscopy and SEM studies help to better understand the preservation state of our specimens, we are unable to confirm the absence of calcite within the coral skeleton using petrographic microscopy and SEM alone.

CL and Raman analyses allow us to better constrain the spatial distribution of calcite in infilled samples. Samples passing our CL and Raman tests are generally characterized by the absence of luminescence (CL) and calcite mineralogy (Raman) within the coral skeleton, despite the presence of highly luminescent and calcite-rich infilling (Fig. 2.4). Some samples that we designate as ‘well preserved’ do contain calcite-rich, luminescent zones near the COCs (Supplementary S9 to S12) consistent with preferential dissolution and recrystallization of the COCs as recognized in our petrographic microscopy studies. While we retain these samples as part of our suite, we note that they are unsuitable for bulk analysis and we discard any SIMS data that overlap with the luminescent or calcite-rich zones. Samples failing our CL and Raman tests are typically characterized by domains of calcite intercalated with aragonite at the micron-scale, as shown in Frankowiak et al. (2013). Because both bulk and SIMS measurements of these corals would include a diagenetic component, we excluded such samples from our seawater chemistry reconstructions (see Supplementary S2).

2.4.1.3 Mn/Ca Ratios

Mn/Ca ratios measured concurrently with other metal/calcium (Me/Ca) ratios using SIMS further ensure that we identify small diagenetic domains that may not have been detected by our other tests (SEM, petrographic microscopy, CL, and Raman). The partition coefficient for
Mn in calcite is greater than that for Mn in coral aragonite (Pingitore, 1978; Shen et al., 1991) and so diagenetic calcite will usually be enriched in Mn. In addition, if recrystallization occurs in reducing waters, those diagenetic fluids should contain far more dissolved Mn than seawater, leading to very high concentrations of Mn in the diagenetic phase (Brand and Veizer, 1980).

For some samples older than Miocene in age, one or more SIMS spot measurements had anomalously high Mn/Ca ratios outside of the range measured in modern corals (Mn/Ca_{ModernCoral} \approx 0.01 - 10 \mu mol/mol; Shen et al. 1991). We attribute these high Mn/Ca ratios to small-scale recrystallization of the skeleton. The highest Mn/Ca ratio measured was 3700 \mu mol/mol for a Triassic age specimen. This is at least 3 orders of magnitude higher than the highest Mn/Ca ratios reported for modern specimens. Similarly high Mn/Ca ratios have recently been measured and identified as the contaminant phase, kutnahorite, in foraminifera shells (Pena et al., 2005). As our criterion for small-scale recrystallization, we used the maximum Mn/Ca ratio measured in Shen et al.: Mn/Ca = 10.3 \mu mol/mol. Any spots with Mn/Ca > 10.3 \mu mol/mol were excluded from reconstructions of seawater Mg/Ca and Sr/Ca. In practice, decreasing our exclusion threshold to values lower than 10.3 \mu mol/mol has very little impact on average Mg/Ca and Sr/Ca ratios.

Fig. 2.5 shows Mn/Ca, Mg/Ca and Sr/Ca measurements across representative SIMS transects from two different Cretaceous age specimens (K1 and K3) and illustrates how we used Mn/Ca to recognize fine scale recrystallization. Also shown are plots of Mg/Ca vs. Mn/Ca for all of the SIMS spot analyses measured for these samples across multiple transects (Fig. 2.5c,d). Both K1 and K3 were determined to be well preserved based on XRD, petrographic microscopy and SEM. Mn/Ca ratios in K1 fall below the threshold value of 10.3 \mu mol/mol at all spots measured across the transect shown in Fig. 2.5a except for a single SIMS point that overlaps with
the COC. The COC is judged to be recrystallized, and the average Mg/Ca and Sr/Ca ratios for this sample are calculated from the remaining SIMS data.

**Figure 2.5** Mg/Ca, Mn/Ca, and Sr/Ca ratios from two Cretaceous age fossil corals. Standard errors for Mg/Ca, Sr/Ca, and Mn/Ca for data shown here are on average 3%, 1%, and 10%, respectively (2σ S.E.). (a) Transect across the septum of the scleractinian coral K1, Trochocyathus egeri (White 1879) from Pierre shale, Dry Creek, Black Hills (South Dakota, USA). (b) Transect across the septum of scleractinian coral K3, Rennensismilia complanata (Goldfuss 1826), from Gosau, Austria. (c) Relationship between Mg/Ca and Mn/Ca (log scale) for sample K1. (d) Relationship between Mg/Ca and Mn/Ca (log scale) for sample K3. Fewer analyses are excluded from the sample K1 than for sample K3, reflecting the more pristine nature of sample K1.
In contrast, Mn/Ca in K3 is elevated across the entire transect shown in Fig. 2.5b (especially at spots 1-4, 7, 10, and 11) although in other regions of sample K3 we identify spots with Mn/Ca below 10.3 µmol/mol (Fig. 2.5d). For most of the spots where we observe high Mn/Ca ratios, we observe that Sr/Ca ratios are low and Mg/Ca ratios are high. This general pattern is consistent with diagenetic alteration to calcite, which lowers Sr/Ca while raising Mg/Ca and Mn/Ca (Brand and Veizer, 1980; Webb et al., 2009).

We also find that rejected samples with micron-scale, intercalated domains of calcite and aragonite (as indicated by CL and Raman; e.g., samples R1, R3, and R4) all have Mn/Ca >10.3 µmol/mol. This result shows that our quantitative studies of Mn/Ca agree with CL imaging and Raman spectroscopy studies, and helps create a consistent pattern of preservation across our sample set.

We make three conclusions from our SIMS studies of Mn/Ca. First, despite careful study by XRD, SEM, and petrographic microscopy, we document local alteration through SIMS measurements of Mn/Ca. CL and Raman confirm these results (Annex S9 to S12). Second, even when specimens are partially altered, it is possible to access and characterize pristine domains, avoiding Mn-rich regions according to the criterion described above. Third, bulk geochemical measurements for specimens with high Mn/Ca SIMS spots reflect a combination of primary and secondary material, and thus cannot provide robust paleoenvironmental information; microanalysis techniques are necessary to recover the original geochemical signatures from these specimens (these samples are marked by asterisks in Table 2.1).
Figure 2.6 Representative plots of Sr/Ca vs. Mg/Ca for fossil corals of various ages. Approximately 80% of corals in our sample set display an inverse relationship similar to that observed by Gagnon et al. (2007). Data shown in grey represent spots corresponding to low Mn/Ca ratios whereas data plotted in black represent spots corresponding to high Mn/Ca ratios. In the case of the Triassic age sample, high Mn/Ca spots represent SIMS analyses that were measured both in the calcite matrix in which the coral skeleton was embedded, and within the coral skeleton itself (representing recrystallization of the skeleton). Standard errors for Mg/Ca and Sr/Ca SIMS spot analyses are 3% and 1%, respectively (2σ S.E.).
2.4.1.4 Trace element patterns

As another test of diagenesis, we determine whether element/Ca ratios in fossil corals exhibit the same patterns as in modern corals. Sr/Ca ratios vary inversely with Mg/Ca ratios in aragonite drilled from modern coral fibers, although this pattern is not observed in the COCs (Gagnon et al., 2007; Gaetani et al., 2011). We generally expect to find a relationship between Sr/Ca and Mg/Ca in our fossil corals if they are well preserved. However, we do not reject samples that fail to show the relationship due to its absence in some modern corals measured by SIMS (e.g., Allison et al., 2010). NanoSIMS studies that measure Mg/Ca and Sr/Ca at a finer scale (spot size <1 µm) also fail to observe this pattern, suggesting that the relationship may be scale dependent (Meibom et al., 2007; 2008). In addition to the relationship between Mg/Ca and Sr/Ca, Recent corals and other aragonites also show a positive relationship between S/Ca and Na/Ca ratios (Busenberg and Plummer, 1985; Bar-Matthews et al., 1993), which we expect to see in our samples if they are well preserved.

Results of SIMS element/Ca analyses (Mg/Ca, Sr/Ca, Mn/Ca, Na/Ca, and S/Ca) for each sample in our study set are listed in Supplementary S5. Approximately 80% of all fossil corals exhibit an inverse relationship between Sr/Ca and Mg/Ca, similar to that observed by Gagnon et al., (2007), supporting the primary nature of our samples (Fig. 2.6, Supplementary S13). Previous studies have suggested that, while Sr substitutes directly into the aragonite crystal lattice, a significant portion of coral Mg may exist in either organic or disordered inorganic compounds (Finch and Allison, 2008). This distribution of Mg raises concerns about the stability of Mg in corals over the timescales we are investigating. The preservation of Sr/Ca-Mg/Ca relationships across our fossil suite supports the conclusion that both Sr and Mg are preserved at
a fine scale within the coral skeleton. Moreover, we fail to observe evidence for loss or gain of Mg from the boundaries of the coral skeleton that would raise concerns about preservation.

Figure 2.7 (a) S/Ca vs. Na/Ca ratios of modern and fossil corals (Bar-Matthews et al., 1993; Busenberg and Plummer, 1985), and inorganic aragonites (Bar-Matthews et al., 1993). Bar Matthews et al. data represent averages of ~30, 1 µm spots measured by electron microprobe. Uncertainties are 6% (2σ) for Na/Ca data and 7% (2σ) for S/Ca data. (b) S/Ca vs. Na/Ca ratios measured in fossil corals (this study). Each spot corresponds to a single SIMS spot analysis. Standard errors for Na/Ca and S/Ca are approximately 2% and 3%, respectively (2σ). S/Ca and Na/Ca generally show a positive correlation.
An inverse correlation between Sr/Ca and Mg/Ca could also be imparted by
diagenetic alteration, as described above (Brand and Veizer, 1980). This diagenetic trend is
typically distinct from primary patterns between Sr/Ca and Mg/Ca in that the diagenetic Sr/Ca-
Mg/Ca trends exhibit much shallower slopes (Fig. 2.6). In addition, Mg/Ca ratios measured by
SIMS in our modern corals vary by a factor of 2-5 while variability in altered fossils can be
much greater (e.g., the variation exhibited within the high-Mn/Ca zones of the Triassic age
sample shown in Fig. 2.6 is about a factor of 10).

We also observe a general positive correlation between Na/Ca and S/Ca in our fossil
and modern corals. This pattern is similar to that observed by Busenberg and Plummer (1985)
and Bar-Matthews et al. (1993) for various modern corals, recent fossil corals, and other
inorganic aragonites (Fig. 2.7). Additional plots of Na/Ca vs. S/Ca relationships from within a
few individual coral specimens can be found in Supplementary S14. While corals and aragonites
measured in previous studies show a tight positive correlation (Fig. 2.7a), both modern and fossil
corals from this study exhibit a larger spread in both Na/Ca and S/Ca space (Fig. 2.7b). Our data
represent individual SIMS spot measurements whereas data from Busenberg and Plummer
(1985) and Bar-Matthews et al. (1993) represent bulk measurements made on powder samples
and averages of electron microprobe data, respectively. The different scales of observation
explain some, but not all, of the greater variability in our samples.

Data from Busenberg and Plummer (1985) and Bar-Matthews et al. (1993) also show
that modern corals exhibit the highest Na/Ca and S/Ca, while Pleistocene-age fossil corals
(younger than almost all of our fossil coral samples) are more depleted in Na and S relative to Ca
(Fig. 2.7). Secondary aragonite and other inorganic aragonites (fibrous, acicular, and oolitic) are
characterized by the lowest Na/Ca and S/Ca ratios. Bar-Matthews et al. (1993) suggest that this
pattern may indicate a relationship between Na and S concentrations and preservation, where lower Na/Ca and S/Ca ratios indicate poor preservation. Similar to Bar-Matthews et al., we find that Na/Ca and S/Ca ratios are highest in our Recent coral samples, but most fossil corals ranging in age from Pleistocene through Jurassic retain S/Ca ratios within the range of our modern specimens. This aspect of the data suggests good preservation. Some SIMS measurements of S/Ca and Na/Ca ratios in fossil corals also fall outside the modern field. Two factors likely contribute to this departure. One is that our modern field is based on only 2 specimens and is unlikely to cover all variability. The other is that departures are expected as seawater [Ca$^{2+}$] and possibly [SO$_4^{2-}$] varies through time (Paytan et al., 1998, 2004; Lowenstein et al., 2003). Indeed, the low Na/Ca ratios in many Mesozoic samples (as well as the lower S/Ca ratios for some samples) may reflect higher seawater [Ca] during the Mesozoic (Lowenstein et al., 2001, 2003, 2005; Horita et al. 2002; Dickson, 2002, 2004; Timofeeff et al., 2006; Brennan et al., 2013; Holt et al., 2014; this work). A few extremely low S/Ca and Na/Ca measurements from Triassic corals may indicate inferior preservation and suggest that other compositional data from these samples should be interpreted with caution. In general, we do not see relationships between low S/Ca or Na/Ca ratios and Mg/Ca ratios that might indicate the latter ratio is diagenetically altered (see Supplementary S15).

2.4.1.5 Carbonate clumped isotopes

Carbonate clumped isotope thermometry studies complement our independent tests of alteration by further supporting the good preservation of most of our samples, and by confirming the poor preservation of samples that we classify as ‘altered’ by other independent tests (Fig. 2.8,
Supplementary S2, S7). Aliquots of powders used in clumped isotope measurements were also measured by XRD (see Table 2.1).

Coral clumped isotope temperatures fall into three groups. First, most samples have clumped isotope temperatures around 25-30°C, consistent with growth in warm surface waters. The clumped isotope temperatures of these samples give additional evidence for their excellent preservation.

**Figure 2.8** Measured clumped isotope temperature in fossil corals vs. geologic age projected into the absolute reference frame of Dennis et al. (2011) and re-projected calibration of Ghosh (2006). Temperatures above 40°C indicate burial diagenesis. Red arrows indicate samples for which clumped isotope temperatures are unreasonably high. Samples E7 and Tr3 - both marked by a ‘?’- are plotted as red squares in Fig. 10 to convey uncertainties in their preservation. Data represent the average and 1σ S.E. (n>2) or 1σ S.D. (n=2) of replicate measurements.
Second, specimens E7, R1, R9, and R10 give average clumped isotope temperatures ≥40°C, which are likely incompatible with early Cenozoic and Mesozoic surface ocean temperatures (Zachos et al., 2001; Pearson et al., 2001, 2007; Keating-Bitonti et al., 2011). We assume R1, R9 and R10 underwent burial diagenesis, and exclude these samples from our seawater chemistry reconstructions. Sample E7 was shown to be well preserved based on our other tests. This sample was infilled with calcite cement that could not be separated in drilling the powder sample, and the high clumped isotope temperature probably results from contamination by this secondary calcite (35%; Table 2.1). The powder from Sample Tr3, which also produced a relatively high clumped isotope temperature (38°C), is characterized by a high percentage of calcite derived from infilling cement (37%) as well. We retain both samples in our reconstructions of Sr/Ca and Mg/Ca based on SIMS data, but flag the points in Fig. 2.10 (red squares instead of red circles) to indicate some ambiguity in the quality of their preservation.

Third, some specimens yield relatively cold clumped isotope temperatures. These temperatures could result from growth in cool subsurface waters, meteoric diagenesis, or coral vital effects; for some species of shallow water coral, clumped temperatures have been found to underestimate true growth temperatures by up to ~12°C (Ghosh et al., 2006; Saenger et al., 2012). We suggest that our clumped isotope measurements give robust minimum temperatures for well-preserved samples but cannot be used to infer absolute temperatures until vital effects in shallow water corals are better understood.

2.4.1.6 Sr Isotopes

Sr isotopes measured on a subset of fossil corals also indicate good preservation of our specimens (Fig. 2.9, Supplementary S8). Our Sr isotope criterion for good preservation is
that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured in a coral must agree (within analytical uncertainty) with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater at the stratigraphic age of the sample. The ages of most of our samples are independently known within ±5 My or better, but in some cases ages are only constrained to a geologic epoch. While other studies have found a small fraction of well preserved fossil aragonites (though not corals) that apparently deviate from the Sr isotope curve for reasons other than poor preservation (McArthur et al., 1994; Ivany et al., 2008; Marcano et al., 2009), we make the conservative assumption that anomalous Sr isotope ratios signify diagenetic alteration.

**Figure 2.9** (a) $^{87}\text{Sr}/^{86}\text{Sr}$ of coral samples vs. geologic age, overlying the Sr isotope seawater curve of McArthur et al. (2001). (b) Enlarged version of the last 60 Ma. Dashed black lines correspond to the mismatch between the Sr isotope age for sample Pa2 and the expected age.

Using independently estimated ages, all but one of the ~45 powders analyzed give $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are within error of those predicted by the McArthur et al. (2001) Sr isotope curve (Fig. 2.9, Supplementary S8). It is surprising that even samples containing some calcite give Sr isotope ages consistent with the expected age. There are three possible explanations for this observation. First, and most likely, the Sr content of the secondary calcite is too low to shift
the original the Sr isotope ratio preserved in the primary aragonite phase. Second, precipitation of secondary minerals may have occurred relatively soon after the coral built its skeleton in a solution with a similar composition as contemporaneous seawater. Third, the calcite may have precipitated later, but from a diagenetic fluid with the same Sr isotope composition as the original skeleton.

A single coral, the Paleocene-age specimen Pa2, gave an $^{87}\text{Sr}/^{86}\text{Sr}$ age that disagreed with the expected age; the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured was too high by about 0.00005. This deviation is small and the measured value falls nearly within the range of input data to the Sr isotope curve for the Paleocene (McArthur et al., 2001). Leaching of radiogenic Sr from silicate minerals having a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio may also account for the slightly elevated composition observed, as the powder XRD pattern for this specimen indicates the presence of quartz and/or other aluminosilicate minerals (Supplementary, S4). We retain this sample as part of our suite, but flag it in Fig. 2.10 (red square instead of red circle) to show that it has failed our Sr isotope test.

Overall, our studies indicate that, by using multiple diagenetic indicators, it is possible to find well preserved scleractinian corals, or domains within skeletons exhibiting good preservation, as old as Triassic in age. These specimens appear to retain their original chemical and isotopic composition and can be used for paleoenvironmental reconstructions. Many samples with partially preserved skeletons may not be suitable for bulk analysis of powders, but it is possible to obtain primary geochemical signatures from these specimens using microanalysis techniques such as SIMS (marked by asterisks in Table 2.1). We find that some other samples containing a mixture of primary and secondary material (e.g. R1, R3 and R4) are too
compromised to extract original paleoenvironmental signatures even with the use of microanalysis techniques.

**Figure 2.10** (a) Seawater Mg/Ca and (b) Sr/Ca inferred from various proxies. (c) Seawater Mg/Ca (as in a) for the last 50 Ma. Error bars represent 2σ S.E. of the mean. Red circles correspond to results from well preserved fossil corals (this study). Red squares with black borders represent fossil corals (this study) that passed all but one of our diagenetic tests. Brine inclusion data are from Lowenstein et al., (2001; 2003; 2005), Horita et al. (2002), Brennan et al. (2004), Timofeeff et al. (2006), Brennan et al. (2013).
2.4.2 Secular variations in seawater Mg/Ca

The average Mg/Ca ratio of 2 modern surface dwelling corals measured in this study using SIMS is 4.0 ± 0.3 mmol/mol, which is similar to values reported in other SIMS studies of modern coral (Allison and Finch, 2007) and bulk measurements of modern surface corals (n=123) (Supplementary S16). Using these modern SIMS and bulk Mg/Ca data, we calculated a partition coefficient \( K_{D}^{Mg/Ca} = \frac{(Mg/Ca)_{coral}}{(Mg/Ca)_{seawater}} = 7.0 \times 10^{-4} \), which we applied to reconstruct seawater Mg/Ca from fossil coral data.

Our reconstruction of the seawater Mg/Ca ratio, calculated from the average Mg/Ca composition of individual fossil corals and the distribution coefficient, is shown in Fig. 2.10a. This history is qualitatively and quantitatively consistent with histories derived from other archives, including brine inclusions in halite, hydrothermal CaCO₃ veins, fossil echinoderms, and a few studies of other fossil corals. Seawater Mg/Ca ratios inferred from corals are lowest during the Jurassic and Cretaceous, and exhibit a nearly 5-fold increase from the Late Mesozoic to the present.

Because coral Mg/Ca is sensitive to temperature (Mitsuguchi et al. 1996), we have assessed the impact of temperature variability for our reconstruction. Coral Mg/Ca ratios are positively correlated with temperature and exhibit a dependence of ~0.13 mmol/mol °C⁻¹ (Mitsuguchi et al., 1996), or about 3% °C⁻¹. Based on our knowledge of growth environments (see Supplementary S1), we estimate that fossil coral growth temperatures ranged between 20 and 35°C for the bulk of our sample set (Keating-Bitonti et al., 2011; Littler et al., 2011). As a result, we should expect to find ±25% variability about the average of our Mg/Ca ratios for corals of the same geologic age, which is roughly compatible with our data. This range of ±25%, although large as illustrated by the spread in the modern data, is far smaller than the Mg/Ca
increase since the Late Cretaceous (about 400%). There are also a few specimens in our dataset (Pa4 from Seymour Island and Mi7 from Poland) that likely grew at temperatures <20°C. Evidence for sample Pa4 comes from clumped isotope analyses of Eocene-age bivalve shells from Seymour Island (Douglas et al., 2014). Evidence for sample Mi7 comes from estimates of middle Miocene sea surface temperatures summarized in You et al. (2009). Cold growth temperatures have the potential to bias Mg/Ca ratios in these samples toward lower values. However, we find that neither sample defines the minimum of our Mg/Ca record and both fall well within the range of values measured for fossil corals of similar geologic age.

We also consider how Cenozoic cooling may affect fossil coral Mg/Ca ratios. If we conservatively estimate that tropical temperatures were ~4°C higher during the Early Cenozoic than today (Keating-Bitonti et al., 2011), and if we remove the temperature dependence of coral Mg/Ca associated with this change, we calculate that reconstructed Mg/Ca ratios during the Cretaceous should be ~13% lower than the measured values suggest. In this way, accounting for the temperature change related to Cenozoic cooling slightly amplifies (by about 0.1 mol/mol) the difference between low seawater Mg/Ca ratios in the Mesozoic and high seawater Mg/Ca ratios in the late Cenozoic. This calculation confirms that trends observed in the coral Mg/Ca data cannot be explained by a response to temperature change.

To further illustrate the robustness of the Mg/Ca change inferred from fossil corals, we plot three additional representations of Mg/Ca ratios measured in corals against their geologic age (Fig. 2.11). Fig. 2.11a shows averages of coral Mg/Ca ratios including high-Mn analyses and demonstrates the impact of using Mn/Ca as a diagenetic indicator. Data are colored according to Mn content. While it may still be possible to observe the general trend toward higher Mg/Ca ratios between the Cretaceous and today, many of the average Mg/Ca ratios plotted (especially
for samples of Eocene age and older) are skewed toward higher values. The highest Mg/Ca ratios plotted in Fig. 2.11a correspond to samples with high Mn/Ca ratios, consistent with the observation that high Mn/Ca ratios occur with high Mg/Ca ratios (as well as low Sr/Ca ratios: see Fig. 2.5). These observations reinforce two conclusions made previously. First, Mn/Ca is a strong indicator of small-scale recrystallization in aragonitic fossil corals. Second, it is clear that some generally well preserved corals exhibit small-scale recrystallization. Microanalysis techniques such as those employed here are essential for recovering primary geochemical information from these samples.

Fig. 2.11b plots average coral Mg/Ca ratios (as in Fig. 2.10) on a logarithmic scale. The variance in average Mg/Ca measured in samples of similar geologic age does not appear to greatly change with time, further supporting the good preservation of our samples. Fig. 2.11b also more clearly shows that the rise in seawater Mg/Ca began around 80 Ma. Parenthetically, the linear increase shown in seawater Mg/Ca with time during the Cenozoic (when plotted on a logarithmic scale as in Fig. 2.11b and 2.11c) can be explained by invoking a constant rate of [Mg] rise and [Ca] fall.

Fig. 2.11c shows the minimum Mg/Ca ratio (rather than the mean) of all SIMS spots measured in each coral specimen. This representation would be appropriate if corals precipitate their skeletons from a closed batch of seawater via a Rayleigh distillation process, and the most Sr-rich and Mg-poor spot approximates initial precipitation from unfractionated seawater. Fig. 2.11c still portrays a Mg/Ca change in fossil corals of similar magnitude and timing as observed in the plot of average coral Mg/Ca (Fig. 2.11b), but the scatter is greater. Part of the scatter in minimum Mg/Ca values may result from the fact that we have not always captured the initial phase of the Rayleigh process.
Figure 2.11 (a) Average coral Mg/Ca calculated including spots with high Mn/Ca ratios (log scale). Mg/Ca ratios for older specimens are skewed toward higher values. Error bars represent 2σ S.E. (b) Average coral Mg/Ca (as in Fig. 2.10a) plotted on a log scale. Error bars represent 2σ S.E. (c) Minimum Mg/Ca ratios measured in fossil corals, plotted on a log scale (error bars are not shown because each symbol denotes a single SIMS spot analysis and internal errors are smaller than the symbol size).
Our more complete Mg/Ca record allows us to determine when seawater Mg/Ca began to increase toward its present day value (~80 Ma), and suggests that the Cenozoic transition from calcite to aragonite sea (Mg/Ca = 2 mol/mol according to Hardie, 1987) occurred at ~40 Ma. At least half of the total change in seawater Mg/Ca between the middle Cretaceous and today appears to have occurred within the last 15-20 My. Our data also strengthen the link between low Cretaceous seawater Mg/Ca and the presence of Late Cretaceous-age corals with primary calcite skeletons (Stolarski, 2007).

Surprisingly, the coral archive suggests that Mg/Ca ratios during the Late Triassic were low – about 1/3 of the modern ratio (Fig. 2.10a, Fig. 2.11). This period is generally thought to be a time when inorganic CaCO₃ precipitated from seawater as aragonite (‘aragonite seas’), implying high seawater Mg/Ca ratios. Our results, along with data from brine inclusions and fossil echinoderms (Fig. 2.10a; Lowenstein et al., 2001, 2003, 2005; Horita et al. 2002; Dickson, 2002, 2004; Timofeeff et al., 2006; Brennan et al., 2013), instead suggest that the Triassic transition from high Mg/Ca seawater to low Mg/Ca seawater may have occurred prior to 230 Ma. The apparent mismatch between the timing of Mg/Ca and mineralogical change during the Triassic, which is also observed for the Carboniferous (Holt et al., 2014), may be related to the observation that carbonate mineralogy also depends on seawater SO₄²⁻, temperature, alkalinity, saturation state, and pCO₂ (Burton and Walter, 1991; Morse et al. 1997; Lee and Morse, 2010; Bots et al. 2011). This improved understanding of the timing of changes in seawater Mg/Ca may be useful in helping to test key hypotheses that seek to determine the geologic controls on seawater chemistry and long-term climate (e.g., changes in the rates of dolomitization through time, changes in the rates of either low or high temperature hydrothermal alteration, or changes
in the river flux of Mg relative to Ca: Wilkinson and Algeo, 1989; Holland, 2005; Hardie et al., 1996; Horita et al., 2002; Stanley and Hardie, 1998; Broecker et al., 2013).

### 2.4.3 Secular variations in seawater Sr/Ca

We calculate seawater Sr/Ca ratios using a partition coefficient, $K_{D}^{Sr/Ca} = \frac{(Sr/Ca)_{coral}}{(Sr/Ca)_{seawater}} = 1.13$, based on an average of modern coral SIMS and bulk measurements as in Section 3.2 for Mg/Ca (Fig. 2.10b; Allison and Finch, 2004; Supplementary S16). Because coral Sr/Ca ratios are also slightly temperature sensitive, (~1% decrease in Sr/Ca for every 1°C increase in temperature), we have assessed the effects of temperature on fossil coral Sr/Ca (Beck et al., 1992; Beck et al., 1997; de Villiers et al., 1994; McCulloch et al., 1994; Corrège et al., 2006; Watanabe et al., 2011). Assuming (as noted earlier for the case of Mg/Ca ratios) that most fossil corals in our sample set lived in waters ranging in temperature from 20 to 35°C, we would expect a range in coral Sr/Ca of ±7.7% for corals of similar geologic age. This range of variability is similar to the observed variability in reconstructed Sr/Ca of about ±10% for corals of the same geologic age. We can also calculate the magnitude of temperature-induced Sr/Ca change as a consequence of Cenozoic cooling. A cooling of 4°C between the Early Paleogene and today as estimated previously would result in a ~4% increase in coral Sr/Ca ratios between the Paleogene and today. This temperature-induced change is much smaller than the observed Cenozoic change and in the opposite direction, suggesting that temperature effects do not significantly bias our reconstructions.

Our fossil coral record is generally consistent with other biogenic carbonate-based records of seawater Sr/Ca (Lear et al., 2003; Tripati et al., 2009; Balter et al., 2011; Sosdian et al., 2012; Evans et al., 2013; Fig. 2.10b) but disagrees with two independent records from
hydrothermal calcium carbonate veins (CCV) (Coggon et al., 2010; Rausch et al., 2013). We favor the fossil Sr/Ca records rather than the CCVs. The calculation of seawater Sr/Ca ratios from fossil biogenic carbonates is based on exhaustive observations of Sr/Ca in modern CaCO$_3$ skeletons. It is also based on empirical results from culture experiments showing that the Sr/Ca ratio of CaCO$_3$ skeletons scales with that of seawater (Lewin and Chow, 1961; Swart, 1981; Lorens and Bender, 1980). Such a detailed empirical and mechanistic basis is lacking for Sr/Ca in CCVs, and the precipitation rate-dependence of the Sr/Ca ratio in inorganic calcites (e.g. Lorens, 1981; Tang et al., 2008) is problematic.

Several fossil coral samples dating to the Early Cenozoic have Sr/Ca ratios ~15% higher than modern and Sr/Ca in fossil corals decreases steadily between the Early Cenozoic and present. A single sample dated to ~71 Ma by Sr-isotope stratigraphy has the highest Sr/Ca ratio in our record. This result supports the inference of high seawater Sr/Ca ratios during the Late Cretaceous based on benthic foraminifera and fossil fish teeth (Lear et al., 2003; Balter et al., 2011), but needs to be confirmed with additional samples. Our few samples older than 100 Ma have Sr/Ca ratios similar to modern, consistent with a Mesozoic and Paleozoic record from brachiopods, belemnites and rudists (Steuber and Veizer, 2002).

Despite general agreement between biogenic carbonate records, there also are differences between the various records during the Cenozoic. Although there are large uncertainties in the gastropod seawater Sr/Ca records that overlap with the other biogenic records (Tripati et al., 2009; Sosdian et al., 2012), the gastropods give higher average estimates for seawater Sr/Ca. This may be partly related to uncertainties in interspecific offsets and temperature sensitivities (Sosdian et al., 2012). In addition, there is modest divergence between fossil corals, benthic foraminifera, and fish teeth during the middle Cenozoic (Lear et al., 2003;
Balter et al., 2011). We suggest that the Sr/Ca history of seawater is likely bounded by our fossil corals and the foram and fish teeth records.

2.5 Conclusion

Studies of the mineralogy, crystal habit, clumped isotope composition, Sr isotope composition, and trace element geochemistry (especially Mn/Ca) of fossil corals have allowed us to constrain the extent of diagenetic alteration in ~60 well preserved fossil corals. SIMS studies of Sr/Ca and Mg/Ca in these samples suggest that well preserved fossil corals can produce useful records of seawater paleochemistry. These samples can also be used in future studies to explore additional seawater properties of interest. Many of our samples are from museum or government collections and are essentially in the public domain. We find that seawater Sr/Ca was higher than today during the Late Cretaceous and Early Paleogene, consistent with other biogenic records of Sr/Ca. Our Mg/Ca record agrees with existing records and suggests low seawater Mg/Ca during the Mesozoic and high seawater Mg/Ca ratios today. The initial increase in Mg/Ca towards the present value appears to occur at ~80 Ma, and the Cenozoic transition from calcite to aragonite seas occurs in the mid to Late Eocene. Sr/Ca and Mg/Ca records from well preserved fossil corals may help constrain major element cycling on Earth’s surface and the relationship between seawater chemistry and Earth’s climate state.

2.6 Acknowledgements

We thank Yunbin Guan (California Institute of Technology) for his help with SIMS analyses, Gerald Poirier (Princeton Imaging and Analysis Center) for assistance with SEM and
XRD, and Guillaume Paris (California Institute of Technology) for his help with sulfate concentration analyses. This manuscript has benefitted tremendously from helpful discussions with John M. Eiler (California Institute of Technology), John A. Higgins (Princeton University), Alex C. Gagnon (University of Washington) and helpful comments from Silke Severmann (AE), Tim Lowenstein, and two anonymous reviewers. We also thank Stephen A. Cairns, Tim Coffer (Smithsonian Institution), Roger Portell (Florida Museum of Natural History), the USGS Core Research Center, Bill Thompson (WHOI), Gregory P. Dietl (Paleontological Research Institution), and Linda Ivany (Syracuse University) for contributing samples for this work. The work of JS was supported in part by the Polish-Norwegian Research Programme operated by the National Centre for Research and Development under the Norwegian Financial Mechanism 2009-2014 in the frame of Project Contract No Pol-Nor/196260/81/2013. We gratefully acknowledge support from the Princeton BP Amoco Carbon Mitigation Initiative, and from the Frank Harrison Tuttle Memorial Fund for Invertebrate studies.

2.7 Supplementary

Supplementary materials S1-S17 for this chapter can either be found online, alongside the published version of this article (as Electronic Annexes) or at Princeton DataSpace:

http://arks.princeton.edu/ark:/88435/dsp013f462780m

2.8 Author contributions, and previous presentations of this work

Michael Bender and Anne Gothmann initially planned the project. Anne Gothmann conducted analytical work with the exception of CL and micro-raman, with much input from Michael
Bender, Jess Adkins, Blair Schoene, Kate Dennis, and Dan Schrag. CL and micro-raman work was performed by Jarek Stolarski and Maciej Mazur. Anne Gothmann drafted the manuscript and figures with input from the other co-authors.

This work has been published as:


This work has been presented as:


O’Leary (Gothmann), A.M., Stolarski, J., Adkins, J.F., A.M., Dennis, K.J., Schrag, D.P., Bender, M.L. (June 2013) “SIMS as a tool for measuring primary geochemistry and characterizing vital effects in fossil corals”, High-Resolution Proxies of Paleoclimate Workshop, University of Wisconsin-Madison, Madison, WI.

O’Leary (Gothmann), A.M., Dennis, K.J., Schrag, D.P., Stolarski, J., Adkins, J.F., Bender, M.L. (January 2013) “Clumped Isotopes in corals as an indicator of diagenetic alteration and as
a paleotemperature proxy”, 3rd International Workshop on Clumped Isotopes, Harvard University, Cambridge, MA.

Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry Since the Mesozoic

References


CHAPTER 2. FOSSIL CORALS AS AN ARCHIVE OF SECULAR VARIATIONS IN SEAWATER CHEMISTRY SINCE THE MESozoIC

Acta 55, 777-785.


Getty, S. R., Asmerom, Y., Quinn, T. M., and Budd, A. F. 2001. Accelerated Pleistocene coral extinctions in the Caribbean Basin shown by uranium-lead (U-Pb) dating. Geology 28,
CHAPTER 2. FOSSIL CORALS AS AN ARCHIVE OF SECULAR VARIATIONS IN SEAWATER CHEMISTRY SINCE THE MESOZOIC

639-642.


*Acta* 66, 3733 - 3756.


Chapter 2. Fossil Corals as an Archive of Secular Variations in Seawater Chemistry Since the Mesozoic


CHAPTER 2. FOSSIL CORALS AS AN ARCHIVE OF SECULAR VARIATIONS IN SEAWATER CHEMISTRY SINCE THE MESOZOIC

Nature 305, 19-22.


Timofeeff, M. N., Lowenstein, T. K., Martins da Silva, M. A., and Harris, N. B. 2006. Secular variation in the major-ion chemistry of seawater: Evidence from fluid inclusions in
CHAPTER 2. FOSSIL CORALS AS AN ARCHIVE OF SECULAR VARIATIONS IN SEAWATER CHEMISTRY SINCE THE MESOZOIC


Chapter 3. A Cenozoic record of Mg isotopes from fossil corals

3.1 Abstract

Two published records of Cenozoic seawater $\delta^{26}$Mg give divergent histories. A record derived from bulk foraminifera and limestone suggests that seawater $\delta^{26}$Mg has not varied by more than $\pm 0.2$‰ over the Cenozoic (Higgins and Schrag, 2015). In contrast, a record derived from species-specific planktic foraminifera shows a $\sim 0.8$‰ decrease in seawater $\delta^{26}$Mg since 20 Ma (Pogge von Strandmann et al., 2014).

Previous studies of Mg isotopes in modern scleractinian corals indicate that unaltered fossil corals are likely to be robust archives of past seawater $\delta^{26}$Mg (Wombacher et al., 2011; Saenger et al., 2013). The sensitivity of coral Mg isotopes to temperature is small ($+0.03$‰ °C$^{-1}$; Saenger et al. 2013; Wombacher et al. 2011), and the Mg isotope composition of modern corals is similar to the composition of inorganic aragonite (Wang et al. 2013).

We measured Mg isotopes in a set of excellently preserved fossil scleractinian corals, ranging in age from Paleocene through Recent, to discriminate between the existing records of Cenozoic seawater $\delta^{26}$Mg. We find that fossil corals show little variability in $\delta^{26}$Mg throughout the Cenozoic – consistent with Higgins and Schrag (2015), and different from the record of Pogge von Strandmann et al. (2014). Together, the fossil coral record and the Higgins and Schrag (2015) record indicate that the proportion of Mg removed from seawater as dolomite, relative to the amount removed by Mg uptake in clays, has not changed greatly since the Late
Mesozoic. As a result, a decrease in the rate Mg removed by dolomite cannot, by itself, explain the rise in seawater Mg/Ca since ~80 Ma.

**Figure 3.1** Summary of (a) Reconstructions of seawater Mg/Ca and (b) seawater [Mg] and [Ca]. Mg/Ca data are from Zimmermann et al. (2000), Horita et al. (2002), Lowenstein et al. (2001; 2003; 2005), Timofeeff et al. (2006), Dickson et al. (2002; 2004), Coggon et al. (2010), Rausch et al. (2013), and Gothmann et al. (2015). Mg and Ca concentration data are reconstructed from fluid inclusions in halite (Horita et al. 2002; Lowenstein et al. 2003; Timofeeff et al. 2006; Brennan et al. 2013).
3.2 Introduction

It is well established that there have been dramatic changes in the Mg/Ca ratio of seawater over timescales of tens to hundreds of millions of years (Lowenstein et al. 2001; 2003; 2005; Horita et al., 2002; Timofeeff et al., 2006; Dickson, 2002; 2004; Coggon et al., 2010; Rausch et al., 2013; Gothmann et al., 2015). A complete understanding of the fundamental mechanisms driving these changes has not yet been achieved. However, they are of interest because they are likely related to other major changes in the Earth system – most notably, changes in Earth’s climate between greenhouse and icehouse (Hardie, 1996; Haq et al., 1987; Holland and Zimmerman, 2000; Lowenstein et al. 2001; 2003; 2005; Horita et al., 2002; Timofeeff et al., 2006; Dickson, 2002; 2004; Coggon et al., 2010; Rausch et al., 2013; Gothmann et al., 2015).

The increase in seawater Mg/Ca between ~80 Ma and today results from a decrease in seawater [Ca] and an increase in seawater [Mg] (Fig. 3.1; Zimmermann, 2000; Horita et al., 2002; Lowenstein et al., 2003; Timofeeff et al., 2006; Higgins and Schrag, 2012; Fantle and DePaolo, 2006). These changes point to imbalances in the seawater budgets for both Mg and Ca since the Mesozoic. In the case of Mg, the seawater concentration is determined by the flux of Mg weathered from carbonate and silicate rocks on land relative to the amount of Mg removed via the two main seawater sinks: (1) carbonate rocks (mostly dolomite) and (2) Mg-rich clays (Fig. 3.2; Holland and Zimmerman, 2000; Tipper et al., 2006). This relationship is described by the equation below:

$$d[Mg]_{SW}/dt = F_{RIVER} - F_{DOL} - F_{CLAY} \quad \text{(Eqn. 3.1)}$$
where $F_{\text{RIVER}}$ is the river flux of Mg from carbonate and silicate weathering on land, $F_{\text{DOL}}$ is the amount of Mg removed from seawater by dolomitization, and $F_{\text{CLAY}}$ is the flux of Mg removed from seawater in secondary clay minerals.

![Diagram of seawater Mg isotope mass balance]

**Figure 3.2** Schematic showing the seawater Mg isotope mass balance. $\delta^{26}\text{Mg}$ values are relative to the standard DSM3. The isotope effects associated with the formation of dolomite and with the formation of secondary silicate minerals are distinct, suggesting that changes in the two fluxes relative to one another should impact seawater $\delta^{26}\text{Mg}$. Isotopic values for seawater and rivers are from Galy et al. (2003) and Tipper et al. (2006). Isotope effects for dolomite and clay minerals are from Galy et al. (2002), Pogge von Strandmann et al. (2008), Higgins and Schrag (2010), and Teng et al. (2010).

In line with the equation above, three main hypotheses have been proposed to explain the Cenozoic change in seawater [Mg]. The first hypothesis proposes that a decrease in dolomitization going forward in time, driven by changes in the area of shallow seas, has led to a decrease in the rate of Mg removal from seawater (e.g., Wilkinson and Algeo, 1989; Holland and Zimmerman, 2000; Wallman, 2001). The second hypothesis suggests that the Mg/Ca ratio of the silicate weathering flux has increased since the Mesozoic (Ligi et al. 2013; Kent and Muttoni,
Lastly, it has been proposed that the rate of Mg uptake in clays during hydrothermal alteration has decreased during the Cenozoic, driven either by decreases in the rate of seafloor spreading or by lower ocean bottom water temperatures (e.g., Hardie, 1996; Higgins and Schrag, 2015).

Because the Mg isotopic compositions of carbonate rocks and silicate rocks are distinct, records of seawater $\delta^{26}\text{Mg}$ can be utilized to investigate the importance of dolomitization for changing seawater Mg/Ca, relative to processes related to silicate minerals (Fig. 3.2). Dolomite is $\sim$2‰ depleted in $^{26}\text{Mg}$ relative to seawater ($\delta^{26}\text{Mg}_{\text{seawater}} = -0.82$‰ vs. DSM3), whereas secondary clays are $\sim$0-1‰ enriched in $^{26}\text{Mg}$ (Galy et al., 2002; Tipper et al., 2006; Galy et al., 2003; Foster et al., 2010; Pogge von Strandmann et al., 2008; Higgins and Schrag, 2010; Teng et al., 2010; Geske et al., 2012; Saenger et al., 2014; Li et al., 2015; Geske et al., 2015). Thus, changes in the fraction of Mg removed as dolomite, relative to the fraction removed by uptake in clays, will alter the Mg isotope composition of seawater. This relationship is represented mathematically by Eqn 3.2, which gives the seawater Mg isotope mass balance:

$$d(\delta^{26}\text{Mg}_{\text{SW}})/dt = (\delta^{26}\text{Mg}_{\text{RIV}}) - f_{\text{DOL}} \times (\delta^{26}\text{Mg}_{\text{SW}} - \varepsilon_{\text{DOL}}) - (1 - f_{\text{DOL}}) \times (\delta^{26}\text{Mg}_{\text{SW}} - \varepsilon_{\text{CLAY}}) \quad (\text{Eqn. 3.2}),$$

where $\delta^{26}\text{Mg}_{\text{SW}}$ is the isotopic composition of seawater, $\delta^{26}\text{Mg}_{\text{RIV}}$ is the isotopic composition of the river flux of Mg, $\varepsilon_{\text{DOL}}$ and $\varepsilon_{\text{CLAY}}$ are the isotope effects associated with the formation of dolomite and secondary clays, and $f_{\text{DOL}}$ is the fraction of Mg that leaves the ocean as dolomite.

The clay Mg sink encompasses the formation of secondary silicate minerals both at high temperatures (i.e., hydrothermal alteration at the mid-ocean ridge axis) and at low temperatures (i.e., hydrothermal alteration on the ridge flanks and clay authigenesis). During
high temperature alteration, where Mg is quantitatively stripped from hydrothermal fluids, the isotopic fractionation associated with clay formation is 0 ‰. Constraints from pore fluid measurements of [Mg] and $\delta^{26}$Mg at a site where sediments are dominated by silicate minerals suggests that low-temperature clays may be enriched by up to 1.25 ‰ in $^{26}$Mg (Higgins and Schrag, 2010). For reference, the isotopic composition of dissolved Mg in rivers is -1.09 ‰ (Tipper et al., 2006), which reflects the combination of Mg derived from carbonate weathering and from silicate weathering.

There currently exist two published records of seawater $\delta^{26}$Mg for the Cenozoic that have been used to investigate the mechanisms responsible for past changes in seawater Mg/Ca (Pogge von Strandmann et al., 2014; Higgins and Schrag, 2015), but the records give extremely different histories. Pogge von Strandmann et al. reconstructed seawater $\delta^{26}$Mg from species-specific planktic foraminifera and found that seawater $\delta^{26}$Mg decreased by ~0.8 ‰ between ~20 Ma and today. Based on this record, the authors suggest a large decrease in dolomitization rates toward the present. Higgins and Schrag measured $\delta^{26}$Mg in deep-sea pelagic carbonates from two different ocean basins. Their results suggest that seawater $\delta^{26}$Mg has remained relatively constant over the last ~60 Myr.

The objective of the present study is to discriminate between the two existing records of seawater $\delta^{26}$Mg. We present a supplementary record of seawater $\delta^{26}$Mg from a set of well preserved fossil corals previously described in Gothmann et al. (2015), and discuss why this record likely gives a faithful representation of the Mg isotope composition of Cenozoic seawater.
3.3 Methods

Fossil coral samples measured in this study range in age from Paleocene through Recent, and were collected from a variety of geologic localities. Bulk powders of coral carbonate weighing ~2-5 mg were prepared using a mortar and pestle, and were dissolved in 1N HNO₃. To isolate Mg from the CaCO₃ matrix, samples were processed using either a two-step ion exchange gravity column method modified from Higgins and Schrag (2010), or using a Thermo Dionex DCS5000+ ion chromatography (IC) system (Husson et al., 2015). For the traditional ion-exchange separation method, dissolved coral samples were dried down and loaded onto a column filled with BioRad X12 resin. Mg and alkali metals including Na and K were eluted with 9N HCl, and collected, to separate them from Ca and Sr. Subsequently, the Mg fraction was dried down in preparation for elution through a second column (also filled with BioRad X12 resin). For the second column pass, Mg was eluted using 1N HNO₃ (and collected) in order to achieve separation from Na and K.

For the IC method, dissolved samples were dried down and redissolved in 0.2% HNO₃. The sample was then injected through a CS-16 cation exchange column and eluted with methanesulfonic acid (MSA). Mg fractions were collected using a Dionex AS-AP autosampler and yields were monitored through measurements of sample conductivity. Purified samples corresponding to 300-500 ng Mg were dried down in preparation for mass spectrometry.

Magnesium isotope analyses were performed using a Thermo Scientific Neptune Plus Multicollector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at Princeton University as described in Husson et al. (2015) and Blättler et al. (2015). Briefly, in preparation for isotopic analysis, purified Mg samples were dried down and redissolved in 2% HNO₃.
Samples were then diluted to a concentration of 150 ppb, either according to sample conductivity results from the IC, or by direct concentration checks on the MC-ICP-MS. Intensities of $^{24}\text{Mg}$, $^{25}\text{Mg}$, and $^{26}\text{Mg}$ were measured on the faraday cups L3, C, and H3, respectively. L3 and H3 are both three cups away from the center cup on either side. Measurements were conducted using a standard-sample-standard bracketing technique with Dead Sea Metal-3 (DSM3) - a pure Mg metal from the Dead Sea (Young and Galy, 2004). Mg intensities of samples and standards were monitored to ensure that concentrations were within 20% of each other. Triple-isotope plots of $\delta^{25/24}\text{Mg}$ vs. $\delta^{26/24}\text{Mg}$ were also examined for each run to check for mass-dependent behavior (see Supplementary).

In addition to samples, the Mg isotope standard Cambridge-1, an in-house modern coral standard, and an in-house dolomite standard were taken through the entire chemical procedure and measured to assess accuracy and precision. We measured a value of $-2.63 \pm 0.13 \, ^\circ\text{oo}$ (2σ SD) for Cambridge-1, consistent with the previously published values of $-2.58 \, ^\circ\text{oo}$ and $-2.62 \, ^\circ\text{oo}$ (Galy et al., 2003; Higgins and Schrag, 2010). The $\delta^{26}\text{Mg}$ of the in-house coral standard was $-1.87 \pm 0.05 \, ^\circ\text{oo}$ (2σ SD), in agreement with values measured for other modern corals (Saenger et al., 2013; Wombacher et al., 2011). The long-term external reproducibility of $\delta^{26}\text{Mg}$ for our in-house dolomite standard was $0.11 \, ^\circ\text{oo}$ (2σ SD). All results are reported relative to DSM3.

Aliquots of dissolved powders analyzed for Mg isotopes were also measured for Mg/Ca ratios on ThermoFinnegan Element-2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The Mg/Ca ratios of samples were determined using a set of matrix-matched in-house standards with Mg/Ca ratios spanning the sample range (Rosenthal et al. 1999). A carbonatite standard, OKA-II, was used to assess the accuracy and precision of our measurement. We
CHAPTER 3. A CENOZOIC RECORD OF Mg ISOTOPES FROM FOSSIL CORALS

measured a value of 4.75 mmol/mol for OKA-II ±6% 2σ SD – within uncertainty of the value reported by Gabitov et al. (2013) as measured by Isotope Dilution ICP-MS.

3.4 Results

Results of fossil coral Mg isotope analyses are presented in Table 3.1 and Fig. 3.3. Data were converted to inferred seawater values by assuming a constant fractionation factor between coral carbonate and seawater equal to -0.9 ‰, in line with fractionations observed in previous studies (Saenger et al., 2013; Wombacher et al., 2011). Fossil corals of similar geologic age span a range of ±0.2 ‰, which is twice as large as the long-term reproducibility of our method. The scatter may be due to the presence of small vital effects for δ²⁶Mg and/or the influence of a small dependence of coral δ²⁶Mg on temperature (+0.03 ‰ °C⁻¹; Saenger et al., 2013), combined with variations in growth temperature for our samples (20 - 30 °C; Gothmann et al., 2015).

Our record of seawater δ²⁶Mg inferred from fossil corals shows minor variability over the Cenozoic – about 0.3 ‰ (Fig. 3.3). These results agree well with the existing seawater δ²⁶Mg record inferred from ODP Site 807 (Ontong Java Plateau, Pacific Ocean) and Site 1265 (Walvis Ridge, Southern Atlantic Ocean) bulk forams and limestones (Higgins and Schrag, 2015). However, they are offset from the record inferred from ODP Site 1262, 1263, and 1264 (Walvis Ridge, Southern Atlantic Ocean) species-specific planktic forams (Pogge von Strandmann et al., 2014). In the following sections, we discuss evidence supporting the use of fossil corals as archives of seawater δ²⁶Mg. We also discuss the implications of our record for the mechanisms controlling seawater Mg/Ca.

102
### Table 3.1 Results of Mg isotope analyses for fossil corals.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Age (Myr)</th>
<th>δ²⁶Mg (^a)</th>
<th>2σ SD (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.0</td>
<td>-1.89</td>
<td>-</td>
</tr>
<tr>
<td>Pl3</td>
<td>0.1</td>
<td>-1.84</td>
<td>0.20</td>
</tr>
<tr>
<td>Pl5</td>
<td>0.1</td>
<td>-2.16</td>
<td>-</td>
</tr>
<tr>
<td>Pl2</td>
<td>1.4</td>
<td>-1.77</td>
<td>-</td>
</tr>
<tr>
<td>Pl7</td>
<td>2.0</td>
<td>-1.92</td>
<td>-</td>
</tr>
<tr>
<td>Pl8</td>
<td>2.2</td>
<td>-1.97</td>
<td>-</td>
</tr>
<tr>
<td>Pli3</td>
<td>2.3</td>
<td>-1.81</td>
<td>-</td>
</tr>
<tr>
<td>Pli2</td>
<td>3.1</td>
<td>-1.98</td>
<td>0.08</td>
</tr>
<tr>
<td>Pli1</td>
<td>3.5</td>
<td>-1.69</td>
<td>-</td>
</tr>
<tr>
<td>Mi6</td>
<td>5.4</td>
<td>-1.57</td>
<td>-</td>
</tr>
<tr>
<td>Mi11</td>
<td>9.3</td>
<td>-1.82</td>
<td>-</td>
</tr>
<tr>
<td>Mi7</td>
<td>14</td>
<td>-1.99</td>
<td>0.32</td>
</tr>
<tr>
<td>Mi1</td>
<td>18</td>
<td>-1.90</td>
<td>-</td>
</tr>
<tr>
<td>Mi3</td>
<td>18</td>
<td>-1.87</td>
<td>0.02</td>
</tr>
<tr>
<td>O11</td>
<td>29</td>
<td>-2.08</td>
<td>-</td>
</tr>
<tr>
<td>O14</td>
<td>30</td>
<td>-1.98</td>
<td>-</td>
</tr>
<tr>
<td>O15</td>
<td>30</td>
<td>-2.09</td>
<td>-</td>
</tr>
<tr>
<td>O16</td>
<td>30</td>
<td>-1.86</td>
<td>-</td>
</tr>
<tr>
<td>O13</td>
<td>32</td>
<td>-1.92</td>
<td>0.03</td>
</tr>
<tr>
<td>E6</td>
<td>35</td>
<td>-1.70</td>
<td>0.06</td>
</tr>
<tr>
<td>E8</td>
<td>36</td>
<td>-1.85</td>
<td>-</td>
</tr>
<tr>
<td>E2</td>
<td>37</td>
<td>-1.78</td>
<td>-</td>
</tr>
<tr>
<td>O12</td>
<td>38</td>
<td>-1.78</td>
<td>0.10</td>
</tr>
<tr>
<td>E1</td>
<td>38</td>
<td>-1.71</td>
<td>-</td>
</tr>
<tr>
<td>E4</td>
<td>45</td>
<td>-1.56</td>
<td>-</td>
</tr>
<tr>
<td>E3</td>
<td>50</td>
<td>-1.80</td>
<td>0.06</td>
</tr>
<tr>
<td>Pa2</td>
<td>56</td>
<td>-1.60</td>
<td>-</td>
</tr>
<tr>
<td>Pa1</td>
<td>60</td>
<td>-1.70</td>
<td>-</td>
</tr>
<tr>
<td>Pa3</td>
<td>62</td>
<td>-1.52</td>
<td>-</td>
</tr>
<tr>
<td>J1</td>
<td>160</td>
<td>-1.84</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Mg isotope composition relative to the standard DSM3 in ‰ notation.

\(^b\) Standard deviation of replicate analyses from different analytical sessions. Samples for which no standard errors are reported were only measured once.
Figure 3.3 Cenozoic records of the Mg isotope composition of seawater. Fossil coral data from this study are shown as red circles. All coral data are converted to seawater values by assuming a constant fractionation of -0.9 ‰ (based on modern coral data from this study, Saenger et al., 2013 and Wombacher et al., 2011). Records from Higgins and Schrag (2015) and Pogge von Strandmann et al. (2014) are also shown (in grey asterisks and black diamonds, respectively). As for the case of fossil corals, the bulk foraminifera, limestone, and species-specific foraminifera Mg isotope data are converted to seawater values using modern fractionation factors. The error-bar on the modern planktic foraminifera average corresponds to the uncertainty in the fractionation applied for the Pogge von Strandmann et al. (2014) record, based on a core-top calibration with Orbulina universa. Errors for fossil coral data are ±0.11 ‰ (2σ S.D.).
3.5 Discussion

3.5.1 Preservation of fossil coral $\delta^{26}\text{Mg}$

The fossil coral samples studied here for Mg isotopes were previously screened for diagenetic alteration by Gothmann et al. (2015), using a range of techniques: optical microscopy, scanning electron microscopy, cathodoluminescence microscopy, micro-raman spectroscopy, X-ray diffraction, and analyses of trace element and isotope systems sensitive to diagenesis. Results indicate that both the mineralogy and geochemistry of fossil coral samples measured for Mg isotopes in this study are excellently preserved, and that records of seawater $\delta^{26}\text{Mg}$ are likely free of biases due to diagenesis.

Gothmann et al. (2015) also measured Mg/Ca ratios in the same fossil coral samples measured for Mg isotopes, using Secondary Ion Mass Spectrometry (SIMS) (Fig. 3.1). The observation that fossil coral Mg/Ca as measured by SIMS faithfully tracks the Mg/Ca ratio of Cenozoic seawater lends further support that the Mg contained in the fossil corals skeletons is primary. Results of Mg isotopes from this study cannot be directly compared to samples measured for Mg/Ca by SIMS because the Mg isotope measurements are performed on bulk powders whereas SIMS is a microanalysis technique. As a result, here we also present measurements of Mg/Ca ratios in the same bulk powders analyzed for Mg isotopes and compare them with SIMS Mg/Ca to check for consistency (Fig. 3.4).

We find that Mg/Ca ratios measured on bulk powders by ICP-MS are generally compatible with ratios measured by SIMS. However, there are many powder samples that disagree with the measured SIMS Mg/Ca ratio beyond our analytical uncertainty. The lack of a relationship between the magnitude of Mg/Ca disagreement and $\delta^{26}\text{Mg}$ suggests that offsets in
Mg/Ca between bulk and SIMS are not related to a diagenetic contribution in bulk samples. Instead, these offsets could be due to heterogeneity in Mg/Ca within coral samples.

**Figure 3.4** Comparison of Mg/Ca measurements made on bulk powders by ICP-MS and by Secondary Ion Mass Spectrometry (SIMS). (a) Bulk powder measurements vs. average Mg/Ca ratios measured by SIMS. SIMS data are from Gothmann et al. (2015). Error bars for bulk powder ICP-MS data represent the external reproducibility based on repeat measurements of OKA-II - a carbonatite standard (~6% 2 S.D.). Error bars for SIMS data represent 2 S.E. of multiple SIMS spots measured within a single sample. (b) The percent difference between Mg/Ca measurements made on bulk powders and by SIMS vs. the measured Mg isotope composition for powder samples. There is no relationship between the offset in Mg/Ca between the two measurement methods and δ^{26}Mg.

Diagenetic testing performed by Gothmann et al. (2015), as well as Mg/Ca results on bulk powders, suggest that fossil coral samples are well preserved. Nevertheless, it is also not clear whether the differences between the fossil coral seawater δ^{26}Mg record and the Pogge von Strandmann et al. (2014) record are related to differential preservation. Pogge von Strandmann et al. (2014) and Higgins and Schrag (2015) both screen their archives for alteration. Pogge von
Strandmann et al. avoid picking foraminifera samples with diagenetic overgrowths. They also use foraminifera Sr/Ca and Mg/Ca ratios as a constraint on diagenesis, with Sr/Ca ratios <1.2 mmol/mol and Mg/Ca ratios >5.5 mmol/mol suggestive of alteration. These tests do not reveal any signs of diagenetic alteration in the planktic foraminifera measured for Mg isotopes. We note, however, that the small size of planktic foraminiferal tests makes it difficult to conduct many of mineralogical and geochemical tests that have been used to screen fossil corals.

Higgins and Schrag (2015) combine measurements of pore-fluid [Mg] and Mg isotopes, together with a model of sediment diagenesis, to constrain recrystallization in their samples (Higgins and Schrag, 2012; Fantle and DePaolo, 2006). They find that sedimentary recrystallization occurs within the first 5 to 10 My of burial. Despite significant exchange between pore fluid and sediment Mg during early diagenesis, their model suggests that alteration should impart little change in sediment $\delta^{26}$Mg. This is largely because of the similarity of the equilibrium calcite fractionation to the average fractionation for foraminiferal calcite, which makes up a large component of the sediments studied (Mavromatis et al., 2013; Higgins and Schrag, 2012; Pogge von Strandmann et al. 2008). As also argued by the authors, another piece of evidence suggestive of the absence of local diagenetic overprinting is that the bulk foraminifera and limestone data come from two different sediment cores (in different ocean basins – Pacific and Atlantic), and follow the same trend in $\delta^{26}$Mg.

### 3.5.2 Absence of significant coral Mg isotope vital effects

The absence of significant vital effects in modern coral also suggests that well preserved fossil corals are likely to be good archives of seawater Mg isotopes. ‘Vital effects’ are defined as departures in the geochemical composition of biomineral carbonates from the
composition expected based on inorganic distribution coefficients. Corals exhibit large vital effects for many elemental and isotopic parameters, such as δ¹⁸O, δ¹³C and Mg/Ca (Tambutté et al., 2011). The presence of these vital effects can be problematic because they have the potential to bias or obscure environmental signatures (Weiner and Dove, 2003; Tambutté et al. 2011). However, recent work suggests that coral Mg isotope vital effects are small. As summarized in Saenger and Wang (2014), corals exhibit a relatively constant fractionation factor of ~0.9 ‰ regardless of species, which is within uncertainty of the inorganic aragonite fractionation (Wang et al. 2013; Saenger and Wang, 2014; Wombacher et al. 2011). There is also only ~0.4 ‰ variability in the compositions of all corals measured to date (n = 51), which is comparable to the range of ~0.3 ‰ in δ²⁶Mg measured for inorganic aragonites precipitated from free-drift growth experiments (n = 8; Wang et al., 2013). Moreover, both coral and inorganic aragonites show a minor dependence on temperature (~+0.03 ‰ °C⁻¹; Wang et al., 2013; Saenger and Wang, 2014; Wombacher et al., 2011).

While Mg isotopes do not seem to exhibit vital effect behavior, the factor of ~2 variability in Mg/Ca ratios measured on bulk powders of modern coral suggests considerable biological control over Mg incorporation (Mitsuguchi et al., 2003; Cohen et al., 2006; Inoue et al., 2007; Gagnon et al., 2007). The presence of vital effects for coral Mg/Ca and the absence of vital effects for coral δ²⁶Mg could be related to a reservoir effect of biomineralization. For example, Rayleigh distillation of the solution from which corals calcify has been suggested to play an important role in coral trace element uptake (Gagnon et al., 2007; Gaetani et al., 2011). Coral calcification from an isolated ‘calcifying fluid’ would lead to an increase in the Mg/Ca ratio of the fluid as calcification proceeds because Mg is heavily discriminated against relative to Ca (K_D⁰⁻¹ Mg/Ca ≈ 10⁻⁴; Gagnon et al., 2007). Assuming a constant partition coefficient for Mg/Ca,
such an increase in the Mg/Ca of the calcifying fluid would yield concomitant changes in the Mg/Ca of the coral aragonite precipitated from that fluid. While the Mg/Ca of the fluid increases, however, the Mg concentration of the fluid will not change greatly. As a result, there should be negligible distillation of the calcifying fluid Mg isotope composition and a lack of variability in coral $\delta^{26}\text{Mg}$. A similar effect on coral Mg/Ca and $\delta^{26}\text{Mg}$ would arise if the calcifying fluid existed instead as a steady state system that was continually open to external seawater.

Unlike scleractinian corals, measurements of biogenic calcites, including foraminifera and coccolithophores, suggest the presence of significant Mg isotope vital effects both between and within species (Pogge von Strandmann et al., 2008; Wombacher et al., 2011; Muller et al., 2011; Saenger and Wang, 2014; Pogge von Strandmann et al., 2014). The range in modern planktic foraminifera is >1.5 ‰ (Pogge von Strandmann et al., 2008). This range is similar to the range of values measured for inorganic calcite precipitation experiments, but is much greater than the range for corals (Saenger and Wang, 2014). Planktic foraminifera exhibit Mg isotope fractionations from seawater that are similar on average (~ -4.0 ‰) to the equilibrium fractionation estimated for calcite (-3.5 ‰; Mavromatis et al. 2014). However, average Mg isotope compositions of individual planktic foraminifera species can be offset from one another, and also can exhibit, on average, fractionations up to -1 ‰ greater than the equilibrium fractionation (Immenhauser et al., 2010; Li et al., 2012; Mavromatis et al., 2013; Saulnier et al., 2012; Pogge von Strandmann et al., 2014).

Pogge von Strandmann et al. (2014) attempt to account for the presence of Mg isotope vital effects in planktic foraminifera, and their potential to bias records of seawater Mg isotopes. First, they characterized the core-top variability in *Orbulina universa*, which is the species they use to reconstruct their seawater $\delta^{26}\text{Mg}$ record back to ~15 Ma. They find variability
of only ±0.18 ‰ for the core-top samples, which is small compared with the range of all modern planktic foraminifera measured to date (Saenger and Wang, 2014). However, the offset of this species from seawater is large (~4.8 ‰) compared with the estimated equilibrium calcite fractionation (Mavromatis et al., 2013). Pogge von Strandmann et al. use the fractionation for this species to convert their data to seawater values, assuming that the vital effect offset for this species stays constant over time. As stated in Section 3.4, we make the same assumption for fossil corals. We conclude that although forams generally exhibit larger Mg isotope vital effects than corals, it is unclear whether a vital effect problem can explain the difference between our fossil coral record and the Pogge von Strandmann et al. (2014) record.

### 3.5.3 Mg isotope records and their implications for controls on seawater [Mg]

Although the reason for the deviation of the Pogge von Strandmann et al. record, is uncertain, the good agreement between our record and the record of Higgins and Schrag (2015) also suggests that these two datasets likely provide faithful histories of seawater $\delta^{26}$Mg. The contrasting mineralogies of the aragonitic corals and deep-sea sediments, as well as their distinct preservational environments, preclude the possibility of consistent biases between the two records due to diagenesis, mineralogy and vital effects. Below, we discuss the implications of these records for the controls on seawater Mg/Ca since the Mesozoic.

As discussed in Higgins and Schrag (2015) and in Section 3.2, seawater $\delta^{26}$Mg is sensitive to (1) changes in the fraction of Mg removed from seawater by dolomitization versus uptake in clays, and (2) changes in the fraction of Mg delivered to seawater from carbonate versus silicate weathering. This behavior is due to the relatively large fractionation associated with dolomite formation (and the light Mg isotopic composition of carbonates) as compared with
the small fractionation associated with clay formation (Fig. 3.2). The fact that the fossil coral record and the record of Higgins and Schrag (2015) show little change in seawater $\delta^{26}$Mg, suggests that the amount of Mg removed from seawater as dolomite, relative to the amount removed by clays, has not changed significantly since the Late Mesozoic. Similarly, the amount of Mg delivered by rivers from carbonates, relative to the amount delivered by silicates, is unlikely to have changed very much.

This result is explored more quantitatively in Higgins and Schrag (2015) using a numerical model of the global carbon cycle, coupled with the global cycles of magnesium and calcium. The authors calculate the change in seawater $\delta^{26}$Mg expected if (1) all of the increase in seawater [Mg] between the Late Mesozoic and present were attributed to a decrease in dolomitization, and (2) if all of the increase in seawater [Mg] between the Late Mesozoic and present were attributed to clays. They show that the first scenario (changes in dolomite) would result in a large decrease in the fraction of Mg removed from seawater by dolomite relative to the amount removed by clays between, resulting in a concomitant $\sim$0.8‰ decrease in the $\delta^{26}$Mg of seawater. In contrast, the second scenario (changes in Mg uptake in clays) would result in only small changes in the fraction of Mg removed as dolomite and small changes in seawater $\delta^{26}$Mg.

We replicate the result of Higgins and Schrag (see Supplementary, Figure 3.6; Table 3.2) using a simple 1-box model incorporating only Mg chemistry and following from Eqns. 3.1, 3.2, and Fig. 3.2. Overall, our records, together with the calculations described above, suggest that changes in dolomitization alone cannot explain the seawater Mg/Ca record; changes in Mg cycling in silicate minerals must have been important since the Mesozoic. Complementary records of additional seawater properties, including seawater $\delta^7$Li, [Li], and $\delta^{11}$B (among others) may further elucidate the mechanistic controls on seawater [Mg] and $\delta^{26}$Mg.
3.6 Conclusions

Well preserved aragonitic fossil corals are good candidates for reconstructing past seawater $\delta^{26}\text{Mg}$. We measured $\delta^{26}\text{Mg}$ in fossil coral samples previously described by Gothmann et al. (2015) to distinguish between two existing records of Cenozoic seawater Mg isotopes that give conflicting results. Our coral record is inconsistent with the record of Pogge von Strandmann et al. (2014), but agrees with the published record of Higgins and Schrag (2015). In the context of model results from Higgins and Schrag (2015), the fossil coral results suggest that the fraction of Mg removed from seawater as dolomite has not changed significantly over the Cenozoic. As a result, the increase in seawater [Mg] between the Early Cenozoic and today must have been driven, at least in part, by changes in Mg cycling in silicate rocks.

3.7 Author contributions and previous presentations of this work

Michael Bender, John Higgins, and Anne Gothmann planned the project. Anne Gothmann conducted analytical work, interpreted data, and drafted the chapter with input from Michael Bender, John Higgins, Jess Adkins, and Jarek Stolarski. Jarek contributed many of the samples that were analyzed as part of this work.

This work was presented as:

3.8 Supplementary

Figure 3.5 Triple-isotope plot showing results of Mg isotope measurements. The slope of the $\delta^{26/24}\text{Mg} (\%o)$ vs. $\delta^{25/24}\text{Mg}$ relationship is 0.522, consistent with the value reported in previous studies (Young and Galy, 2004; Husson et al. 2015).
Figure 3.6 Results of model calculations showing the magnitude of change in (a, c) seawater [Mg] and (b, d) seawater $\delta^{26}\text{Mg}$ that would result from driving secular variations in seawater [Mg] by invoking either (1) changes in Mg uptake in clay minerals (panels a and b with data shown in red), or (2) changes in dolomitization rates (panels c and d with data shown in blue). Seawater magnesium concentration data are taken from reconstructions from fluid inclusions trapped in halite and plotted in (a) and (b) along with model curves (Zimmermann, 2000; Horita et al., 2002; Timofeeff et al., 2006; Brennan et al., 2013). Fossil coral Mg isotope data are shown in (b) and (d). The model (constructed following Eqns 3.1, 3.2, and Fig. 3.2) is initially run to steady state. Then, the clay Mg sink, or the dolomite Mg sink is varied (while holding the other fluxes
constant) to drive changes in seawater [Mg] consistent with fluid inclusion data. In addition, the $\delta^{26}$Mg of Modern seawater in the model is required to match measured values of Modern seawater $\delta^{26}$Mg (Galy et al., 2003), which is presented as a green line in (b) and (d). The plots convey that seawater $\delta^{26}$Mg is insensitive to changes in Mg uptake in clays, but responds to changes in dolomitization rates.

Table 3.2 Parameters and initial conditions chosen for the 1-box model of the Mg cycle used to generate Fig. 3.6.

<table>
<thead>
<tr>
<th>Model Parameters</th>
<th>Initial Conditions (Paleogene Seawater): Case 1 - constant dolomite flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater [Mg]</td>
<td>30 mM$^a$</td>
</tr>
<tr>
<td>River Mg Flux</td>
<td>(+) 4.5e12 mol/yr$^b$</td>
</tr>
<tr>
<td>Clay Mg Flux</td>
<td>(−) 3.7e12 mol/yr$^c$</td>
</tr>
<tr>
<td>Dolomite Mg Flux</td>
<td>(−) 0.8e12 mol/yr$^c$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Initial Conditions (Paleogene Seawater): Case 2 - constant clay flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater [Mg]</td>
</tr>
<tr>
<td>River Mg Flux</td>
</tr>
<tr>
<td>Clay Mg Flux</td>
</tr>
<tr>
<td>Dolomite Mg Flux</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Isotope Compositions/Fractionations (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Rivers</td>
<td>-1.09$^b$</td>
</tr>
<tr>
<td>Clay ($\varepsilon$)</td>
<td>(−) 0.5$^*$$^d$</td>
</tr>
<tr>
<td>Dolomite ($\varepsilon$)</td>
<td>(+) 2.0$^*$$^d$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Additional Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern Seawater $\delta^{26}$Mg</td>
</tr>
</tbody>
</table>

$^*\varepsilon$ is defined as $\delta_{sw} - \delta_{sink}$, such that a negative $\varepsilon$ results in a product that is heavier than seawater

$^a$ Chosen based on Zimmermann (2000), Horita et al. (2002, Lowenstein et al. (2003), Timofeff et al. (2006)

$^b$ Chosen based on Wilkinson and Algeo (1989), Tipper et al. (2006), and Higgins and Schrag (2015)

$^c$ Chosen to fit the condition that Modern seawater $\delta^{26}$Mg $\approx$ -0.82 ‰ vs. DSM3

$^d$ From Higgins and Schrag (2010), Higgins and Schrag (2015), and Geske et al. (2015)

$^e$ From Galy et al. (2003)
CHAPTER 3. A CENOZOIC RECORD OF Mg ISOTOPES FROM FOSSIL CORALS

References


CHAPTER 3. A CENOZOIC RECORD OF Mg ISOTOPES FROM FOSSIL CORALS


CHAPTER 3. A CENOZOIC RECORD OF Mg ISOTOPES FROM FOSSIL CORALS

Diagenesis and low grade metamorphism on isotope ($\delta^{26}$Mg, $\delta^{13}$C, $\delta^{18}$O and $^{87}$Sr/$^{86}$Sr) and elemental (Ca, Mg, Mn, Fe and Sr) signatures of Triassic sabkha dolomites. *Chemical Geology* 332-333, 45-64.


Chapter 3. A Cenozoic Record of Mg Isotopes from Fossil Corals

Cosmochimica Acta 66, 3733-3756.


Kent, D.V., Muttoni, G., 2013. Modulation of Late Cretaceous and Cenozoic climate by variable drawdown of atmospheric pCO$_2$ from weathering of basaltic provinces on continents drifting through the equatorial humid belt. Climate of the Past 9, 525-546.


CHAPTER 3. A CENOZOIC RECORD OF Mg ISOTOPES FROM FOSSIL CORALS


Müller, M.N., Kisakürek, B., Buhl, D., Gutperlet, R., Kolevica, A., Riebesell, U., Stoll, H., Eisenheuer, A., 2011. Response of the coccolithophores *Emiliania huxleyi* and *Coccolithus braarudii* to changing seawater Mg$^{2+}$ and Ca$^{2+}$ concentrations: Mg/Ca, Sr/Ca ratios and $\delta^{44/40}$Ca, $\delta^{26/24}$Mg of coccolith calcite. *Geochimica et Cosmochimica Acta* 75, 2088-2102.


120
Chapter 3. A Cenozoic Record of Mg Isotopes from Fossil Corals


Chapter 4.

Variations in seawater uranium concentrations during the Cenozoic reconstructed from well preserved aragonitic fossil corals

4.1 Abstract

We measured U/Ca ratios, $^4$He concentrations, $^{234}$U/$^{238}$U, and $^{238}/^{235}$U in a subset of well preserved scleractinian fossil corals previously described by Gothmann et al. (2015). Comparisons of calculated fossil coral He/U ages with the expected stratigraphic age suggest the good preservation of fossil coral uranium geochemistry. These studies also demonstrate the ability of well preserved coral aragonite to retain most of its radiogenic He over million year timescales. Measurements of $^{234}$U/$^{238}$U and $^{238}/^{235}$U further help to evaluate the preservation of uranium across our sample set.

From measurements of fossil coral U/Ca, we infer a history of seawater [U] over the Cenozoic. Reconstructed seawater [U] shows a factor of ~2 increase between the Early Cenozoic and today. Possible explanations for the observed increase include (1) a decrease in uranium removal due to an increase in seawater [CO$_3^{2-}$], and a resulting increase in UO$_2$-CO$_3$ complexation as originally suggested by Broecker (1971), (2) a decrease in the rate of low-temperature hydrothermal alteration over the Cenozoic, or (3) a small decrease in uranium removal in reducing sediments.
4.2 Introduction

The geochemistry of uranium in seawater has long been of interest due to the use of uranium and its daughter isotopes as dating tools (Henderson and Anderson, 2003), and because of uranium’s redox sensitive behavior (Anderson, 1987; Barnes and Cochran, 1990; Morford and Emerson, 1999; Weyer et al., 2008). Over the last decade in particular, with the development of high-precision mass spectrometry, there has been a considerable effort to access the past seawater $\delta^{238\text{U}}$ as an indicator of paleo-redox conditions (Weyer et al., 2008; Montoya-Pino et al., 2010; Brennecka et al., 2011; Kendall et al., 2013; Goto et al., 2014). In order to apply this proxy quantitatively, a thorough understanding of the controls on seawater U is essential. However, key aspects of the controls on uranium removal processes from seawater remain unclear.

Uranium exists in seawater mainly as binary UO$_2$-CO$_3$ and ternary Ca-UO$_2$-CO$_3$ complexes (Langmuir et al., 1978; Djogic et al., 1986; Endrizzi and Rao, 2014). The tendency for uranium to complex strongly with carbonate and with cations such as Ca dramatically increases its solubility (Langmuir et al., 1978; Bernhard et al., 2001; Dong and Brooks, 2006), leading to the conservative nature of uranium in seawater and its long residence time (3.5-5.6×10$^5$ yrs) (Chen et al., 1986). Uranium is also redox sensitive. U(VI) is present in well-oxygenated seawater, with reduction to U(IV) in reducing sediments (Langmuir, 1978; Anderson, 1987; Cochran et al. 1986; Anderson et al., 1989).
Chapter 4. Variations in seawater uranium concentrations during the Cenozoic reconstructed from well preserved aragonitic fossil corals

Table 4.1 Summary of sources and sinks of seawater U.

<table>
<thead>
<tr>
<th>Flux (Mmol/yr)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sources of uranium to seawater:</strong></td>
<td></td>
</tr>
<tr>
<td>riverine</td>
<td>42.0 ± 14.5</td>
</tr>
<tr>
<td></td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>45 ± 15</td>
</tr>
<tr>
<td>submarine groundwater</td>
<td>9.3 ± 8.7</td>
</tr>
<tr>
<td>aeolian</td>
<td>1.8 ± 1.1</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>53.1 ± 16.9</strong></td>
</tr>
<tr>
<td><strong>Sinks for uranium from seawater:</strong></td>
<td></td>
</tr>
<tr>
<td>suboxic sediments</td>
<td>15.3 ± 10.6</td>
</tr>
<tr>
<td></td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>12</td>
</tr>
<tr>
<td>coastal zone sediments</td>
<td>11.2 ± 5.6</td>
</tr>
<tr>
<td>basalt alteration</td>
<td>5.7 ± 3.3</td>
</tr>
<tr>
<td></td>
<td>16 ± 4</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>11.2 ± 17.8</td>
</tr>
<tr>
<td></td>
<td>12.5 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>19 ± 7</td>
</tr>
<tr>
<td>anoxic sediments</td>
<td>11.6 ± 6.0</td>
</tr>
<tr>
<td>carbonate sediments</td>
<td>13.3 ± 5.6</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
</tr>
<tr>
<td>metalliferous sediment</td>
<td>1.0 ± 0.8</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>58.1 ± 14.9</strong></td>
</tr>
</tbody>
</table>

1 assuming high-T hydrothermal water fluxes calculated from the seawater $^{87}$Sr/$^{86}$Sr budget and quantitative consumption of U during high-T basalt alteration
2 assuming a river flux of 32 Mmol/yr
3 compiled from estimates made by Chen et al. (1986) and Hart and Staudigel (1982)
4 using the shallow water carbonate budget of Milliman (1993)
5 also used for Barnes and Cochran (1990) and Morford and Emerson (1999) U budgets

Rivers are the principal source of uranium to seawater, and the dissolved uranium in rivers themselves is primarily derived from carbonate rocks and black shales (Palmer and Edmond, 1993). Additional sources of U include wind-blown dust and groundwater discharge, but these fluxes are poorly constrained (Dunk et al. 2002; Henderson and Anderson, 2003). The main seawater uranium sinks are uptake into suboxic sediments and low-temperature
hydrothermal alteration of basalt (Dunk et al., 2002; Mills and Dunk, 2010; Kinkhammer and Palmer, 1991, Henderson and Anderson, 2003; Barnes and Cochran, 1990). Additional sinks include uptake in coastal wetland sediments, uptake in anoxic sediments, high-temperature hydrothermal alteration, and co-precipitation with carbonate minerals and ferromanganese crusts (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Dunk et al., 2002; Wheat et al., 2003; Mills and Dunk, 2010). Published estimates for the magnitudes of each of these source and sink terms exhibit a wide range (Table 4.1), which further emphasizes existing ambiguities in the seawater uranium mass balance.

Here, we present data on U/Ca, $^{234}$U/$^{238}$U, $^{238}$U/$^{235}$U, $^4$He, and calculated $^4$He/U ages from a set of well preserved aragonitic fossil corals. The fossil coral sample set was previously screened for diagenesis using x-ray diffractometry, scanning electron microscopy, petrographic microscopy, cathodoluminescence microscopy, micro-raman spectroscopy, $^{87}$Sr/$^{86}$Sr measurements, carbonate clumped isotope thermometry, and measurements of trace elements sensitive to diagenesis (Gothmann et al., 2015). He/U dating calculations from this study, as well as measurements of U isotopes, allow further evaluation of the integrity of fossil coral specimens. Results of U/Ca measurements have implications for our understanding of the controls on seawater [U] through time.

4.3 Methods

4.3.1 U/Ca measurements

Small pieces of coral skeleton were cut using a dremel tool and crushed into ~1 mm chunks using a mortar and pestle. Aliquots of approximately 10 mg of coral were dissolved in 1N nitric acid (HNO$_3$) for U/Ca analyses. Dissolved samples were centrifuged, inspected for
insoluble residues, and diluted to a concentration of 60 ppm Ca in preparation for mass spectrometry. U/Ca measurements were conducted using a Thermo Finnigan Element-2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at Princeton University. Ratios were calibrated using a set of matrix-matched in-house standards whose U/Ca ratios spanned our sample range as in Rosenthal et al. (1999). The external reproducibility of an in-house deep-sea coral standard was ~6% 2σ S.D.

### 4.3.2 \(^4\)He measurements

Additional ~10 mg aliquots were weighed and wrapped in foil in preparation for He extraction. Samples were loaded into a vacuum furnace and heated to 1200°C to degas He. The evolved gas was then purified cryogenically and inlet to a MAP 215-50 noble gas mass spectrometer at the California Institute of Technology to measure \(^4\)He concentrations. Sensitivity was calibrated through frequent measurements of air standards run at \(^4\)He concentrations spanning the expected range of our samples. The reproducibility of standards run throughout the analysis session was <1% 2σ S.D. for \(^4\)He. Hot blanks and sample re-extracts were run routinely throughout the analysis session. He measured in re-extracted samples derives from the blank rather than incomplete extraction in the first heating. The \(^4\)He blank in re-extracts was 0.1-0.2 ncc, which corresponds to <1% of sample \(^4\)He for most corals. The only exception is for samples with ages <2 My, for which the re-extracted \(^4\)He signal contributed up to 10% of the total \(^4\)He due to the low amount of accumulated \(^4\)He.


4.3.3 Uranium isotope analyses

Residual ~1 mm chunks of coral sample were powdered using a mortar and pestle in preparation for uranium isotope analyses. Using estimates of coral [U] from U/Ca measurements, coral powders corresponding to 50-100 ng U were weighed and dissolved in 10 mL of 0.5 N HNO₃. These samples were centrifuged and the supernatant was poured off to avoid small amounts of organics and/or insoluble silicate residue. Samples were then spiked with 25-50 µL of an in-house 233U-236U double-spike. After drying down the spiked samples, they were re-dissolved in 3N HNO₃ in preparation for uranium purification. Uranium was separated by eluting through a column filled with Eichrom UTEVA resin. First, sample matrix was eluted using 3N HNO₃. Thorium was eluted in two steps using 10N HCl and 5N HCl, and U was eluted and collected with 0.05 N HCl. Purified U samples were dried down once more, and diluted to ~50 ppb U using 5% HNO₃ for mass spectrometry.

Measurements were conducted at Yale University using a Thermo Scientific Neptune Plus multicollector inductively coupled mass spectrometer (MC-ICP-MS) with an ESI Apex-IR sample introduction system. Sensitivity for ²³⁸U was ~35 V for a 50 ppb solution, and baseline measurements and gain calibrations were performed prior to every analytical session. Beam intensities for ²³²Th (L3), ²³³U (L2), ²³⁴U (L1), ²³⁵U (C), ²³⁶U (H1), and ²³⁸U (H3) were measured in low resolution. Data were acquitted in 5 blocks of 10 cycles each, with 3s integration per cycle. Instrumental mass bias was accounted for using the ²³³U-²³⁶U double-spike and δ²³⁸/²³⁵U compositions were reported relative to the average composition of the standard CRM112a, measured during the same analytical session. One CRM112a standard was measured for every 3 samples. In addition to samples, we measured an in-house Fe-Mn crust standard and procedural blanks, which were taken through the entire chemical procedure, to assess the accuracy and long-
CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS

term reproducibility of the method. For BHVO-2, a basalt standard, we measured a composition of $\delta^{238/235}U = -0.26 \pm 0.12 \% (2 \text{ S.D.})$, and $^{234}U/^{238}U = 0.997 \pm 0.032 \% (2 \text{ S.D.}); n = 12$. For Nod-A-1, an in-house Fe-Mn nodule standard, we measured a value of $\delta^{238/235}U = -0.59 \pm 0.10 \% (2 \text{ S.D.})$, and $^{234}U/^{238}U = 1.087 \pm 0.030 \% (2 \text{ S.D.}); n = 7$. These results are consistent with values published previously (Weyer et al., 2008; Tissot and Dauphas, 2015).

4.4 Results and Discussion

4.4.1 He/U dating of fossil corals

During precipitation from seawater, corals incorporate uranium such that their U/Ca ratios are similar to seawater (Swart and Hubbard, 1982; Thompson et al., 2003; Robinson et al., 2006). After precipitation, $^{238}U$ and $^{235}U$ in coral decay to their lead daughters ($^{206}Pb$ and $^{207}Pb$) by alpha-decay, producing $^4He$ (described below by Eqn. 4.1).

$$[^4He] = 8[^{238}U](e^{\lambda^{238}t} - 1) + 7[^{235}U](e^{\lambda^{235}t} - 1) + 6[^{232}Th](e^{\lambda^{232}t} - 1), \text{(Eqn. 4.1)}$$

Because negligible amounts of Th are incorporated in coral carbonate, the third term in Eqn. 4.1 above can be ignored (Bender, 1973; Thompson et al., 2003). Previous studies have shown that ~70-100% of radiogenic $^4He$ produced by uranium decay is retained in well preserved fossil corals (Bender, 1973). With this background, He/U dating can be applied as a diagenetic indicator.

It is necessary to correct calculated He/U ages for He-loss associated with alpha particle ejection from coral aragonite (Bender, 1973; Farley et al., 1996). In Bender’s (1973) sample suite, alpha ejection losses as high as 20-30% were calculated from the geometry of the samples. This is due to similarities in magnitude between the alpha stopping distance for aragonite (15 µm; Bender, 1973; Schroeder et al., 1970) and the width of some features of the
Assuming a homogenous uranium distribution in the skeleton, Bender calculated the fraction of $^4\text{He}$ ($F$) that should be lost for a given thickness of coral skeleton. We estimate the degree of He-loss from our samples based on their skeletal geometry in an effort to correct for alpha ejection as in Bender (1973). We acknowledge that this correction has a large uncertainty for two main reasons: (1) because our treatment of the geometry of the coral skeleton is oversimplified, and (2) because the assumption of homogeneous [U] in the coral skeleton is inaccurate (see, for example, Robinson et al., 2006). Not all of the samples studied here require a He-loss correction because we were sometimes able to sample dense, massive (non-porous) skeletal material from the base of the coral calyx. Table 4.2 gives $F$-values for samples investigated in this study. In addition to specifying a value for $F$, Bender used an ‘intersection correction’ ($I$) to account for the observation that coral features intersect. These intersections effectively decrease the percentage of $^4\text{He}$ lost. We give values for $I$ in Table 4.2 as well. The corrected $^4\text{He}$ age can then be calculated as:

$$\text{Corrected He-age} = \frac{\text{uncorrected age}}{1 - F \times (1 - I)} \quad (\text{Eqn. 4.2}).$$

Fig. 4.1 shows a comparison of our calculated, corrected He/U ages relative to the expected age of the sample. For a full details regarding sample identification, provenance, and ages, see Table 2.1 or Table 5.4 in this thesis. The majority of these samples agree with the expected age, but a few still give He ages 20-30% younger than expected (italicized samples in Table 4.2). The young ages may indicate yet-unrecognized alteration – specifically, addition of diagenetic $^{238}\text{U}$ and $^{235}\text{U}$. However, these young samples also have U/Ca ratios comparable to samples of similar geologic age, which give correct He/U ages. As a result, we retain these samples as part of our
sample set but flag them in our U/Ca record. The exception is for sample Mi11, which has a higher U/Ca ratio than corals of comparable geologic age, which we exclude.

There are also 5 fossil coral samples that give He-ages 20-30% older than expected (bold-faced samples in Table 4.2). Such ages may result from He implantation due to infilling clay-rich muds or sediment. Alternatively, this He may derive from the decay of Th adsorbed onto the surface of the skeleton throughout the coral’s existence (Cheng et al., 2000; Thompson et al., 2003; Robinson et al. 2006). Because He implantation and decay of adsorbed Th should only affect the He-age (and not the coral U/Ca ratio), we do not remove these samples from our U/Ca record. The exception is for sample Mi8, which we exclude. This sample’s $^4$He measurement did not replicate well and the sample had a U/Ca ratio slightly higher than samples of similar geologic age (see Table 4.2).

Surprisingly, for 3 samples that have been identified as the same species and that share the same geologic locality and geologic age (Oligocene samples Ol4, Ol5, and Ol6; marked with an asterisk in Table 4.2), we observe a range of variability greater than analytical uncertainty (~20%) in calculated He-ages. According to previous diagenetic tests, these samples are also similarly well preserved (Gothmann et al., 2015). The existence of multiple diffusion domains (which can occur if there are a range of crystal sizes present within a mineral), has been suggested to be important for He-loss in calcite (Copeland et al. 2007; Cros et al. 2014; Cherniak et al. 2015; Amidon et al. 2015). This may account for some of the variability in He-loss from one sample to another.
Table 4.2 Summary of U/Ca results, He/U dating experiments, and alpha ejection correction calculations. Alpha ejection correction calculations are after Bender (1973). Samples for which the correction was not applied were massive, and so the magnitude of He loss from alpha ejection is assumed to be insignificant. Italicized samples correspond to those for which the corrected He age is still younger than the expected age. Bold-faced and italicized samples contain a mixture of pristine aragonite and secondary calcite infilling.

<table>
<thead>
<tr>
<th>ID</th>
<th>Expected Age (Ma)</th>
<th>Expected Age Uncertainty (Ma)</th>
<th>U/Ca (µmol/mol)</th>
<th>2σ S.D.</th>
<th>4He (ncc/g CaCO₃)</th>
<th>2σ S.D.</th>
<th>Uncorrected He Age (Myr)</th>
<th>2σ S.D. (%)</th>
<th>F*</th>
<th>I**</th>
<th>Corrected He Age (Myr)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.0</td>
<td>0</td>
<td>1.08</td>
<td>0.08</td>
<td>84.0</td>
<td>-</td>
<td>0.28</td>
<td>-</td>
<td>0.10</td>
<td>0.01</td>
<td>0.31</td>
<td>porous</td>
</tr>
<tr>
<td>P13</td>
<td>0.1</td>
<td>0.05</td>
<td>1.14</td>
<td>-</td>
<td>127</td>
<td>-</td>
<td>0.36</td>
<td>39.1</td>
<td>0.25</td>
<td>0.10</td>
<td>0.46</td>
<td>porous</td>
</tr>
<tr>
<td>P12</td>
<td>1.4</td>
<td>0.05</td>
<td>0.86</td>
<td>0.03</td>
<td>312</td>
<td>36</td>
<td>1.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.30</td>
<td>massive</td>
</tr>
<tr>
<td>P18</td>
<td>2.2</td>
<td>0.09</td>
<td>1.08</td>
<td>0.11</td>
<td>569</td>
<td>-</td>
<td>1.94</td>
<td>-</td>
<td>0.12</td>
<td>0.01</td>
<td>2.20</td>
<td>porous</td>
</tr>
<tr>
<td>P17</td>
<td>2.3</td>
<td>0.06</td>
<td>1.42</td>
<td>0.10</td>
<td>685</td>
<td>-</td>
<td>1.76</td>
<td>-</td>
<td>0.20</td>
<td>0.01</td>
<td>2.19</td>
<td>porous</td>
</tr>
<tr>
<td>P13i</td>
<td>2.3</td>
<td>0.08</td>
<td>1.04</td>
<td>0.03</td>
<td>773</td>
<td>-</td>
<td>2.61</td>
<td>-</td>
<td>0.20</td>
<td>0.10</td>
<td>3.19</td>
<td>porous</td>
</tr>
<tr>
<td>P11i</td>
<td>3.5</td>
<td>1</td>
<td>0.62</td>
<td>0.00</td>
<td>957</td>
<td>-</td>
<td>5.52</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.52</td>
<td>massive</td>
</tr>
<tr>
<td>P12i</td>
<td>3.8</td>
<td>0.35</td>
<td>1.00</td>
<td>-</td>
<td>965</td>
<td>-</td>
<td>3.11</td>
<td>-</td>
<td>0.20</td>
<td>0.10</td>
<td>3.79</td>
<td>porous</td>
</tr>
<tr>
<td>Mi6</td>
<td>5.4</td>
<td>0.07</td>
<td>0.66</td>
<td>0.00</td>
<td>888</td>
<td>-</td>
<td>4.79</td>
<td>-</td>
<td>0.20</td>
<td>0.01</td>
<td>5.97</td>
<td>porous</td>
</tr>
<tr>
<td>Mi11</td>
<td>9.0</td>
<td>0.2</td>
<td>1.15</td>
<td>0.22</td>
<td>1617</td>
<td>-</td>
<td>5.36</td>
<td>-</td>
<td>0.10</td>
<td>0.01</td>
<td>5.94</td>
<td>porous</td>
</tr>
<tr>
<td>Mi13</td>
<td>9.4</td>
<td>0.23</td>
<td>0.58</td>
<td>-</td>
<td>1526</td>
<td>201</td>
<td>13.7</td>
<td>6.2</td>
<td>0.02</td>
<td>0.01</td>
<td>10.0</td>
<td>porous</td>
</tr>
<tr>
<td>Mi7</td>
<td>14.0</td>
<td>0.59</td>
<td>0.8</td>
<td>0.0</td>
<td>2660</td>
<td>201</td>
<td>13.7</td>
<td>6.2</td>
<td>0.02</td>
<td>0.01</td>
<td>13.9</td>
<td>some pore space</td>
</tr>
<tr>
<td>Mi8</td>
<td>15.0</td>
<td>9</td>
<td>0.96</td>
<td>-</td>
<td>5931</td>
<td>4423</td>
<td>22.4</td>
<td>70.1</td>
<td>0.12</td>
<td>0.01</td>
<td>25.4</td>
<td>silicate residue</td>
</tr>
<tr>
<td>Mi2</td>
<td>17.8</td>
<td>0.08</td>
<td>0.48</td>
<td>0.01</td>
<td>1972</td>
<td>80</td>
<td>14.3</td>
<td>4.0</td>
<td>0.20</td>
<td>0.01</td>
<td>17.9</td>
<td>porous</td>
</tr>
<tr>
<td>Mi1</td>
<td>18.0</td>
<td>0.14</td>
<td>0.33</td>
<td>0.04</td>
<td>1707</td>
<td>-</td>
<td>17.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17.3</td>
<td>massive</td>
</tr>
<tr>
<td>Mi3</td>
<td>18.2</td>
<td>0.13</td>
<td>0.60</td>
<td>0.06</td>
<td>3024</td>
<td>967</td>
<td>17.5</td>
<td>30.1</td>
<td>0.08</td>
<td>0.01</td>
<td>19.0</td>
<td>some pore space/some silicate residue</td>
</tr>
<tr>
<td>O13</td>
<td>31.8</td>
<td>0.51</td>
<td>0.34</td>
<td>-</td>
<td>2767</td>
<td>-</td>
<td>24.9</td>
<td>-</td>
<td>0.02</td>
<td>0.01</td>
<td>25.4</td>
<td>some pore space</td>
</tr>
<tr>
<td>O14*</td>
<td>32.5</td>
<td>0.13</td>
<td>0.27</td>
<td>0.06</td>
<td>2024</td>
<td>-</td>
<td>24.6</td>
<td>-</td>
<td>0.02</td>
<td>0.01</td>
<td>25.1</td>
<td>some pore space</td>
</tr>
<tr>
<td>O16*</td>
<td>32.5</td>
<td>0.13</td>
<td>0.29</td>
<td>0.04</td>
<td>2515</td>
<td>-</td>
<td>28.5</td>
<td>-</td>
<td>0.02</td>
<td>0.01</td>
<td>29.0</td>
<td>some pore space</td>
</tr>
</tbody>
</table>
## Chapter 4. Variations in seawater uranium concentrations during the Cenozoic reconstructed from well preserved aragonitic fossil corals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uranium Concentration</th>
<th>Coral Texture</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>O15*</td>
<td>32.6 0.17 0.22 0.06</td>
<td>2083 123 31.3 6.3</td>
<td>0.02 0.10 31.9</td>
</tr>
<tr>
<td>E6</td>
<td>35.0 0.48 0.81 0.03</td>
<td>5148 295 20.2 5.5</td>
<td>0.30 0.01 28.8</td>
</tr>
<tr>
<td>E8</td>
<td>37.0 0.63 0.24 -</td>
<td>3026 - 38.2 -</td>
<td>- - - 38.2</td>
</tr>
<tr>
<td>O12</td>
<td>37.7 0.83 0.25 -</td>
<td>2578 23 28.6 1.1</td>
<td>0.02 0.01 29.2</td>
</tr>
<tr>
<td>E1</td>
<td>39.2 0.5 0.38 0.04</td>
<td>3772 621 33.4 16.5</td>
<td>0.10 0.01 37.1</td>
</tr>
<tr>
<td>E7</td>
<td>45.0 10 0.13 -</td>
<td>1281 - 30.7 -</td>
<td>- - - 30.7</td>
</tr>
<tr>
<td>E3</td>
<td>45.7 9.03 0.37 0.02</td>
<td>3032 286 28.1 9.3</td>
<td>0.08 0.01 30.5</td>
</tr>
<tr>
<td>E5</td>
<td>45.9 10.13 0.26 0.05</td>
<td>3634 58 45.8 1.7</td>
<td>0.10 0.01 50.8</td>
</tr>
<tr>
<td>E4</td>
<td>46.7 6.68 0.30 0.02</td>
<td>3510 - 40.3 -</td>
<td>- 0.02 0.01 41.1</td>
</tr>
<tr>
<td>Pa1</td>
<td>60.0 4 0.49 0.00</td>
<td>11059 322 74.4</td>
<td>2.8 - -</td>
</tr>
<tr>
<td>Pa3</td>
<td>60.1 1.68 0.45 0.01</td>
<td>8229 265 62.4</td>
<td>3.1 0.02 0.01 63.6</td>
</tr>
<tr>
<td>K2</td>
<td>86.6 0.05 0.14 -</td>
<td>2936 24 54.8 1.0</td>
<td>- - - 54.8</td>
</tr>
<tr>
<td>J1</td>
<td>160.3 0.08 0.44 0.10</td>
<td>16518 101 137.7 0.5</td>
<td>0.10 0.01 152.8</td>
</tr>
<tr>
<td>J4</td>
<td>161.5 0.38 0.56 -</td>
<td>20774 - 127.3 -</td>
<td>- 0.12 0.01 144.4</td>
</tr>
</tbody>
</table>

*F is based on coral skeleton thickness

**I is based on the number of intersections between different coral skeleton components
Finally, we measured two samples containing a mixture of coral skeleton and secondary cement infilling. These samples give ages that agree to within ~30% of the expected age (Fig. 4.1; colored grey in Table 4.2). These samples are also characterized by relatively low U/Ca ratios. We interpret this result as indicating good preservation of the original coral skeleton combined with a minor U contribution from the secondary cement. Due to the presence of a diagenetic component, these samples, as well as the few samples that give He-ages that underestimate the expected age by more than 30%, are excluded from our coral U/Ca record.

4.4.2 $^{234}\text{U}/^{238}\text{U}$ and $\delta^{238/235}\text{U}$ compositions of fossil corals

Modern seawater $^{234}\text{U}/^{238}\text{U}$ is enriched in $^{234}\text{U}$ ($^{234}\text{U}/^{238}\text{U} = 1.146$; Chen et al. 1986) relative to secular equilibrium ($^{234}\text{U}/^{238}\text{U} = 1$). This can be explained by $\alpha$-recoil of $^{234}\text{U}$ from minerals on land, and $\alpha$ loss of $^{234}\text{U}$ from oceanic sediments (Ku, 1965; Chen et al., 1986; Henderson and Anderson, 2003; Cheng et al., 2000; Pogge von Strandmann et al., 2010). $^{234}\text{U}$ lost from minerals on land accumulates in surface waters and is delivered to seawater by rivers while $^{234}\text{U}$ lost from oceanic sediments can diffuse back to seawater. Modern coral $^{234}\text{U}/^{238}\text{U}$ should be identical to modern seawater. However, because the decay constant for $^{234}\text{U}$ is large compared with the decay constant for $^{238}\text{U}$ (its ultimate source), the activity ratio of $^{234}\text{U}$ to $^{238}\text{U}$ in corals approaches secular equilibrium after ~1 My (assuming closed system behavior). Because almost all fossil corals studied here have geologic ages >1 Myr, measured $^{234}\text{U}/^{238}\text{U}$ ratios greater or less than one for our fossil corals should indicate post-depositional alteration of primary U. In this way we can use measurements of $^{234}\text{U}/^{238}\text{U}$ in our fossil corals as an additional constraint on preservation. More specifically, higher $^{234}\text{U}/^{238}\text{U}$ could indicate addition of U, for example from groundwaters. Instead, lower $^{234}\text{U}/^{238}\text{U}$ might indicate $\alpha$-recoil loss of $^{234}\text{U}$.


**Figure 4.1.** Corrected He/U ages vs. expected stratigraphic age (Myr). Expected ages are from radiogenic Sr isotope measurements or from independent constraints on the age of the geologic formation from which fossil coral samples were collected (Gothmann et al., 2015). He ages generally fall to within 20-30% of the expected age. Black circles correspond to samples retained for our U/Ca record. Grey circles correspond to samples that are retained (but flagged due to questionable He/U ages). Grey triangles correspond to samples that are excluded from our U/Ca record due to the presence of calcite in drilled powders or due to anomalous He/U ages. Y-axis error bars correspond to the 1 S.D. of those samples that were analyzed in replicate for $[^{4}\text{He}]$. X-axis error bars correspond to uncertainties in the stratigraphic age.
Chapter 4. Variations in Seawater Uranium Concentrations During the Cenozoic Reconstructed from Well Preserved Aragonitic Fossil Corals

Figure 4.2a shows results of $^{234}\text{U}/^{238}\text{U}$ measurements. About half the samples are enriched in $^{234}\text{U}/^{238}\text{U}$ as is also common for otherwise well-preserved Pleistocene samples (e.g., Thompson et al. 2003; Robinson et al. 2006). However, there is no apparent trend in $^{234}\text{U}/^{238}\text{U}$ vs. age or [U]. Most likely, $^{234}\text{U}$ from groundwaters is added to samples by absorption. This absorbed component may enhance He production rates by a few percent. The exception is for the sample with the greatest $^{234}\text{U}/^{238}\text{U}$ ratio, E6 ($^{234}\text{U}/^{238}\text{U} = 1.58$), which also has uranium concentrations greater than samples of similar geologic age. We exclude this sample from our fossil coral U/Ca record.

The $\delta^{238/235}\text{U}$ compositions of fossil corals also provide insight into U preservation. Modern seawater has a $\delta^{238/235}\text{U}$ composition of $-0.392 \pm 0.005\%$ (Stirling et al., 2007; Weyer et al., 2008; Tissot and Dauphas, 2015). Published measurements of modern coral (n=6) display a similar isotopic composition to modern seawater – spanning a range of $\sim -0.38$ to $-0.5\%$ (Stirling et al., 2007; Weyer et al. 2008; Tissot and Dauphas, 2015). Variations in fossil coral $\delta^{238/235}\text{U}$ could result from diagenesis (e.g., Romaniello et al. 2013), or from secular changes in seawater $\delta^{238/235}\text{U}$ (e.g., Brennecka et al. 2011).

As shown in Fig. 4.2b, we observe a wide range in fossil coral $\delta^{238/235}\text{U}$ of $\sim 0.5\%$, but no monotonic trend in fossil coral $\delta^{238/235}\text{U}$ with geologic age. While the majority of our fossil corals are similar to the modern coral measured in this study, some fossil coral samples are also shifted to $\delta^{238/235}\text{U}$ values lighter and heavier than modern samples. These shifts may be reflective of diagenesis.
Chapter 4. Variations in Seawater Uranium Concentrations during the Cenozoic Reconstructed from Well Preserved Aragonitic Fossil Corals

Figure 4.2. Summary of fossil coral uranium isotope results. (a) $^{234}\text{U}/^{238}\text{U}$ in fossil corals vs. sample age. Colors correspond to fossil coral $[\text{U}]$. Black arrow corresponds to one sample that lies off the scale, with $^{234}\text{U}/^{238}\text{U} = 1.58$. (b) $\delta^{238/235}\text{U}$ in fossil corals vs. sample age. Colors as in (a). Error bars in (a) and (b) correspond to 2s S.D. for the Mn nodule standard Nod-A-1.

Three samples have $\delta^{238/235}\text{U}$ composition heavier than modern corals. Romaniello et al. (2013) found that diagenesis of carbonate sediments in the presence of reducing pore fluids caused an increase in carbonate $[\text{U}]$ and a $\sim 0.2\%$ increase in $\delta^{238/235}\text{U}$. The magnitude of change in $\delta^{238/235}\text{U}$ we see in the heavier population of fossil corals is consistent with the shift observed by Romaniello et al. (2013). However, those samples do not appear to have U concentrations greater than samples of similar geologic age (and with $\delta^{238/235}\text{U}$ similar to modern corals). If our heavy coral $\delta^{238/235}\text{U}$ are, indeed, not primary, then their compositions either reflect the addition of a small amount of secondary U that is extremely enriched in $^{238}\text{U}$. Alternatively (and more improbably) their compositions could be explained by replacement of primary coral uranium with a fluid of different $\delta^{238/235}\text{U}$ and similar $[\text{U}]$. 

137
We also measured 2 fossil corals – one of Pleistocene age and one of Eocene age – with much lighter $\delta^{238/235}$U compositions than modern corals. Stirling et al. (2007) measured $\delta^{238/235}$U in a set of Pleistocene fossil corals and found that some fossils exhibited values as light as $\sim -0.6 \%$ – similar to the lightest two of our specimens. They did not interpret those light values as reflecting alteration of primary U, and the origin of the isotopically light U for these specimens remains unclear. However, Tissot and Dauphas (2015) note that $\delta^{238/235}$U tends to be light in minerals where U is incorporated by adsorption.

It is clear that if both light and heavy fossil coral samples reflect some alteration, then the mechanism by which the diagenetic U is added or exchanged must be very different for each case. We retain samples with anomalous $\delta^{238/235}$U in our U/Ca record, but flag them in Fig. 4.3. Additional measurements of modern corals and carbonates from different diagenetic environments may help shed light on the results presented here.

### 4.4.3 Fossil coral U/Ca record

Fossil coral U/Ca data are presented in Table 4.2 and Fig. 4.3a. U/Ca ratios are low for Early Cenozoic samples, and increase by a factor of 4-5 between the Eocene and the present. Our coral U/Ca record must reflect either (1) large changes in U uptake dynamics in coral aragonite through time, or (2) changes in the U/Ca ratio of seawater. We evaluate these two possibilities below.

It has been shown both in culture experiments and in surveys of natural coral samples that the U/Ca ratio of the aragonitic coral skeleton is inversely proportional to the pH and/or $[\text{CO}_3^{2-}]$ of the seawater in which it grows (Armid et al. 2008; Inoue et al., 2011; Anagnostou et al., 2011; Raddatz et al., 2014). A similar dependence has been demonstrated for inorganic
A number of previous studies examined the relationship between U/Ca with pH and/or [CO$_3^{2-}$]. The sensitivity of coral U/Ca to [CO$_3^{2-}$] (or pH), differs between surface and deep-sea corals. Deep-sea corals exhibit a large dependence of U/Ca (umol/mol) on [CO$_3^{2-}$] and pH, with up to a factor of 3 variability in the U/Ca ratio among natural samples (Anagnostou et al., 2011; Raddatz et al., 2014). In contrast, culture experiments with symbiotic (zooxanthellate) surface corals suggest a much more moderate dependence of U/Ca on seawater pH, with a slope of -0.21 µmol/mol pH$^{-1}$ (Inoue et al., 2011). The sensitivity of inorganic aragonite to seawater [CO$_3^{2-}$] is also about an order of magnitude less than the sensitivity observed for deep-sea corals (DeCarlo et al., 2015). Many of our fossil coral samples may have been asymbiotic (azooxanthellate). However, none of our fossil corals can be classified as deep-sea corals. There are no data available (either from natural samples or culture experiments) regarding behavior in shallow water azooxanthellate corals. As a result, for the remainder of this study, we assume that our samples follow the behavior of surface corals.

A number of studies have concluded that, during the Early Cenozoic, seawater pH was ~0.4 units lower than present (Ridgwell and Zeebe, 2005; Hönisch et al., 2012; Hain et al., 2015) and [CO$_3^{2-}$] was a factor of ~3 lower than present (Tyrrell and Zeebe, 2004; Zeebe, 2012). As detailed in Hain et al. (2015), these changes are compatible with existing estimates of high pCO$_2$ for the Early Cenozoic, seawater DIC similar to present, and elevated seawater [Ca] (Horita
CHAP TER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS

If there had been no change in seawater U/Ca, and applying the -0.21 µmol/mol pH\(^{-1}\) dependence from modern shallow-water zooxanthellate corals (Inoue et al., 2011), we estimate that coral U/Ca would have been \(~0.08\) µmol/mol greater during the Early Cenozoic than today. This small change would be difficult to resolve given the natural range of variability observed for modern surface corals – (0.8 - 2 µmol/mol) (Swart and Hubbard, 1982; Min et al., 1995). We observe much lower coral U/Ca ratios in Early Cenozoic-age samples. Thus, the sense of the observed change is opposite to that predicted from inferred pH and \([\text{CO}_3^{2-}]\) change. As a result, our coral U/Ca data cannot be explained by changes in coral U uptake as a result of changes in seawater pH or \([\text{CO}_3^{2-}]\). Instead, the data likely reflect secular variations in the U/Ca ratio of seawater over the last \(~60\) Myr. In fact, the magnitude of this change may be underestimated by our data.

While some previous studies have proposed that coral U/Ca is predominantly dependent on seawater [U] (Sward and Hubbard, 1982; Shen and Dunbar, 1995), other studies suggest a dependence of aragonite U/Ca on the seawater U/Ca ratio (Broecker, 1971; Meece and Benninger, 1993; Gabitov et al., 2008). In fact, the U/Ca ratio of corals is very close to that of seawater (Shen and Dunbar, 1995; Amiel et al., 1973; Swart and Hubbard, 1982), indicating minor discrimination of coral aragonite for or against uranium. If coral U/Ca tracks the U/Ca ratio of seawater, then either changes in seawater [Ca], changes in seawater [U], or both may be responsible for the coral chemistry changes we observe.

Seawater [Ca] has decreased by a factor of \(~3\) since \(~100\) Ma (Lowenstein et al. 2001; 2003; Horita et al. 2002; Timofeeff et al. 2006; Dickson, 2002; 2004; Coggon et al. 2010; Rausch et al. 2013; Gothmann et al. 2015). Assuming constant seawater [U], then both seawater U/Ca and coral U/Ca should increase by a factor of 3 between the Cretaceous and today. That our
CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS

coral record displays an even larger change in U/Ca (closer to a factor of 4-5 increase in U/Ca between the Early Cenozoic and present) suggests additional variations in seawater [U].

Fig. 4.3b plots seawater [U] inferred from fossil corals assuming that coral U/Ca = seawater U/Ca, and a linear decrease in seawater [Ca] from 26 mmol/kg to 10.6 mmol/kg between 100 Ma and today (Lowenstein et al., 2003; Horita et al. 2002; Timofeeff et al. 2006; Sarmiento and Gruber, 2006). We choose 100 Ma as the start of the seawater [Ca] decline because there are no estimates for seawater [Ca] from fluid inclusions between 100 Ma and ~35 Ma (Zimmerman, 2000; Horita et al., 2002; Lowenstein et al., 2003; Timofeeff et al., 2006; Brennan et al., 2013). However, we note that our inferred history of seawater [U] will evolve slightly as seawater [Ca] becomes better constrained. After removing the [Ca] dependence, our coral data suggest seawater [U] increased by a factor of ~2 between the Eocene and present.
Figure 4.3. (a) Fossil coral U/Ca vs. geologic age. Coral U/Ca increases by a factor of 4-5 since ~30 Ma. Error bars correspond to 2s S.D. (6% for U/Ca). (b) Calculated seawater [U] assuming a linear decrease in seawater [Ca] based on the chemical composition of brine inclusions trapped in halite (Lowenstein et al., 2003; Horita et al., 2002; Timofeeff et al., 2006) and a constant U/Ca distribution coefficient of 1.00 (Broecker, 1971; Meece and Benninger, 1993).
4.4.4 Secular variations in seawater [U]

As summarized below in equations for the ocean uranium mass balance, the variations in seawater [U] we infer suggest imbalances in either the seawater uranium sources and/or sinks over the Cenozoic:

\[
\frac{d[U]}{dt}_{SW} = F_{\text{inputs}} - F_{\text{outputs}}, \quad (\text{Eqn. 4.3})
\]

\[
\frac{d[U]}{dt}_{SW} = F_{\text{River}} - (F_{\text{Low-T Hydrothermal}} + F_{\text{Anoxic}} + F_{\text{Suboxic}} + F_{\text{Oxic}}), \quad (\text{Eqn. 4.4})
\]

The term \([U]_{SW}\) represents the concentration of uranium in seawater, and the different \(F_x\) terms represent the U mass fluxes of the uranium inputs and outputs. \(F_{\text{River}}\) represents the river flux of U to seawater, \(F_{\text{Low-T Hydrothermal}}\) corresponds to the low-temperature hydrothermal sink of U from seawater, \(F_{\text{Anoxic}}\) and \(F_{\text{Suboxic}}\) correspond to the anoxic and suboxic U sinks, respectively. The term \(F_{\text{Oxic}}\) corresponds to the U flux into oxic sinks including carbonates and Fe-Mn crusts. Most estimates for the size of the coral carbonate U sink are small in comparison with the total seawater U sink, suggesting that changes in coral U uptake should not greatly affect the seawater U budget (Morford and Emerson, 1999; Klinkhammer and Palmer, 1990; Barnes and Cochran, 1990). However, we note that the size of the carbonate sink is estimated to be comparable to the suboxic U sink in a study by Dunk et al. (2002) (see also Table 4.1). In the following sections, we discuss the possible controls on Cenozoic seawater [U] in further detail.

4.4.4.1 A relationship between seawater [U] and seawater \([CO_3^{2-}]\)

First, we consider a hypothesis proposed by Broecker (1971) and Broecker (2013), which suggests that the removal flux of uranium by the major oceanic sinks is a function of seawater \([CO_3^{2-}]\). Broecker’s hypothesis is grounded in studies of the U concentration of highly
alkaline Mono Lake, which has a \([\text{CO}_3^{2-}]\) concentration 100 times greater than seawater (Thurber, 1965; Simpson, 1982; Anderson et al., 1982). Uranium’s propensity to complex with carbonate in natural waters, and with cations such as Ca, greatly increases its solubility (Langmuir et al., 1978; Bernhard et al., 2001; Dong and Brooks, 2006). The dominant form of uranium in seawater at pH > 6 is \(\text{Ca}_2\text{UO}_2(\text{CO}_3)_3\) (~60% of total uranium), with other Ca-Mg-UO\(_2\)-CO\(_3\) and UO\(_2\)-CO\(_3\) complexes exhibiting secondary importance (Endrizzi and Rao, 2014).

In contrast to the uranium-carbonate complexes, the abundances of uranium-hydroxide complexes and uncomplexed uranium species are low in seawater (Langmuir, 1978; Djogic et al., 1986; Reeder et al., 2000; Endrizzi and Rao, 2014). As a result of this behavior, \([\text{U}]\) in Mono Lake – like \([\text{CO}_3^{2-}]\) – is ~100 times higher than in seawater (Thurber, 1965; Anderson et al. 1982). Similarly high U concentrations have been observed in alkaline surface waters of Eastern and Western Mongolia (Linhoff et al. 2011; Shvartsev et al. 2012).

Broecker reasoned that if \([\text{CO}_3^{2-}]\) was an important factor in setting the \([\text{U}]\) concentration of natural surface waters like Mono Lake, then secular variations in the \([\text{CO}_3^{2-}]\) of seawater may also cause proportional variations in seawater \([\text{U}]\). Importantly, because of the long residence time of U in seawater (~400,000 yrs; Chen et al. 1986), these variations should only be evident on million-year timescales. Following from Broecker (1971), we suggest that the changes in seawater \([\text{U}]\) inferred from fossil corals may be a result of the factor of ~3 increase in seawater \([\text{CO}_3^{2-}]\) between the Early Cenozoic and today (Tyrrell and Zeebe, 2004; Zeebe, 2012). The idea is that higher \([\text{CO}_3^{2-}]\) and a greater fraction of complexed U would slow kinetic reactions associated with major U sinks.

Experiments of uranium adsorption on ferrihydrite and uranium reduction give additional insight into the mechanisms through which a relationship between \([\text{U}]\) and \([\text{CO}_3^{2-}]\) in
seawater could arise. Wazne et al. (2003) found that the amount of U(VI) adsorbed on ferrihydrite was a strong function of the concentration of carbonate ion in solution. At a concentration of $[\text{CO}_3^{2-}] = 0$ M and at pH = 6, 0.125 mol U(VI) was removed from solution for every mol Fe(III). In contrast, at a concentration of $[\text{CO}_3^{2-}] = 1.68$ mM, only 0.034 mol U(VI) was removed from solution for every mol Fe(III). The authors attributed this observation to (1) a higher abundance of uranium-carbonate complexes relative to total U at high $[\text{CO}_3^{2-}]$, and (2) the lower affinity of uranium-carbonate complexes for adsorption relative to free uranium and uranium-hydroxides.

Studies have also shown that reduction of U(VI) to U(IV) – a potentially large removal pathway for U in reducing sediments – is inhibited by higher $[\text{CO}_3^{2-}]$ (Hua et al., 2006; Belli et al., 2015). Hua et al. (2006) conducted U(VI) reduction experiments with sulfide, and found that reduction rates were highly sensitive to the carbonate ion concentration and pH of the solution. Speciation calculations done for these experiments also reveal a strong relationship between initial reaction rates of U(VI), and the abundance of uranium-hydroxyl species in solution. The authors concluded that uranium-hydroxyl species are the dominant species available for reduction. As a result, the presence of $[\text{CO}_3^{2-}]$ in solution limits uranium reduction because the fractional abundance of uranium-hydroxyl species is lower at high $[\text{CO}_3^{2-}]$ (Hua et al. 2006; Wazne et al. 2003). Belli et al. (2015) conducted similar experiments with *S. putrefaciens* – a uranium reducing bacterium. They found that the highest rate constants for U reduction in the experiments were associated with ‘free’ uranium and uranium-hydroxide species, while lower rate constants were associated with UO$_2$-CO$_3$ species. It is unclear how quantitatively translatable these studies are to seawater, but they do suggest that multiple
seawater uranium removal pathways may be strongly affected by changes in the abundance of 

\( \text{UO}_2\text{CO}_3 \) complexes relative to total seawater \([\text{U}]\). 

Broecker (1971) and (2013) further suggested that if seawater \([\text{U}]\) is indeed controlled by seawater \([\text{CO}_3^{2-}]\), then coral \( \text{U}/\text{Ca} \) should scale with past seawater \([\text{CO}_3^{2-}]\) and/or seawater \([\text{Ca}]\). As shown in the equations below, this relationship assumes that (1) the \( \text{U}/\text{Ca} \) ratio of corals records the \( \text{U}/\text{Ca} \) ratio of seawater, and (2) that seawater \([\text{U}]\) is proportional to seawater \([\text{CO}_3^{2-}]\):

\[
\frac{\text{U}}{\text{Ca}_{\text{corals}}} = \frac{\text{U}}{\text{Ca}_{\text{SW}}} \text{ and } [\text{U}]_{\text{SW}} \propto [\text{CO}_3^{2-}]_{\text{SW}}, \hspace{1cm} (\text{Eqn. 4.5})
\]

\[
\frac{\text{U}}{\text{Ca}_{\text{corals}}} \propto \frac{[\text{CO}_3^{2-}]_{\text{SW}}}{[\text{Ca}]_{\text{SW}}}, \hspace{1cm} (\text{Eqn. 4.6})
\]

\[
[\text{Ca}]_{\text{SW}} \times [\text{CO}_3^{2-}]_{\text{SW}} = \text{constant}, \hspace{1cm} (\text{Eqn. 4.7})
\]

\[
\frac{\text{U}}{\text{Ca}_{\text{corals}}} \propto \frac{1}{[\text{Ca}]_{\text{SW}}^2}, \hspace{1cm} (\text{Eqn. 4.8})
\]

We also use the relationship proposed by Broecker (1971, 2013) and detailed in Eqns. 4.5 - 4.8 to reconstruct a history of seawater \([\text{Ca}]\) inferred from coral \( \text{U}/\text{Ca} \) (Fig. 4.4). The history for seawater \([\text{Ca}]\) we calculate using Broecker’s \( \text{U}-\text{CO}_3 \) relationship is in agreement with independent estimates from fluid inclusions in halite (Lowenstein et al., 2003; Horita et al., 2002; Timofeeff et al., 2006). As a result, it seems that the carbonate ion dependence suggested by Broecker can account for the changes in coral \( \text{U}/\text{Ca} \) we observe both in direction and magnitude, and that \([\text{CO}_3^{2-}]\) may be an important control on seawater \([\text{U}]\) over geologic timescales.
Figure 4.4. Seawater [Ca] inferred from fossil coral U/Ca ratios. Brine inclusion data are from Zimmermann (2002), Horita et al. (2002), Lowenstein et al. (2003), and Timofeeff et al. (2006). Fossil coral data are consistent with results from brine inclusions.

4.4.4.2 Changes in the uranium river flux

In addition to the dependence of uranium removal on seawater \([\mathrm{CO}_3^{2-}]\), it is also important to consider other mechanisms by which seawater uranium sources and sinks could have changed. Rivers – the main input sources of U to seawater (Eqn. 4.3) – carry uranium derived mostly from the weathering of carbonates and uraniferous black shales (Palmer and Edmond, 1993). The Ganges and Brahmaputtra rivers are particularly enriched in uranium, likely due to the weathering of black shales and radiogenic uranium-rich and strontium-rich rocks, and so it is important to consider the implications of Himalayan uplift for the U river flux (Sarin et al., 1990; Palmer and Edmond, 1993; Peucker-Ehrinbrink et al., 1995; Chabaux et al., 2001; Dunk et al., 2002).
The global U river flux is estimated to be between 30 and 60 Mmol/yr (Palmer and Edmond, 1993; Dunk et al., 2002). Single measurements of uranium in the Ganges-Brahmaputra river system that were made during the monsoon season yielded a U flux estimate of ~12 Mmol/yr from the Himalayan rivers – up to 40% of the global flux (Palmer and Edmond, 1993). However, studies of seasonally-averaged [U] in the Ganges and Brahmaputra rivers indicate more moderate fluxes (5.2 Mmol/yr; Sarin et al., 1990; Chabaux et al., 2001; Dunk et al., 2002) as compared with the global average (42 Mmol/yr; Dunk et al., 2002). Therefore, although Himalayan uplift may have contributed to the rise in seawater [U] between the Early Cenozoic and present, it is unlikely that it can account for the majority of the increase we observe.

4.4.4.3 Changes in low-temperature hydrothermal alteration

Changes in hydrothermal alteration through time – independent of the carbonate ion control – may also be able to drive the changes in seawater [U] we infer from our coral record. Uranium is quantitatively stripped from hydrothermal fluids during high-temperature hydrothermal alteration at the ridge axis (Michard et al. 1983; Michard and Albarede, 1985). However, due to the relatively small water flux associated with high-temperature hydrothermal alteration (2.3-4.2 × 10^{12} m^3/yr as compared with the river flux: 4-5 × 10^{13} m^3/yr), this sink of uranium is only a small fraction of the river input (Elderfield et al., 1996; Dunk et al., 2002). In contrast, low-temperature hydrothermal alteration, for which the water flux is estimated to range from 4.8 – 21.0 × 10^{12} m^3/yr, constitutes a major sink of uranium from seawater (Table 4.1; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Dunk et al., 2002; James et al., 2003; Wheat et al., 2003; Mills and Dunk, 2010). The alteration products in which U is
Chapter 4. Variations in seawater uranium concentrations during the Cenozoic reconstructed from well preserved aragonitic fossil corals

Incorporated are likely palagonites, smectites, and Fe-oxides (MacDougall, 1977; Mills and Dunk, 2010; Noordmann et al., 2015).

Figure 4.5. Schematic of the modern seawater uranium mass balance used for the 1-box model in this study, adapted from Barnes and Cochran (1990), Klinkhammer and Palmer (1991), and Dunk et al. (2002) in accordance with updated constraints on the low-T hydrothermal and anoxic sinks (Wheat et al., 2003; Mills and Dunk, 2010; Montoya-Pino et al., 2010; Brennecke et al., 2011; Noordmann et al. 2015). $\delta^{238}$U compositions relative to CRM112a and isotope effects used in model calculations are as follows: $\delta^{238}$U$_{\text{river}} = -0.24 \, \%_o$, $\delta^{238}$U$_{\text{ModernSW}} = -0.39 \, \%_o$, $\Delta^{238}$anoxic = +0.60 \, \%_o$, $\Delta^{238}$suboxic = +0.10 \, \%_o$, $\Delta^{238}$hydrothermal = +0.10 \, \%_o$, $\Delta^{238}$carb/FeMn = -0.05 \, \%_o$ (Montoya-Pino et al., 2010; Weyer et al., 2008; Noordmann et al. 2015).
Recent studies have highlighted the potential importance of variations in low-temperature ridge-flank hydrothermal alteration rate for the seawater budgets of elements like Mg, Sr, Ca, and Li. Some studies suggest that variations in rates of low-temperature alteration could be driven by changes in mid-ocean ridge length, and the resulting change in the area of ocean crust where low-temperature hydrothermal alteration occurs (Van der Meer et al., 2014; Müller et al., 2013). However, the decrease in low-temperature hydrothermal alteration rates predicted between the Early Cenozoic and present from recent model reconstructions of ridge length is only 20-50% (Van der Meer et al. 2014; Müller et al., 2013). This decrease is not large enough to drive the factor of ~2 increase in seawater [U] we observe.

An alternative hypothesis is that changes in ocean bottom water temperatures could have led to changes in U removal via a temperature-dependent hydrothermal alteration relationship (Coogan and Gillis, 2013; Coogan and Dosso, 2015; Higgins and Schrag, 2015). This hypothesis was recently invoked to explain observed variations in Cenozoic seawater Mg/Ca and δ²⁶Mg (Higgins and Schrag, 2015). Indeed, the observation that [Mg] and [U] are correlated in low-T hydrothermal fluids (Wheat et al., 2003; Noordmann et al. 2015) suggests that similar kinetics may govern the removal of both elements.

Using a simple 1-box model (Eqn. 4.3, Eqn. 4.4, Fig. 4.5) we investigate the magnitude of change in the low-temperature hydrothermal alteration uranium sink required to drive a factor of ~2 change in seawater [U] between the Early Cenozoic and today. We then compare this change to the predicted hydrothermal flux change for Mg from Higgins and Schrag (2015). In our model, we assume that the modern low-temperature hydrothermal sink constitutes ~35% of the total U output flux – well within in the range of 15-70% estimated by Barnes and Cochran (1990), Wheat et al. (2003), Morford and Emerson (1999), Mills and Dunk (2010) and
We also assume that the riverine U input remains constant through time, and that all seawater sinks are first-order with respect to the seawater [U]:

\[ F_{\text{sink}} = k_{\text{sink}} \times [U]_{\text{seawater}}, \quad (\text{Eqn. 4.9}) \]

where \( F_{\text{sink}} \) is the flux of U into the seawater sink (e.g., \( F_{\text{Low-T Hydrothermal}} \), \( F_{\text{Anoxic}} \), and \( F_{\text{Suboxic}} \) in Eqn. 4.4) and \( k_{\text{sink}} \) is the rate removal constant associated with each sink.

In order to change seawater [U] in the model, we systematically decrease the rate constant, \( k_{\text{Low-T Hydrothermal}} \), associated with the hydrothermal sink between the between the Early Cenozoic and today. The prescribed decrease in \( k_{\text{Low-T Hydrothermal}} \) results in a flux imbalance between U sources and sinks (with sources > sinks), and as a result, seawater [U] in the model increases. While we prescribe changes in \( k_{\text{Low-T Hydrothermal}} \), the rate constants associated with the other seawater sinks are held constant. The U fluxes associated with those sinks only evolve in response to changing seawater [U] (see Eqn. 4.9).

A factor of ~2 increase in seawater [U] in the model requires a factor of ~4.5 decrease in \( k_{\text{Low-T Hydrothermal}} \). These changes correspond to a factor of ~2 decrease in the low-temperature hydrothermal flux since the Early Cenozoic (Fig. 4.6a and b). At the same time, \( F_{\text{Suboxic}} \), \( F_{\text{Anoxic}} \), and \( F_{\text{oxic}} \), increase in response to increasing seawater [U] (Fig. 4.6b). The magnitude of change in the hydrothermal flux we calculate in the model is consistent with the factor of 2 change in low temperature hydrothermal Mg flux modeled by Higgins and Schrag (2015) to explain observed variations in seawater Mg/Ca and \( \delta^{26}\text{Mg} \). These model calculations allow for the possibility that changes in the hydrothermal flux are responsible for the inferred variations in seawater [U]. However, we note that it is also unclear whether temperature (as is the case for Mg), or redox condition, is the main factor in determining the uptake of U from seawater during low temperature hydrothermal alteration (James et al., 2003; Dunk et al., 2002; Mills and Dunk,
Variations in seawater uranium concentrations during the Cenozoic reconstructed from well preserved aragonitic fossil corals (2010). Most recently, based on $\delta^{238}\text{U}$ isotope analyses of basalt altered at low temperatures and hydrothermal fluids, Noordmann et al. (2015) and Andersen et al. (2015) suggested that some hydrothermal U removal likely occurs via oxic weathering – where temperature may determine reaction kinetics – and some occurs through reduction of U(VI) to U(IV) by reducing hydrothermal fluids. Additional studies of the controls on the hydrothermal U sink may better help determine the importance of this flux in changing seawater [U] over the Cenozoic.

4.4.4.4 A dependence of seawater [U] on ocean oxygen

Finally, we explore the possibility that a decrease in the uranium flux to suboxic and anoxic sediments (also independent of seawater [CO$_3^{2-}$]) can explain our record. Like low-temperature hydrothermal alteration, suboxic and anoxic sediments are important sinks for seawater U (Fig. 4.5 and Table 4.1). Here, consistent with Berner (1981), we define suboxic sediments as having no oxygen or H$_2$S (e.g., the Peru margin), while anoxic sediments are defined as having H$_2$S present but no oxygen (e.g., the Black Sea). The U concentration of suboxic and anoxic sediments has been linked to a variety of factors including: (1) the magnitude of the organic matter flux and organic carbon burial (McManus et al., 2005; McManus et al., 2006; Morford et al., 2009), (2) uranium adsorbed to organic material in the surface ocean that escapes remineralization at depth (Zheng et al., 2002), and (3) microbiually-mediated reduction of U(VI) to U(IV) with subsequent precipitation of solid uranium phases (Lovley et al., 1991). To first order, however, the dominant control on U removal in suboxic and anoxic sediments is likely the oxygen concentration of sedimentary pore waters (Anderson, 1987; Barnes and Cochran, 1990; Morford and Emerson, 1999; Weyer et al., 2008).
**Figure 4.6.** (a) Modeled history of seawater [U] for the case invoking only changes in the rate of hydrothermal alteration. Changes in the size of the hydrothermal U flux relative to the other seawater U sinks for the case shown in (a) are plotted in (b). (c) Modeled history of seawater [U] for the case invoking changes in the rate of U removal in anoxic and suboxic sediments. Changes in the size of the suboxic and anoxic U fluxes relative to other seawater U sink for the case shown in (c) are plotted in (d). (e) Modeled seawater U isotope composition for the case shown in (c), plotted along with a record of seawater $\delta^{238/235}$U from Goto et al. (2014).

Changes in the fluxes of U to anoxic and suboxic sediments, resulting (for example) from changes in ocean oxygenation or productivity, may drive changes in seawater [U]. Using the same 1-box model as in Section 4.4.4.2, we can calculate the magnitude of change in the suboxic and anoxic fluxes required to drive our inferred change in seawater [U]. Also similar to Section 4.4.4.2, we prescribe decreases in $k_{\text{anoxic}}$ and $k_{\text{suboxic}}$ since the Early Cenozoic in the model, but hold all other k’s constant such that they only respond to changes in model seawater
CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS

[U]. For simplicity, we link the suboxic and anoxic fluxes (i.e., increasing the suboxic sink increases by 10%, also increases the anoxic sink by 10%). In addition, we include a U isotope mass balance, following from Eqn. 4.4:

\[
\frac{d(\delta^{238/235}U_{SW})}{dt} = \left(\delta^{2238/235}U_{River}\right) - F_{HYD} \times \left(\delta^{2238/235}U_{SW} - \epsilon_{HYD}\right) - F_{Anoxic} \times \left(\delta^{2238/235}U_{SW} - \epsilon_{Anoxic}\right) - F_{Suboxic} \times \left(\delta^{2238/235}U_{SW} - \epsilon_{Suboxic}\right) \quad \text{(Eqn. 4.10)}
\]

Our model calculations indicate that the suboxic and anoxic fluxes of U must have decreased by ~35% between the Early Cenozoic than today in order to account for the changes in seawater [U] we observe (Fig. 4.6c and d). This magnitude of decrease in the suboxic and anoxic sinks between the Early Cenozoic and today only corresponds to a ~0.04 ‰ increase in the $\delta^{238}$U composition of seawater (Fig. 4.6e).

Recently, a record of seawater $\delta^{238/235}$U derived from ferromanganese crusts has been published (Goto et al. 2014; Fig. 4.6e), showing no clear variation in seawater $\delta^{238/235}$U. This result is broadly consistent with the model output, but we note that $^{234}\text{U}/^{238}\text{U}$ measured in the ferromanganese crusts suggest that the $\delta^{238/235}$U compositions may be biased by diagenesis (Goto et al. 2014). Measurements of $\delta^{238/235}$U from fossil corals measured in this study (Fig. 4.2b) show more scatter than the record from Goto et al. (2014), but also show no detectable changes in $\delta^{238/235}$U since 40 Ma, but the coral data cannot rule out smaller magnitude variation in seawater $\delta^{238/235}$U.
4.5 Conclusions

Measurements of $^4$He, and U isotopes from well preserved scleractinian fossil corals allow us to constrain preservation of fossil coral U geochemistry and suggest the absence of recrystallization. U/Ca ratios measured in these samples show a factor of 4-5 between the Early Cenozoic samples and Recent samples. We interpret this change as indicative of variations in seawater $[U]$. An increase in seawater $[U]$ between the Early Cenozoic and present is consistent with a carbonate ion control over U removal rates, as originally suggested by Broecker (1971). In addition, it is also possible that seawater $[U]$ has changed as a result of: (1) changes in rates of low-temperature hydrothermal alteration over the Cenozoic, or (2) a small decrease in removal of U in suboxic and anoxic sediments over the last ~60 Myr.

4.6 Acknowledgements

We would like to thank Stephen Cairns and Tim Coffer (Smithsonian Institution), Linda Ivany (Syracuse University), Roger Portell (Florida Museum of Natural History), Anne Cohen and Bill Thompson (WHOI), the USGS, and Gregory Dietl (Paleontological Research Institution) for loaning samples. We thank Elizabeth Lundstrom (Princeton University) and Lindsey Hedges (California Institute of Technology) for analytical support. We also thank Wally Broecker (Lamont Doherty Earth Observatory), Sarah Jane White (Princeton University), Francois Morel (Princeton University) and Will Amidon (Middlebury College) for helpful discussions.
4.7 Author contributions and previous presentations of this work

Michael Bender, Anne Gothmann, and John Higgins planned this work. Anne Gothmann conducted U/Ca measurements. 4He measurements were made by Anne Gothmann with much help from Ryan McKeon and Ken Farley. U isotope measurements were made by Anne Gothmann and Xiangli Wang, with much help from Noah Planavsky. Anne Gothmann drafted the chapter with input from Michael Bender, John Higgins, Jess Adkins, and Jarek Stolarski. Jarek Stolarski contributed many of the samples that were analyzed as part of this work.

This work is in prep for submission to Geochimica et Cosmochimica Acta.

This work was presented as:


Chapter 4. Variations in seawater uranium concentrations during the Cenozoic reconstructed from well preserved aragonitic fossil corals

References


Chapter 4. Variations in seawater uranium concentrations during the Cenozoic reconstructed from well preserved aragonitic fossil corals


CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS


CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS


CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS


CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS


Keul, N., Langer, G., de Nooijer, L., Nehrke, G., Reichart, F.-J., and Bijma, J., 2013,
Incorporation of uranium in benthic foraminiferal calcite reflects seawater carbonate ion concentration. *Geochemistry Geophysics Geosystems* G3 14, 102-111.


CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS


Chapter 4. Variations in seawater uranium concentrations during the Cenozoic
reconstructed from well preserved aragonitic fossil corals

underlying bottom waters with high oxygen content. *Geochimica et Cosmochimica Acta*
73, 2920-2937.

supercontinent assembly, breakup, and dispersal. *Geology* 41, 907-910.

crustal material, rivers and products of hydrothermal alteration: new insights on the oceanic
U isotope mass balance. *Isotopes in Environmental and Health Studies*, 1-23.


Acta* 57, 4947-4955.


Pogge von Strandmann, P.A.E., Burton, K.W., James, R.H., van Calsteren, P., Gislason, S.R.,
2010. Assessing the role of climate on uranium and lithium isotope behaviour in rivers
draining a basaltic terrain. *Chemical Geology* 270, 227-239.

Raddatz, J., Rüggeberg, A., Flögel, S., Hathorne, E. C., Liebetrau, V., Eisenheuer, A., and Dullo,
W.-C., 2014. The influence of seawater pH on U/Ca ratios in the scleractinian cold-water

Rausch, S., Böhm, F., Bach, W., Klugel, A., and Eisenhauer, A., 2013. Calcium carbonate veins
in ocean crust record a threefold increase of seawater Mg/Ca in the past 30 million years.

CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS


CHAPTER 4. VARIATIONS IN SEAWATER URANIUM CONCENTRATIONS DURING THE CENOZOIC RECONSTRUCTED FROM WELL PRESERVED ARAGONITIC FOSSIL CORALS


Chapter 5.

Calcium isotopes in scleractinian fossil corals since the Mesozoic: implications for vital effects and biomineralization through time

5.1 Abstract

We present a 160 Myr record of $\delta^{44/40}$Ca from well preserved scleractinian fossil corals, as well as a complementary ~80 Myr record of $\delta^{44/40}$Ca from bulk pelagic carbonates. The same fossil corals used for this study were previously shown to be excellently preserved, and to be faithful archives of past seawater Mg/Ca and Sr/Ca since ~200 Ma (Gothmann et al., 2015). We find that the $\delta^{44/40}$Ca compositions of bulk pelagic carbonates from ODP Site 807 (Ontong Java Plataeu) and DSDP Site 516 (Rio Grande Rise) have remained relatively constant over the last ~80 My. In contrast, the $\delta^{44/40}$Ca compositions of Mesozoic and Early Cenozoic fossil corals are ~1‰ lighter than $\delta^{44/40}$Ca in Modern corals.

The observed change in coral $\delta^{44/40}$Ca does not likely reflect secular variations in seawater $\delta^{44/40}$Ca. Instead, we propose that it reflects a vital effect of calcification – specifically, a sensitivity of coral Ca isotope discrimination to changing seawater [Ca] and/or pH. Support for this hypothesis comes from the presence of an empirical correlation between our coral $\delta^{44/40}$Ca record and records of seawater [Ca] and pH since the Mesozoic (Lowenstein et al. 2003; Hönisch et al. 2012). We explore various mechanisms that could give rise to such a vital effect, including:
(1) changes in calcification rate, (2) changes in proton pumping in exchange for Ca$^{2+}$, (3) variable Rayleigh distillation from an isolated calcifying fluid, and (4) changes in the calcium mass balance of the extracellular calcifying fluid (termed here the “leaky Ca model”). We test for the dependence of seawater δ$^{44/40}$Ca on external seawater [Ca] by measuring the δ$^{44/40}$Ca of cultured corals grown in seawater solutions with [Ca] ranging from 10 to 15 mmol/kg. Corals grown under elevated [Ca] conditions show a slight, ~0.15‰ depletion of δ$^{44/40}$Ca at higher seawater [Ca] – a supportive but not definitive result. Together, our data provide new geochemical constraints on the response of coral calcification to changes in seawater carbonate chemistry since the Mesozoic.

5.2 Introduction

Diagenetically unaltered scleractinian fossil corals are useful archives of a variety of paleoenvironmental properties across a range of geologic timescales (McCulloch et al., 1994; Beck et al. 1992; Marshall and McCulloch, 2002; Beck et al., 1997; Cohen et al., 2006; Shen and Boyle, 1987; Corrège, 2006; Mertz-Kraus et al., 2009; Thiagarajan et al., 2011; Gaetani et al. 2011; McCulloch et al. 2012). For example, coral-based paleothermometers (Sr/Ca, δ$^{18}$O, and Δ$^{47}$) have been successfully applied to reconstruct high-resolution records of past climate (McCulloch et al., 1996; Guilderson et al., 1998; Tudhope et al., 2001; Guilderson et al., 2001; Mertz-Kraus et al., 2009; Thiagarajan et al., 2014). They have also been used to reconstruct the geochemical evolution of seawater (i.e., seawater Mg/Ca and Sr/Ca) on timescales of millions of years (Ivany et al., 2004; Griffiths et al., 2013; Gothmann et al., 2015). The application of corals as paleoenvironmental indicators, however, can sometimes be confounded by the presence of
‘vital effects’ (McConnaughey, 1989; de Villiers et al., 1995; Adkins et al., 2003; Sinclair et al., 2006).

“Vital effects” refer to departures in skeletal geochemistry away from the composition expected based on inorganic distribution coefficients (Epstein, 1951; Adkins et al., 2003; de Villiers et al., 1995; Cohen et al., 2006; Sinclair et al., 2006; McCulloch et al., 2012). They are thought to result from biological control by the coral organism over skeletal calcification (Weiner and Dove, 2003; Tambutte et al., 2011). Problematically, they may also vary between and within coral species, in which case constant correction factors cannot be employed (Marshall and McCulloch, 2002; Corrège, 2006; McCulloch et al., 2012; Jones et al., 2009).

The existence of vital effects in scleractinian coral has been very well documented, but a full mechanistic understanding of the origin of vital effects in corals has yet to be achieved (McConnaughey, 1989; Adkins et al., 2003; Meibom et al., 2004; Sinclair et al., 2006; Cohen et al., 2006; Gagnon et al. 2007; Tambutte et al. 2011). Mechanisms that have been identified as potential sources of vital effects include, but are not limited to (1) Rayleigh fractionation from an isolated calcifying fluid and/or other reservoir effects (e.g., Gaetani et al., 2011; Gagnon et al., 2007; Gagnon et al., 2012), (2) biologically-mediated ionic transport into the calcifying space (e.g., Zoccola et al., 2004; Böhm et al., 2006; Meibom et al., 2007), (3) variable calcification rates (e.g., Cohen et al., 2001; de Villiers et al., 1995) and (4) the influence of an organic matrix (e.g., Allemand et al., 1998; Clode and Marshall, 2003). Element/Ca ratios such as Mg/Ca and Sr/Ca as well as the stable isotopes of oxygen, carbon, and boron are examples of geochemical parameters that display significant vital effect behavior (Meibom et al. 2004; Gagnon et al. 2007;

Figure 5.1 Sketch of key skeletal compartments and reservoirs that play a role in coral calcification, modeled after Böhm et al. (2006). Seawater transport to the site of calcification can occur paracellularly via direct exchange with seawater, or can occur transcellularly by active transport with Ca-ATPase.

Existing measurements of $\delta^{44/40}$Ca in modern corals also suggest the presence of significant vital effects for Ca isotopes. Modern coral $\delta^{44/40}$Ca is on average ~0.4‰ heavier than inorganic aragonite (Chang et al., 2004; Böhm et al., 2006; Pretet et al., 2013). For reference, inorganic aragonite is offset from seawater by about -1.7‰ (Blättler et al., 2012; Gussone et al., 2005). In addition, modern corals exhibit a wide range (~0.6‰) of $\delta^{44/40}$Ca compositions (Blättler et al., 2012; Pretet et al., 2013). This range cannot be attributed to variations in coral taxonomy, or environmental changes in salinity or temperature.
Ca isotopes may be able to offer unique insight into the biomineralization mechanisms generating coral vital effects because calcium plays a critical role in calcification (Zoccola et al., 2004; Al-Horani et al., 2003). There are two main pathways by which Ca may arrive at the site of coral calcification (Fig. 5.1). Ca may be transported paracellularly (i.e., via open channels or conduits) from seawater directly to the site of calcification (Zoccola et al. 2004; Gagnon et al. 2012). Also, Ca that has diffused into the coelenteron (the mouth of the coral animal) may be actively transported by Ca-ATPase to the site of calcification (Zoccola et al. 2004; Al-Horani et al. 2003). The calcification site may exist as a thin, seawater-like “calcifying fluid” beneath the calicoblastic layer (McConnaughey, 1989; Adkins et al., 2003; Gagnon et al., 2007; Cohen et al. 2009). Alternatively, calcification may occur directly from an organic matrix (Allemand et al. 1998; Clode and Marshall, 2002; Cuif and Daupin, 2005; Cuif et al. 2008).

Moreover, external seawater carbonate chemistry and seawater [Ca] may influence each of these pathways and the isotope effects associated with them. As proposed for other trace elements and isotope systems, reservoir effects such as Rayleigh distillation may lead to a dependence of coral Ca isotopes on seawater [Ca] (Gagnon et al., 2007; Gaetani et al., 2011). Alternatively, coral Ca isotope fractionation may be dependent on seawater [Ca] in a way similar to the dependence of carbon isotope fractionation on pCO₂ in plants (Farquhar, 1982). For reference, in plants, the CO₂ that is eventually fixed as organic carbon by RuBisCO is transported from the surrounding environment (atmosphere or ocean) into plant cells. Once present in the cell, CO₂ is either fixed as biomass, or it leaks back out to the atmosphere by diffusion (Farquhar, 1982; Pagani, 2014). Because the isotopic fractionations associated with carbon fixation by RuBisCO and diffusion are distinct, changes in the ratio of fixation to
CHAPTER 5. CALCIUM ISOTOPE IN SCLERACTIAN FOSSIL CORALS SINCE THE MESOZOIC: IMPLICATIONS FOR VITAL EFFECTS AND BIOMINERALIZATION THROUGH TIME

diffusion lead to changes in the isotopic composition of the plant biomass. This ratio itself is dependent on the concentration of CO$_2$ in the environment. In corals, the ratio of Ca incorporation into coral aragonite from the calcifying fluid and Ca transported back to seawater from the calcifying fluid, may be dependent on external seawater [Ca]. In this way, the Ca isotope composition of coral aragonite may be a function of seawater [Ca].

In addition, it has been hypothesized that seawater pH, alkalinity, and saturation state play a role in setting the proportion of skeletal Ca that comes from seawater relative to the amount derived from Ca-ATPase (Gagnon et al., 2012; 2013). Further evidence for this dependence comes from studies of boron isotopes, pH-sensitive dyes, and transcriptometric modifications in cultured corals (Vidal-Dupoil et al. 2013; McCulloch et al. 2012; Venn et al., 2013). The proportion of Ca derived from seawater relative to Ca derived from active pumping by Ca-ATPase is also likely to be a function of seawater [Ca] itself.

We measured Ca isotopes in a suite of well preserved fossil aragonitic corals (Gothmann et al., 2015), and bulk pelagic carbonates from ODP Site 807 and DSDP Site 516. Together, the data allow us to examine how coral Ca isotope fractionation has responded to natural variations in seawater [Ca] and pH since the Mesozoic (Lowenstein et al., 2001; 2003; Horita et al., 2002; Timofeeff et al. 2006; Tyrrell and Zeebe, 2004; Hönisch et al., 2012). In particular, it is possible to compare coral Ca isotope fractionation with the average fractionation of pelagic carbonate, which is the dominant seawater Ca sink today. We show that bulk carbonate $\delta^{44/40}$Ca remains roughly constant over the last 80 Myr. However, the Ca isotopic composition of aragonitic corals has increased by ~ 1‰ since the Mesozoic. Collectively, our
results provide new insights into the relationship between coral calcification and secular variations in seawater chemistry over million-year timescales.

5.3 Materials and methods

5.3.1 Samples

The fossil and modern corals samples (n=40) that are the subjects of this study were previously described by Gothmann et al. (2015). Fossil corals measured for Ca isotopes are as old as Jurassic in age and have been obtained from a variety of geologic localities to ensure that variations through time reflect global rather than local signatures. While our sample set includes a range of different species of coral, there are no trends in our sample set between coral taxonomy and geologic age. Samples were screened for diagenesis by a combination of X-ray diffractometry, cathodoluminescence, and Raman spectroscopy. Additional measurements of trace elements, carbonate clumped isotopes and $^{87}\text{Sr}/^{86}\text{Sr}$ in these samples give support that their original geochemical composition is retained, which suggests that their Ca isotope composition should also be primary (Gothmann et al., 2015).

Bulk limestone samples from ODP Site 807 (Ontong Java Plateau, ~2800 m water depth) and DSDP Site 516 (Rio Grande Rise, ~1300 m water depth) were also measured for $\delta^{44/40}\text{Ca}$. Samples range in age from Late Cretaceous to Recent. Both cores are generally carbonate-rich although some intervals of claystone and radiolarian siltstone are also present (Berger et al., 1991; Fantle and DePaolo, 2007; Barker et al., 1983). Sediments of Eocene age and younger are dominated by foraminifer ooze, nannofossil ooze, and chalk. Eocene and older sediments are dominated by lithified limestone (Berger et al., 1991; Barker et al., 1983). Bulk
limestone samples were washed and sieved prior to geochemical analysis as described in Higgins et al., (2015).

Cultured coral samples were grown for 9 weeks under controlled laboratory conditions at the University of Miami’s Experimental Hatchery. Concentrations of calcium in the culture solutions were varied to assess the effect of past changes in seawater [Ca] on coral Ca isotope discrimination. Calcium concentrations of the growth solutions ranged from modern seawater concentrations (~10 mmol/kg) to concentrations similar to those expected for the late Oligocene or early Miocene (~15 mmol/kg) (Horita et al., 2002; Lowenstein et al., 2003; Brennan et al., 2013). For reference, Early Cenozoic seawater [Ca] was ~25-30 mmol/kg, 250-300% of present (Lowenstein et al., 2001; 2003; Horita et al., 2002). While some colonies were only subjected to elevated [Ca], others were also subjected to elevated [Mg] and [Sr].

Prior to starting experiments, 2 branches (>1.5 cm in length) of Pocillopora damicornis were fragmented from coral colonies using wire cutters. These fragments were then glued to PVC tiles with CorAffix™ Cyanoacrylate Adhesive and allowed to recover for 4 weeks in flow-through seawater. Seawater was pumped from Bear Cut, a tidal channel that connects Biscayne Bay to the Atlantic Ocean. The composition of this water varied naturally each day. Temperature ranged from 21-25°C, with an average of 22.6°C, and salinity ranged from 31-35 psu, with an average of 34 psu. The average alkalinity for the experiments was 2.261 ± 0.061 meq/kg (1σ S.D.) and pH varied between 7.9-8.0. Calcification rates were quantified with the alkalinity anomaly method and normalized to buoyant weights. Only data generated in the last 5 weeks of the experiments were used for calcification rate quantification to ensure that corals were fully acclimated to the treatments. For the alkalinity anomaly measurements, experimental
jars were filled with water and water samples were taken. Then, corals were transferred into the experimental jars. A second set of water samples were taken 24 hours later, after the addition of corals. Water samples were filtered with glass microfiber filters (VWR, Grade 691, 0.45 μm) and preserved with mercuric chloride (HgCl₂). The change in total alkalinity between water samples was measured with an automated titrator (Brinkmann Metrohm 665 Dossimat) and the corresponding amount of carbonate precipitated was determined according to Chrisholm and Gattuso (1991). The buoyant weight method (Jokiel et al. 1978) was used to determine the dry skeletal weights at the beginning of the fifth week of the experiment, using a skeletal density of 2.703 g/cm³ (previously reported for *P. damicornis*; Spinaze et al. 1996). Dry skeletal weights were used to normalize the amount of carbonate precipitated each week. Calcification rates were determined using the slope of the normalized amount of carbonate precipitated. The errors for alkalinity measurements and buoyant weights were propagated using the Monte Carlo method to determine the total standard deviation of calcification rates (~4.5 % RSD; Anderson, 1976).

The start of the experiment was marked with Alizarin Red S biological stain and fragments were moved to jars with 2.5 L of seawater in which concentrations of Ca, Mg and Sr were increased incrementally over 24 hours by adding calcium, magnesium, and strontium chloride salts. Flow was maintained in these jars with aquarium pumps and seawater treatments were changed daily. Saturation state for each experiment was calculated with CO2SYS (van Heuven et al. 2011) using results of alkalinity, pH, temperature, and salinity measurements. Carbonate dissociation constants used in the calculation were from Mehrbach et al. (1973) refitted by Dickson and Millero (1987). Throughout the experiment, corals were kept on a 12hr/12hr light/dark cycle (average light intensity of 257 ± 39 μmol m⁻² sec⁻¹) and fed a mixture
of 100-150 μm and <100 μm larval AP100 diet (Ziegler) twice weekly. Coral tissues were removed from skeletons with an airbrush, and skeletons were oven dried at 40°C for 24 hours. Areas of new growth (above the Alizarin stain line) were ground to a powder for Ca isotope analysis. Culture seawater solutions were also collected, filtered, and analyzed for $\delta^{44/40}$Ca.

### 5.3.2 Ca isotope analyses

Powders weighing 2-5 mg were drilled from fossil coral skeletons and dissolved in 1N nitric acid (HNO$_3$). The exception was for cultured coral samples, for which ~100 µg of CaCO$_3$ was dissolved in 1 mL 1N HNO$_3$. Bulk limestone samples (~5 mg) were powdered and dissolved in buffered 0.1N acetic acid (pH ≈ 5). The latter dissolution technique dissolves carbonate phases, but is gentle enough such that silicate phases remain insoluble (Tessier et al., 1979). Ca in dissolved carbonates and seawaters was purified by ion exchange chromatography as described in Blättler et al. (2012) and Blättler and Higgins (2014), and also using a Thermo Dionex DCS5000+ Ion Chromatograph (IC). The IC system offers a more efficient means (30-50 minute separation per sample) by which to separate and collect cations such as Ca for isotopic analysis.

Samples were prepared for separation on the IC by diluting to ~30 ppm Ca with 0.2% HNO$_3$. Samples (200 µL in volume) were then injected, and Ca was separated from other cations (Na, Mg, K, Sr) using an in-line CS16 cation exchange column. After eluting with methanesulfonic acid (MSA), Ca fractions were collected using a Dionex AS-AP autosampler. Cation separation and yields were verified by measurements of sample conductivity. Accuracy
and precision of the method were assessed by repeated measurements of carbonate standards (in-house and SRM 915b) and modern seawater standards.

Separated Ca fractions were then analyzed for Ca isotopes (44/42, 44/43, 43,42) at a concentration of 2 ppm Ca. Measurements were made using a ThermoFinnegan Neptune Plus inductively-coupled plasma mass spectrometer (ICP-MS) at Princeton University with an ESI Apex-IR sample introduction system. Beam intensities were measured in medium resolution for masses 44, 43 and 42. Mass 43.5 was also monitored to check for Sr interferences. Three-isotope plots of $\delta^{44/43}$ vs. $\delta^{44/42}$ for each analytical session were examined to check for mass-dependent behavior. Raw $\delta^{44/42}$Ca results were converted to $\delta^{44/40}$Ca and calibrated relative to modern seawaters measured in the same analytical session (i.e., $\delta^{44/40}$Ca$_{\text{modern seawater}} = 0$ by definition).

The $\delta^{44/40}$Ca of an in-house Ca standard, taken through the full chemical procedure with each batch of samples in order to monitor long-term external reproducibility, is $-1.11 \pm 0.18\%$ (2 S.D.; n=14) relative to modern seawater. Measurements of SRM 915b yield $\delta^{44/40}$Ca values of $-1.18 \pm 0.18\%$ (2 S.D.; n=11) relative to modern seawater, indistinguishable from values reported in previous studies as measured by MC-ICP-MS ($-0.96\%$ and $-1.16\%$: Heuser and Eisenhauer, 2008; Morgan et al. 2011) and by thermal ionization mass spectrometry (TIMS) ($-1.13\%$: Lehn et al., 2013; Jacobson et al., 2015). A modern Porites sp. coral gives a $\delta^{44/40}$Ca value of $-1.01 \pm 0.13\%$ (2 S.D.; n=3) relative to modern seawater – within the range of values measured for other modern Porites sp. (Pretet et al., 2013).
5.4 Results

Results of $\delta^{44/40}$Ca measurements in Modern and fossil corals are given in Table 5.1 and Fig. 5.2. We measure $\delta^{44/40}$Ca compositions in Modern and Late Pleistocene corals ranging from -1.24 ‰ to -1.01 ‰ (vs. modern seawater), consistent with previous studies (Chang et al., 2004; Pretet et al., 2013; Böhm et al., 2006; Blättler et al., 2012). Ca isotope compositions measured in fossil corals become systematically lighter with increasing geologic age (Fig. 5.2). Jurassic-age samples exhibit the lightest Ca isotope compositions with an average of -2.22 ‰, which is approximately 1‰ lighter than the $\delta^{44/40}$Ca measured for Modern corals. The apparent Jurassic coral $\delta^{44/40}$Ca offset from modern seawater also exceeds the inorganic aragonite fractionation factor of -1.7 ‰ (Blättler et al., 2012; Gussone et al., 2005).
Figure 5.2 (a) Records of seawater $\delta^{44/40}$Ca vs. time (Farkaš et al., 2007; Steuber and Buhl, 2006, Sime et al., 2007; Heuser et al., 2005; Soudry et al., 2004; 2006; Schmitt et al., 2003; Griffith et al., 2008; Blättler and Higgins, 2014) including our record from fossil corals. (b) Same as in (a), but enlarged to show only the last 40 Myr. Uncertainties
in fossil coral $\delta^{44/40}\text{Ca}$ are $\pm 0.2\%$ (2$\sigma$ S.D.). Before the Late Eocene, fossil corals disagree with other archives, with the exception of authigenic phosphates. The left-hand axis gives inferred seawater $\delta^{44/40}\text{Ca}$ compositions. The right-hand axis gives measured coral $\delta^{44/40}\text{Ca}$ vs. modern seawater. (c) Records of bulk carbonates from this study (ODP Site 807 and DSDP Site 516), Fantle and DePaolo (2005), and Fantle and DePaolo (2007).

Using the average apparent fractionation between our modern samples and seawater, we convert fossil coral $\delta^{44/40}\text{Ca}$ to seawater $\delta^{44/40}\text{Ca}$ values (Fig. 5.2a and 5.2b – see left-hand axis). Our bulk pelagic carbonates are normalized to modern samples using an offset of $\sim 1.2\%$. This number was chosen based on our Site 807 results (Table 5.2) and data in Fantle and DePaolo (2007). As imposed by our applied offsets, our inferred modern seawater $\delta^{44/40}\text{Ca}$ value from corals overlaps with $\delta^{44/40}\text{Ca}$ compositions inferred from other archives (Fig. 5.2a and 5.2b). However, the fossil coral record departs from other records going back in time to the Mesozoic. In particular, our Mesozoic data are highly divergent from the Farkaš et al. (2007) record reconstructed from brachiopods, belemnites, and rudists (Fig. 5.2a).

Table 5.2 gives results of $\delta^{44/40}\text{Ca}$ measurements in bulk pelagic carbonates from ODP Site 807 and DSDP Site 516. In contrast with fossil corals, the record of bulk carbonate $\delta^{44/40}\text{Ca}$ shows little variability between the Late Mesozoic and today (Fig. 5.2c), with an average $\delta^{44/40}\text{Ca}$ of $-1.33 \pm 0.2 \%$ (2$\sigma$ S.D.; n=48). Our bulk pelagic carbonate record is also in good agreement with other ODP Site 807 and DSDP Site 590 carbonates measured by Fantle and DePaolo (2005) and Fantle and DePaolo (2007).
### Table 5.1. Results of Ca isotope analyses in recent and fossil corals.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Estimated Age (Ma)</th>
<th>$\delta^{44/40}$Ca vs. SW</th>
<th>2σ S.D./S.E.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>ERP</td>
<td>0</td>
<td>-1.01</td>
<td>0.13</td>
<td>3</td>
</tr>
<tr>
<td>M1</td>
<td>0</td>
<td>-1.22</td>
<td>0.02</td>
<td>2</td>
</tr>
<tr>
<td>P13</td>
<td>0.1</td>
<td>-1.21</td>
<td>0.01</td>
<td>3</td>
</tr>
<tr>
<td>P14</td>
<td>0.1</td>
<td>-1.24</td>
<td>0.10</td>
<td>2</td>
</tr>
<tr>
<td>P15</td>
<td>0.1</td>
<td>-1.13</td>
<td>0.11</td>
<td>3</td>
</tr>
<tr>
<td>P12</td>
<td>1</td>
<td>-1.12</td>
<td>0.16</td>
<td>3</td>
</tr>
<tr>
<td>P17</td>
<td>2</td>
<td>-1.20</td>
<td>0.14</td>
<td>3</td>
</tr>
<tr>
<td>P18</td>
<td>2.24</td>
<td>-1.33</td>
<td>0.13</td>
<td>3</td>
</tr>
<tr>
<td>P13</td>
<td>2.34</td>
<td>-1.36</td>
<td>0.10</td>
<td>3</td>
</tr>
<tr>
<td>P12</td>
<td>3.1</td>
<td>-1.04</td>
<td>0.14</td>
<td>2</td>
</tr>
<tr>
<td>P11</td>
<td>3.5</td>
<td>-1.22</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>M16</td>
<td>5.4</td>
<td>-1.13</td>
<td>0.04</td>
<td>2</td>
</tr>
<tr>
<td>M19</td>
<td>6</td>
<td>-1.01</td>
<td>0.09</td>
<td>3</td>
</tr>
<tr>
<td>M11</td>
<td>9.3</td>
<td>-1.15</td>
<td>0.05</td>
<td>4</td>
</tr>
<tr>
<td>M13</td>
<td>11.9</td>
<td>-1.18</td>
<td>0.06</td>
<td>3</td>
</tr>
<tr>
<td>M16</td>
<td>12.3</td>
<td>-1.16</td>
<td>0.06</td>
<td>3</td>
</tr>
<tr>
<td>M14</td>
<td>13</td>
<td>-1.09</td>
<td>0.19</td>
<td>3</td>
</tr>
<tr>
<td>M17</td>
<td>14.0</td>
<td>-1.70</td>
<td>0.15</td>
<td>3</td>
</tr>
<tr>
<td>M12</td>
<td>18</td>
<td>-1.35</td>
<td>0.29</td>
<td>2</td>
</tr>
<tr>
<td>M11</td>
<td>18</td>
<td>-1.39</td>
<td>0.16</td>
<td>3</td>
</tr>
<tr>
<td>M13</td>
<td>18.2</td>
<td>-1.48</td>
<td>0.03</td>
<td>3</td>
</tr>
<tr>
<td>O11</td>
<td>28.5</td>
<td>-1.56</td>
<td>0.12</td>
<td>3</td>
</tr>
<tr>
<td>O15</td>
<td>30</td>
<td>-1.48</td>
<td>0.11</td>
<td>3</td>
</tr>
<tr>
<td>O16</td>
<td>30</td>
<td>-1.58</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>O14</td>
<td>30</td>
<td>-1.53</td>
<td>0.21</td>
<td>2</td>
</tr>
<tr>
<td>O12</td>
<td>31</td>
<td>-1.56</td>
<td>0.07</td>
<td>3</td>
</tr>
<tr>
<td>O13</td>
<td>31.8</td>
<td>-1.56</td>
<td>0.07</td>
<td>2</td>
</tr>
<tr>
<td>E6</td>
<td>35</td>
<td>-1.84</td>
<td>0.01</td>
<td>2</td>
</tr>
<tr>
<td>E1</td>
<td>35</td>
<td>-1.74</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>E8</td>
<td>36</td>
<td>-1.66</td>
<td>0.17</td>
<td>2</td>
</tr>
<tr>
<td>E2</td>
<td>37</td>
<td>-1.58</td>
<td>0.19</td>
<td>3</td>
</tr>
<tr>
<td>E5</td>
<td>45</td>
<td>-1.55</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>E4</td>
<td>45</td>
<td>-1.80</td>
<td>0.16</td>
<td>2</td>
</tr>
<tr>
<td>E3</td>
<td>50</td>
<td>-1.68</td>
<td>0.20</td>
<td>3</td>
</tr>
<tr>
<td>Pa1</td>
<td>60</td>
<td>-1.80</td>
<td>0.23</td>
<td>3</td>
</tr>
<tr>
<td>Pa3</td>
<td>62</td>
<td>-1.69</td>
<td>0.21</td>
<td>3</td>
</tr>
<tr>
<td>K3</td>
<td>84</td>
<td>-2.00</td>
<td>0.05</td>
<td>3</td>
</tr>
<tr>
<td>J1</td>
<td>160</td>
<td>-2.17</td>
<td>0.14</td>
<td>3</td>
</tr>
<tr>
<td>J2</td>
<td>160</td>
<td>-2.06</td>
<td>0.04</td>
<td>2</td>
</tr>
<tr>
<td>J4</td>
<td>161</td>
<td>-2.26</td>
<td>0.04</td>
<td>2</td>
</tr>
</tbody>
</table>
### Table 5.2. Results of Ca isotope analyses on bulk carbonates from deep sea sediments.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Depth (mbsf)</th>
<th>Age (Ma)</th>
<th>δ^{44/40}Ca vs. SW</th>
<th>2σ.S.D.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>807A-2W-2H</td>
<td>7-16.9</td>
<td>0.5</td>
<td>-1.23</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807A-4H-3</td>
<td>27.35-35.5</td>
<td>3</td>
<td>-1.32</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807A-3W-11H</td>
<td>92-102</td>
<td>3.86</td>
<td>-1.22</td>
<td>0.00</td>
<td>2</td>
</tr>
<tr>
<td>807A-9H-2</td>
<td>74.25-83.25</td>
<td>4</td>
<td>-1.30</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807A-21H-2</td>
<td>188.9-197.0</td>
<td>7</td>
<td>-1.30</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807A-5W-42X</td>
<td>389-399</td>
<td>13.9</td>
<td>-1.19</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807A-50X-3</td>
<td>467.3-474.9</td>
<td>19</td>
<td>-1.32</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807A-6W-53X</td>
<td>495-505</td>
<td>21</td>
<td>-1.26</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807A-2W-72X</td>
<td>678.2-687.8</td>
<td>27.5</td>
<td>-1.31</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807A-1W-84X</td>
<td>793-803</td>
<td>32.8</td>
<td>-1.34</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-1W-2R</td>
<td>789-799</td>
<td>30</td>
<td>-1.39</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-2W-6R</td>
<td>828-838</td>
<td>31</td>
<td>-1.30</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-17R-1</td>
<td>904.2-905.9</td>
<td>34</td>
<td>-1.58</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-1W-25R</td>
<td>948-958</td>
<td>38</td>
<td>-1.34</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-1W-38R</td>
<td>1073-1082</td>
<td>45.4</td>
<td>-1.27</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-1W-42R</td>
<td>1101-1106</td>
<td>54</td>
<td>-1.23</td>
<td>0.33</td>
<td>2</td>
</tr>
<tr>
<td>807C-1W-44R</td>
<td>1116-1125</td>
<td>54.5</td>
<td>-1.26</td>
<td>0.37</td>
<td>2</td>
</tr>
<tr>
<td>807C-2W-46R</td>
<td>1135-1140</td>
<td>55</td>
<td>-1.27</td>
<td>0.38</td>
<td>2</td>
</tr>
<tr>
<td>807C-2W-48R</td>
<td>1145-1150</td>
<td>56.6</td>
<td>-1.39</td>
<td>0.26</td>
<td>2</td>
</tr>
<tr>
<td>807C-1W-50R</td>
<td>1155-1160</td>
<td>57</td>
<td>-1.40</td>
<td>0.10</td>
<td>2</td>
</tr>
<tr>
<td>807C-1W-51R</td>
<td>1160-1169</td>
<td>58.9</td>
<td>-1.30</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-2W-51R</td>
<td>1160-1170</td>
<td>58.9</td>
<td>-1.32</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-1W-52R</td>
<td>1169-1178</td>
<td>60</td>
<td>-1.26</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-2W-52R</td>
<td>1169-1179</td>
<td>60</td>
<td>-1.37</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>807C-4W-52R</td>
<td>1169-1180</td>
<td>60</td>
<td>-1.40</td>
<td>0.34</td>
<td>2</td>
</tr>
<tr>
<td>807C-2W-53R</td>
<td>1179-1188</td>
<td>61.5</td>
<td>-1.35</td>
<td>0.16</td>
<td>2</td>
</tr>
<tr>
<td>807C-2W-54R</td>
<td>1188-1196</td>
<td>67</td>
<td>-1.26</td>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>807C-3W-54R</td>
<td>1188-1197</td>
<td>67</td>
<td>-1.24</td>
<td>0.28</td>
<td>2</td>
</tr>
<tr>
<td>807C-4W-54R</td>
<td>1188-1198</td>
<td>67</td>
<td>-1.18</td>
<td>0.34</td>
<td>2</td>
</tr>
<tr>
<td>807C-1W-55R</td>
<td>1196-1206</td>
<td>67.5</td>
<td>-1.04</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>807C-2W-61R</td>
<td>1251-1261</td>
<td>71</td>
<td>-1.38</td>
<td>0.36</td>
<td>2</td>
</tr>
<tr>
<td>807C-2W-62R</td>
<td>1261-1270</td>
<td>71</td>
<td>-1.35</td>
<td>0.26</td>
<td>2</td>
</tr>
<tr>
<td>807C-2W-63R</td>
<td>1270-1280</td>
<td>72</td>
<td>-1.41</td>
<td>0.17</td>
<td>2</td>
</tr>
<tr>
<td>807C-1W-65R</td>
<td>1290-1299</td>
<td>73</td>
<td>-1.37</td>
<td>0.09</td>
<td>2</td>
</tr>
<tr>
<td>807C-1W-67R</td>
<td>1309-1319</td>
<td>74</td>
<td>-1.47</td>
<td>0.17</td>
<td>2</td>
</tr>
<tr>
<td>807C-2W-69R</td>
<td>1328-1338</td>
<td>75</td>
<td>-1.33</td>
<td>0.23</td>
<td>2</td>
</tr>
<tr>
<td>807C-2W-70R</td>
<td>1338-1348</td>
<td>76</td>
<td>-1.29</td>
<td>0.33</td>
<td>2</td>
</tr>
<tr>
<td>807C-1W-71R</td>
<td>1348-1357</td>
<td>76</td>
<td>-1.27</td>
<td>0.36</td>
<td>2</td>
</tr>
<tr>
<td>516F-15-6</td>
<td>310-311.6</td>
<td>24</td>
<td>-1.44</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>516F-20-4</td>
<td>354-356</td>
<td>27</td>
<td>-1.38</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>516F-45-1</td>
<td>587.1-596.6</td>
<td>35</td>
<td>-1.39</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>516F-50-2</td>
<td>636.1-637.6</td>
<td>39</td>
<td>-1.52</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>516F-55-1</td>
<td>682.1-691.6</td>
<td>41</td>
<td>-1.52</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>516F-83-1</td>
<td>900.6-910.1</td>
<td>57</td>
<td>-1.46</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>516F-90-2</td>
<td>967.1-976.6</td>
<td>66</td>
<td>-1.50</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>516F-98-2</td>
<td>1032.6-1041.1</td>
<td>72</td>
<td>-1.59</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>516F-117-3</td>
<td>1184.1-1185.5</td>
<td>86</td>
<td>-1.34</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>516F-121-1</td>
<td>1212.6-1213.6</td>
<td>87</td>
<td>-1.06</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>
5.5 Discussion

There are three possible explanations for the apparent divergence between our coral record and other $\delta^{44/40}$Ca records during the Mesozoic and Early Cenozoic. Fossil coral $\delta^{44/40}$Ca could reflect (1) progressive diagenetic alteration with increasing sample age, (2) variations in seawater $\delta^{44/40}$Ca that are driven by changes in the average fractionation of the main seawater Ca sink (CaCO$_3$), or (3) changes in coral Ca isotope discrimination over time. We show that explanations (1) and (2) are improbable, and then discuss possible mechanisms for (3) in the context of changes in the major element and carbonate chemistry of seawater since the Mesozoic. We conclude that changes in seawater [Ca] and/or pH may have an effect on coral Ca isotope discrimination, and discuss implications for coral biomineralization models.

5.5.1 Fossil coral and bulk pelagic carbonate preservation

It is not plausible to explain the observed trend in fossil coral $\delta^{44/40}$Ca by invoking progressive diagenetic alteration of samples. The fossil coral samples analyzed here for $\delta^{44/40}$Ca were previously screened for alteration by Gothmann et al. (2015) and shown to be extremely well preserved. Techniques used to test for mineralogical changes indicative of diagenesis include X-ray diffractometry, Scanning Electron Microscopy, petrographic microscopy, Cathodoluminescence, and Micro-Raman. Tests used to constrain preservation of sample geochemistry include measurements of $^{87}$Sr/$^{86}$Sr isotopes, carbonate clumped isotopes, and trace elements sensitive to diagenesis (e.g., Mn/Ca). These corals have also been found to faithfully record other properties of seawater chemistry (Mg/Ca, Sr/Ca: Gothmann et al., 2015). It is difficult to conceive of how the trace element composition of our fossil corals could be retained,
while altering the isotopic composition of Ca, which makes up 40% of coral CaCO₃ by mass and which should therefore be more resistant to diagenesis. Moreover, diagenesis – at least for the case of platform carbonates – is known to shift δ⁴⁴/⁴₀⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰Ca compositions toward heavier values (Fantle and Higgins, 2014). Instead, we observe a shift to lighter coral δ⁴⁴/⁴₀⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰Ca with increasing age.

It is also unlikely that our bulk carbonate δ⁴⁴/⁴₀⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰Ca record is reflective of sedimentary diagenesis. The amount of isotopically heavy seawater Ca incorporated into bulk carbonates during diagenesis is diffusion-limited. In fact, the amount is trivial when considered relative to the Ca content of high-carbonate sediments (Fantle and DePaolo, 2007; Fantle et al., 2010). Both ODP Site 807 and DSDP Site 516 sediments range from 75 to >90 wt % carbonate (Barker et al., 1983; Berger et al., 1991), suggesting that pore fluids at both sites are buffered by the high Ca content of the sediments. In other words, recrystallization does not cause the Ca isotope composition of CaCO₃ to change because the flux of “new” Ca to the sediments is small compared to the sedimentary Ca mass. Indeed, Fantle and DePaolo (2007) modeled pore fluid and sediment geochemistry at ODP Site 807 and calculated maximum diagenetic shifts in carbonate δ⁴⁴/⁴₀⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰Ca of 0.1 to 0.15‰, which is similar to our measurement uncertainty. The agreement between δ⁴⁴/⁴₀⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰Ca compositions of carbonates from Pacific (ODP Site 807) and Atlantic (DSDP Site 516) sites gives further confidence that our δ⁴⁴/⁴₀⁰⁰⁰⁰⁰⁰⁰⁰⁰⁰Ca curve from sedimentary carbonate is free from significant diagenetic alteration.
5.5.2 The seawater Ca isotope mass balance

One possible explanation for the divergent coral and pelagic carbonate records is that the coral record, rather than the sedimentary carbonate record, accurately reflects changes in the Ca isotopic composition of seawater through time (i.e., there was a 1‰ increase in seawater $\delta^{44/40}$Ca between the Mesozoic and present).

This hypothetical change in seawater $\delta^{44/40}$Ca can be considered using a simple steady-state Ca isotope mass balance:

$$\delta^{44/40}C_{\text{input}} = \delta^{44/40}C_{\text{output}} = \delta^{44/40}C_{\text{seawater}} - \varepsilon, \quad (\text{Eqn. 5.1})$$

where $\delta^{44/40}C_{\text{input}}$ represents the Ca isotopic composition of the main source of Ca to seawater (rivers), $\delta^{44/40}C_{\text{output}}$ represents the Ca isotopic composition of the main sink of Ca from seawater (CaCO$_3$), $\delta^{44/40}C_{\text{seawater}}$ is the Ca isotopic composition of seawater, and $\varepsilon$ is the globally averaged fractionation factor for the seawater Ca sink (De La Rocha and DePaolo, 2000; Blättler et al., 2012; Fantle and Tipper, 2014). This mass balance indicates that, on timescales longer than the Ca residence time, changes in $\delta^{44/40}C_{\text{seawater}}$ can result either from changes in the isotopic composition of Ca inputs (from rivers) or from changes in the average $\varepsilon$ of the seawater Ca sink. For reference, the Ca residence time is of order $10^6$ years (Sarmiento and Gruber, 2006).

Because pelagic carbonates are thought to constitute a large fraction of the modern seawater Ca sink (>55% according to Milliman, 1993), our bulk pelagic $\delta^{44/40}$Ca record can provide a constraint on $\delta^{44/40}C_{\text{output}}$ and thus $\delta^{44/40}C_{\text{input}}$ as well (Eqn. 5.1). Our bulk carbonate record indicates that the Ca isotopic composition of the pelagic carbonate sink has likely
remained relatively constant over the last 80 Myr. In addition, records of $\delta^{44/40}\text{Ca}$ records from brachiopods, belemnites, and rudists (Farkaš et al., 2007) and bulk forams (e.g., Sime et al. 2007; Heuser et al., 2007) show little variability in $\delta^{44/40}\text{Ca}$ since the Mesozoic. As a result, it is unlikely that $\delta^{44/40}\text{Ca}_{\text{output}}$ shifted by more than 0.2-0.3‰ is unlikely since the Mesozoic. And considering Eqn. 5.1, this also suggests that $\delta^{44/40}\text{Ca}_{\text{input}}$ has not changed greatly.

Assuming little change in $\delta^{44/40}\text{Ca}_{\text{input}}$, then the only mechanism capable of explaining a $\sim 1\%$ change in $\delta^{44/40}\text{Ca}_{\text{seawater}}$ would be a $\sim 1\%$ change in $\varepsilon$ of $\sim 1\%$ (Eqn. 5.1; Fig. 5.2). Measurements of Modern and cultured coccolithophores, foraminifera, and other calcitic biomineralizers suggest a modern fractionation factor of about $-1.3\%$ (Blättler et al., 2012; Fantle and Tipper, 2014). As a result, a $1\%$ shift in seawater $\delta^{44/40}\text{Ca}$ would require the $\varepsilon$ for Mesozoic foraminifera, coccolithophores, and brachiopods to have been $-0.2$ to $-0.3\%$. Evidence against a $\sim 1\%$ change in $\delta^{44/40}\text{Ca}_{\text{seawater}}$ and $\varepsilon$ comes from the Ca isotopic composition of seawater as inferred from CaSO$_4$ evaporites (Blättler and Higgins, 2014; Farkaš et al., 2007). These archives indicate that seawater $\delta^{44/40}\text{Ca}$ may have been $0.2$-$0.3\%$ lower during the Cretaceous but do not support a large, $>0.5\%$ increase in seawater $\delta^{44/40}\text{Ca}$.

### 5.5.3 Ca isotope discrimination in corals since the Mesozoic

For the reasons described above, we suggest that our coral $\delta^{44/40}\text{Ca}$ record most likely reflects a decrease in coral Ca isotope discrimination since the Mesozoic. Specifically, we propose that this change in coral Ca isotope discrimination results from a response of coral calcification to variations in key seawater carbonate chemistry parameters such as [Ca] and pH. We choose these variables because they empirically correlate with our coral Ca isotope record.
Assuming the Farkaš et al. (2007) data set provides the most robust current representation of seawater δ\(^{44/40}\)Ca during the Mesozoic and Cenozoic, we calculate the apparent fractionation between fossil corals and seawater, and plot those results against seawater [Ca] estimated for the time at which each coral grew (see supplementary text for details; Fig. 5.3). Inferred seawater [Ca] is calculated from a linear interpolation between seawater [Ca] data reconstructed from brine inclusions in halite (Lowenstein et al., 2003; Brennan et al., 2013). We observe an inverse relationship between apparent coral Ca fractionation and the estimated seawater [Ca] at the time of skeletal growth (Fig. 5.3). Seawater [CO\(_3^{2-}\)] and pH also co-vary with [Ca] over this time period (Tyrrell and Zeebe, 2004; Hönisch et al., 2012; Zeebe et al., 2012). As a result, we cannot exclude the possibility that these geochemical variables may also contribute to the change in apparent Ca isotope fractionation we observe. The overall magnitude of change in apparent Ca isotope discrimination between Modern and Mesozoic corals is ~0.8 ‰.
Figure 5.3 Fossil and cultured coral Ca isotope discrimination. (a) Measured fractionation between growth solution and coral skeleton for experiments at modern and elevated seawater [Ca]. Saturation state in experiments also varied. The average saturation state for each [Ca] scenario is presented in grey text. (b) Estimated isotope fractionation between coral and inferred seawater for fossil corals and for seawater [Ca] experiments. Estimates for seawater [Ca] come from Lowenstein et al. (2001) and Brennan et al. (2013). An offset is applied to the seawater [Ca] experiment data such that the apparent fractionations are the same at modern seawater [Ca] (10.6 mmol/kg). Error bars for the average offset (grey squares) of seawater [Ca] experiments represent 2σ standard errors.
To evaluate the hypothesis that coral Ca isotope fractionation may be sensitive to seawater [Ca], we measured Ca isotopes in cultured corals grown in solutions with [Ca] ranging from 10 to 15 mmol/kg (Table 5.3). The apparent fractionation between growth solution and coral skeleton for cultured corals is plotted against growth solution [Ca] in Fig. 5.3. We find that corals cultured at 15 mmol/kg show a ~0.15‰ increase in Ca isotope discrimination relative to the modern controls. This change in discrimination for cultured corals is in the same direction, but of slightly smaller magnitude, than the change we observe in our fossil corals. Given the fossil coral relationship, we would have expected a ~0.25‰ increase (Fig. 5.3). The growth experiment results give some support for our [Ca] hypothesis. However, additional experiments covering the full natural range of seawater [Ca] for the Mesozoic and Cenozoic are necessary to confirm a relationship between Ca isotope discrimination and seawater [Ca]. Although other seawater properties ([Mg] and [Sr]) were also varied in some of the experimental cases, we see no relationship between our cultured coral $\delta^{44/40}$Ca and these properties (see supplementary materials).

**Table 5.3** Results of Ca isotope analyses in cultured corals. Each sample represents the average offset between pairs of seawater solution, and the coral that was grown in that solution.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>[Ca]$_{seawater}$ (mmol/kg)</th>
<th>$\delta^{44/40}$Ca Offset (coral - seawater)</th>
<th>2σ S.D.</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>10</td>
<td>-1.12</td>
<td>0.13</td>
<td>3</td>
</tr>
<tr>
<td>2x_Sr</td>
<td>10</td>
<td>-1.14</td>
<td>0.29</td>
<td>3</td>
</tr>
<tr>
<td>100_Mg</td>
<td>10</td>
<td>-1.15</td>
<td>0.20</td>
<td>3</td>
</tr>
<tr>
<td>200_Mg</td>
<td>10</td>
<td>-1.12</td>
<td>0.14</td>
<td>2</td>
</tr>
<tr>
<td>100Ca100Mg</td>
<td>12.5</td>
<td>-1.27</td>
<td>0.03</td>
<td>2</td>
</tr>
<tr>
<td>100Ca200Mg</td>
<td>12.5</td>
<td>-1.26</td>
<td>0.09</td>
<td>3</td>
</tr>
<tr>
<td>100Ca</td>
<td>12.5</td>
<td>-1.15</td>
<td>0.08</td>
<td>2</td>
</tr>
<tr>
<td>200Ca200Mg</td>
<td>15</td>
<td>-1.28</td>
<td>0.18</td>
<td>3</td>
</tr>
<tr>
<td>200Ca200Mg$_{133}$</td>
<td>15</td>
<td>-1.30</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>200Ca</td>
<td>15</td>
<td>-1.24</td>
<td>0.11</td>
<td>4</td>
</tr>
</tbody>
</table>
In the following sections, we explore various mechanisms that may lead to our hypothesized variation in coral Ca isotope fractionation over geologic timescales. We focus particularly on those that may be dependent on seawater [Ca] and/or pH. This is because both [Ca] and pH may influence calcification dynamics. For example, These mechanisms include (1) changes in coral calcification rates through time, (2) changes in proton pumping in exchange for Ca\(^{2+}\), (3) changes in Rayleigh distillation dynamics, and (4) changes in the steady-state Ca mass balance of the calcifying fluid (which we refer to as the ‘leaky Ca model’).

5.5.3.1 Calcification rate

Calcium isotope fractionation has been shown to be sensitive to calcification rate (Lemarchand et al., 2004; Tang et al., 2008; Gussone et al., 2003, 2005), but different inorganic carbonate precipitation experiments give conflicting results for the \(\delta^{44/40} \text{Ca}\) rate dependence. The Tang et al. (2008) calibration for inorganic calcite shows an inverse relationship between \(\delta^{44/40} \text{Ca}\) and calcification rate. For this relationship, an increase in coral \(\delta^{44/40} \text{Ca}\) between the Mesozoic and present would be consistent with decreasing calcification rates over that time. In contrast, the Gussone et al. (2005) calibration for inorganic aragonite and the Lemarchand et al. (2004) show a positive relationship between calcification rate and \(\delta^{44/40} \text{Ca}\). This relationship would instead be consistent with increasing calcification rates between the Mesozoic and present. Although the direction for the calcification rate dependence differs between published inorganic precipitation experiments, they all generally show that the \(\delta^{44/40} \text{Ca}\) of inorganic calcium carbonate varies by up to 1.5‰ over a two order of magnitude range in precipitation rate (Lemarchand et al. 2004; Gussone et al. 2003; 2005; Tang et al. 2008). This observation suggests
that coral calcification rates would have needed to vary significantly – by about a factor of 10 – between the Mesozoic and today to generate the ~0.8‰ change in apparent fractionation in fossil corals.

Such a large change in calcification rates since the Mesozoic seems unlikely. As inferred from culture experiments, rates of coral aragonite growth seem to correlate most strongly with the saturation state of seawater ($\Omega = [\text{Ca}] \times ([\text{CO}_3^{2-}]/K_{sp})$) with respect to aragonite (Gattuso et al. 1998; Marubini and Atkinson, 1999; Marubini et al. 2008; Maier et al. 2009). Seawater pH and $[\text{CO}_3^{2-}]$ have increased significantly since the Mesozoic (Pearson and Palmer, 1999; Hönisch et al., 2012, Tyrrell and Zeebe, 2004). However, constraints from reconstructions of the calcium carbonate compensation depth through time suggest that seawater $\Omega$ has not changed significantly over this same time interval (Tyrrell and Zeebe, 2004). As a result, we suggest that changes in calcification rate probably cannot account for observed changes in fossil coral $\delta^{44/40}$Ca since the Mesozoic. In addition, a calcification rate dependence does not seem to explain our cultured coral data. Although calcification rates in our culture experiments from this study, as calculated from the alkalinity anomaly method and normalized to buoyant weights, are inversely related to culture [Ca] there is no significant relationship between coral $\delta^{44/40}$Ca and calcification rate (see supplementary materials; Fig. 5.6).

5.5.3.2 Changes in proton pumping – a dependence of Ca-ATPase on external seawater pH

Corals exchange protons for $\text{Ca}^{2+}$ via Ca-ATPase in order to elevate their internal ‘calcifying fluid’ pH and promote calcification (McConnaughey, 1989; Al-Horani et al., 2003; Zoccola et al., 2004; Gaetani et al., 2011). Measurements of boron isotopes and experiments
using pH-sensitive dye suggest that the magnitude of the calcifying fluid pH elevation is inversely related to seawater pH (Venn et al., 2013; McCulloch et al. 2012). Ca isotope fractionation associated with active transport is estimated to be between -1.3 and -1.7‰ (De La Rocha and DePaolo, 2000; Gussone et al. 2006; Böhm et al. 2006; Gussone et al. 2009). This estimate is based on the isotope effect observed for modern coccolithophore calcite because almost all calcium in coccolith calcite is thought to derive from active transcellular transport (Gussone et al., 2006). As such, variations in the fraction of Ca derived from seawater, relative to the amount derived from active transport by Ca-ATPase in exchange for H⁺, could also drive a change in the Ca isotope composition of the coral calcifying fluid.

Recently, a set of coral culture experiments with Porites australiensis was conducted that investigated the effects of pH on coral δ⁴⁴/⁴⁰Ca (Inoue et al. 2015). In the experiments, the pH of growth solutions was varied from 7.4 to 8.1 by bubbling with CO₂. δ⁴⁴/⁴⁰Ca of cultured coral skeleton precipitated in the different pH treatments shows no with culture solution pH (Inoue et al. 2015), which suggests that a sensitivity to pH may not be able to explain the changes we observe in fossil coral δ⁴⁴/⁴⁰Ca since the Mesozoic.

5.5.3.3 A dependence on seawater [Ca] - Rayleigh fractionation

Rayleigh distillation could fractionate Ca isotopes in a manner dependent on seawater [Ca]. The Rayleigh fractionation hypothesis proposes that during calcification, seawater is transported to the calcification site and corals precipitate from the isolated fluid. As calcification proceeds from the fluid, element/Ca ratios, or isotope ratios, become progressively enriched or depleted according to their partitioning behavior into the solid phase. For example, Mg/Ca ratios
become enriched and Sr/Ca ratios become depleted (since the $K_D$ for Sr/Ca $> 1$ and the $K_D$ for Mg/Ca $<< 1$) (Cohen et al., 2006; Gagnon et al., 2007). Inorganic aragonite is isotopically depleted in the heavy isotopes of Ca relative to seawater. Corals fractionate in the same direction as inorganic aragonite, so the $\delta^{44}\text{Ca}$ of both coral aragonite and the residual fluid should become progressively heavy as calcification proceeds.

In the Rayleigh framework, the degree of calcium drawdown during precipitation is represented by the term $f$ - defined as the fraction of Ca remaining in the fluid. At an $f$ of 1, the $[\text{Ca}]$ of the fluid is equal to the original $[\text{Ca}]$. At an $f$ of 0, all of the calcium present in the original fluid has been consumed.

It is currently unclear what determines the amount of Ca remaining in the calcifying fluid ($f$), but it is possible that this parameter depends on the original concentration of Ca in the calcifying fluid. Here, we consider the specific case wherein we assume corals precipitate a fixed mass of Ca from their calcifying fluids regardless of external seawater $[\text{Ca}]$. We acknowledge that in reality, the extent of Ca drawdown may actually depend on a range of other factors. For example, it could be that the corals precipitate CaCO$_3$ until a given calcifying fluid Ca concentration or saturation state is reached. The Rayleigh $f$ has also been hypothesized to be dependent on external seawater pH and/or alkalinity (Gagnon et al., 2013). Such scenarios would yield different predictions for how $f$ changes with variations in external seawater $[\text{Ca}]$, but we do not explore them here.
**Figure 5.4** Results of Rayleigh fractionation calculations. The solid black line corresponds to the instantaneous produce and the black dashed line corresponds to the integrated product of $\delta^{44}\text{Ca}$ in coral for the cases of Modern, Early Cenozoic, and Cretaceous seawater [Ca]. Modern $f$ is assumed to be 0.5. The equilibrium isotope effect for coral is assumed to be the same as the isotope effect for inorganic aragonite, -1.7‰ (Gussone et al., 2003; Blättler et al., 2012). The value for $f$ for each seawater scenario is indicated with the light gray arrows and is set by the requirement that the total mass of Ca precipitated from each ‘batch’ of seawater during distillation remains constant. The value for calculated coral $\delta^{44}\text{Ca}$ in each seawater scenario is indicated by the dark grey arrow on the y-axis.

*Fig. 5.4* shows plots of the instantaneous and integrated products of $\delta^{44}\text{Ca}$ in coral under a Rayleigh fractionation scenario for Modern, Early Cenozoic, and Cretaceous seawater [Ca] conditions (Gaetani et al., 2011; Gagnon et al., 2007). The calculations used to generate each plot assume a Ca drawdown of 5 mmol/L such that the total mass of Ca precipitated from
each ‘batch’ of seawater during distillation remains constant (as stated above) in each case. For
the Modern scenario, where the Ca concentration in the calcifying fluid is assumed to be equal to
modern seawater ([Ca] = 10.6 mmol/L), the total fraction of Ca remaining in the calcifying fluid,
f, is 0.5. This value is compatible with independent estimates for f based on studies of modern
surface corals (e.g., Gaetani et al., 2011). The isotope effect for coral aragonite precipitation is
set to be 1.7 ‰ - equal to the inorganic aragonite fractionation (Gussone et al., 2003; Blättler et
al., 2012). We calculate that f shifts from a value of 0.5 for the case of modern seawater [Ca] to a
value of ~0.8 for Cretaceous seawater [Ca]. This magnitude of change in f leads to a 0.3‰
depletion in the δ44Ca integrated product between the Modern and Cretaceous case. Such a
change cannot account for the full, 0.8‰ decrease in Ca isotope discrimination between the
Mesozoic and today. We conclude that a Rayleigh fractionation response to changes in seawater
[Ca] can contribute to the observed δ44Ca increase in fossil corals, but cannot explain the entire
change. In addition, if f – on average – has remained constant since the Mesozoic, no change in
coral δ44Ca is expected.

5.5.3.4 A response to higher seawater [Ca] – the ‘leaky calcium model’

It is also possible that the calcifying fluid remains open to seawater and can be
modeled as a steady state system with respect to Ca inputs and outputs (e.g., Gagnon et al., 2012;
Fig. 5.5). In this case, the isotopic composition of Ca precipitated from the calcifying fluid
depends on: (1) the exchange rate of Ca between seawater and the calcifying fluid relative to Ca
incorporation into the coral skeleton, and (2) the isotope effects associated with each pathway.
We call this model the ‘leaky calcium model’. Calcium isotope discrimination in this ‘leaky
calcium model’ can be likened to carbon isotope discrimination by RuBisCO in plants – the magnitude of which is dependent on atmospheric CO$_2$ concentrations (Farquhar, 1982; Pagani, 2014).

![Figure 5.5 Schematic showing the steady Ca mass balance of the coral calcifying fluid.](image)

We assume that Ca is sourced to the calcifying fluid by direct transport of seawater, and that contributions from Ca-ATPase are minimal (see Section 5.1.2.2; Figs. 5.1 and 5.5). Ca is removed by skeletal precipitation or by advective or diffusive transport back to seawater. We also assume that the isotope effect associated with skeletal precipitation from the calcifying fluid is equal to the fractionation factor for inorganic aragonite, 1.7‰ (Gussone et al., 2003; Blättler et al., 2012). Following expressions for carbon isotope fractionation by RuBisCo (Farquhar, 1982; Pagani, 2014), we express Ca isotope fractionation for this system as follows:

$$\Delta_{\text{Coral-Arag}} = \varepsilon_{\text{transport}} + (\varepsilon_{\text{ppt}} - \varepsilon_{\text{transport}}) \times F \quad \text{(Eqn. 5.2)}$$

where $\varepsilon_{\text{transport}}$ represents the isotope effect associated with transport of Ca from seawater to the calcifying fluid, $\varepsilon_{\text{ppt}}$ is the isotope effect associated with skeletal precipitation, $F$ represents the
fraction of Ca that is transported (by diffusion or advection) back to seawater from the calcifying fluid, and $\Delta_{\text{Coral-Arag}}$ is the total fractionation expressed in the coral skeleton. We assume that no isotope effect occurs during transport of seawater into the calcifying space, such that $\varepsilon_{\text{transport}} = 0$.

If the mass of CaCO$_3$ precipitated from the calcifying fluid is constant, $\Delta_{\text{Coral-Arag}}$ will increase at higher seawater [Ca] because a greater fraction of Ca will be transported back to seawater relative to the total amount of Ca in the calcifying fluid. In other words, $F$ will increase as seawater [Ca] increases. Alternatively, we can write a steady state equation for the ‘leaky calcium’ scenario:

$$ R^{44/40}\text{Ca}_{\text{coral}} = \frac{\alpha \times R^{44/40}\text{Ca}_{\text{seawater}}}{(F + \alpha \times (1 - F))} \quad \text{(Eqn. 5.3)} $$

where $F$ is the fraction of Ca that exits the calcifying fluid and is transported back seawater (Fig. 5.5, b) relative to the amount transported in (Fig. 5.5, a). Quantitatively, Eqn. 5.3 produces results similar in magnitude to the Rayleigh model. Assuming a modern $F$ of 0.5 (as in Section 5.4.2.3), and assuming again that the mass of Ca precipitated as coral aragonite stays constant through time, we calculate a $\sim 0.3\%$ depletion in the integrated product between the Modern and Cretaceous case – indistinguishable from results calculated for a Rayleigh distillation scenario. We conclude as above, that the ‘leaky Ca model’ can contribute to the observed $\delta^{44}$Ca increase in fossil corals, but cannot explain the entire change.
5.6 Conclusions

We measured the Ca isotope composition of a suite of extremely well preserved aragonitic fossil corals. Results of fossil coral $\delta^{44/40}$Ca measurements, together with data from bulk pelagic carbonates, indicate that coral Ca isotope discrimination has decreased by $\sim 0.8\%$ between the Mesozoic and today. We propose that a decrease in discrimination against the heavy isotopes of Ca is related to a vital effect of calcification – more specifically, to a response of biomineralization dynamics to secular variations in seawater [Ca]. Culture experiments that test for the dependence of coral $\delta^{44/40}$Ca on growth solution [Ca] lend some support for this hypothesis. However, additional experiments are necessary to confirm the sensitivity over the natural range of seawater [Ca] for the Mesozoic and Cenozoic. Changes in Rayleigh fractionation dynamics, or a ‘leaky Ca model’ may be able to explain part of the apparent change in Ca isotope discrimination. Our results provide geochemical constraints on models of coral biomineralization, and emphasize the importance of understanding the mechanisms driving vital effects in biogenic carbonates that are used to reconstruct ancient environmental properties.

5.7 Acknowledgements

We would like to thank Stephen Cairns and Tim Coffer (Smithsonian Institution), Linda Ivany (Syracuse University), Roger Portell (Florida Museum of Natural History), Anne Cohen and Bill Thompson (WHOI), the USGS, and Gregory Dietl (Paleontological Research Institution) for loaning samples. We would also like to thank Alex Gagnon for helpful discussions and Elizabeth Lundstrom for analytical support.
5.8 Author contributions and previous presentations of this work

Initial planning of the project was by Anne Gothmann, Michael Bender, and John Higgins. Anne Gothmann prepared samples, conducted Ca isotope measurements, and analyzed and interpreted the data with help from Michael Bender, John Higgins, Clara Blättler, Jess Adkins, Jarek Stolarski, Peter Swart, and Sharmila Giri. Jarek Stolarski contributed many fossil coral samples used for this work. Sharmila Giri conducted coral growth experiments, which were later analyzed by Anne Gothmann.

This work is in prep for submission to Earth and Planetary Science Letters.

This work was presented as:

5.9 Supplementary

<table>
<thead>
<tr>
<th>ID</th>
<th>Genus</th>
<th>Species</th>
<th>Location (Latitude and Longitude)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td></td>
<td></td>
<td>Guantanamo Bay, Cuba</td>
</tr>
<tr>
<td>P12</td>
<td>Asterosmilia</td>
<td>exarata</td>
<td>Limon Group, Moin Fm., Lomas del Mar Plateau, Costa Rica. Shallowing-upward sequence of coral-rich and silicilastic sediment (10.0° N, 83.1° W)</td>
</tr>
<tr>
<td>P13</td>
<td></td>
<td></td>
<td>Barbados</td>
</tr>
<tr>
<td>P14</td>
<td></td>
<td></td>
<td>Barbados</td>
</tr>
<tr>
<td>P15</td>
<td></td>
<td></td>
<td>Barbados</td>
</tr>
<tr>
<td>P17</td>
<td>Siderastrea</td>
<td>sp.</td>
<td>Caloosahatchee Fm., Florida (26.0° N, 81.7° W)</td>
</tr>
<tr>
<td>P18</td>
<td>Septastrea</td>
<td>marylandica</td>
<td>Waccamaw Fm., North Carolina (33.9° N, 78.8° W)</td>
</tr>
<tr>
<td>P1i</td>
<td>Antillocyathus</td>
<td>maoensis</td>
<td>Gurabo Fm., Dominican Republic (19.5° N, 70.7° W)</td>
</tr>
<tr>
<td>P1ii</td>
<td>Oculina</td>
<td>sarasotana</td>
<td>Tamiami Fm., Pinecrest Beds, Florida (26.9° N, 82.0° W)</td>
</tr>
<tr>
<td>P1iii</td>
<td>Septastrea</td>
<td>crassa</td>
<td>Yorktown Fm., Virginia (37.2° N, 76.9° W)</td>
</tr>
<tr>
<td>M1</td>
<td></td>
<td></td>
<td>Chipola Fm., Florida (30.4° N, 85.0° W)</td>
</tr>
<tr>
<td>M12</td>
<td></td>
<td></td>
<td>Chipola Fm., Florida (30.4° N, 85.0° W)</td>
</tr>
<tr>
<td>M13</td>
<td></td>
<td></td>
<td>Chipola Fm., Florida (30.4° N, 85.0° W)</td>
</tr>
<tr>
<td>M16</td>
<td>Porites</td>
<td>sp.</td>
<td>Dominican Republic (19.5° N, 70.7° W)</td>
</tr>
<tr>
<td>M17</td>
<td>Paracyathus</td>
<td>cupola</td>
<td>Holy Cross Mountains, Korytnica Basin, Poland (50.6° N, 20.5° E)</td>
</tr>
<tr>
<td>M19</td>
<td></td>
<td></td>
<td>Enowetak Atoll, Marshalls Islands. Shallow-water, lagoon sediment rich in carbonate mud and fossils (11.6° N, 162.3° E)</td>
</tr>
<tr>
<td>M11</td>
<td></td>
<td></td>
<td>Enowetak Atoll, Marshalls Islands. Shallow-water, lagoon sediment rich in carbonate mud and fossils (11.6° N, 162.3° E)</td>
</tr>
<tr>
<td>M13</td>
<td></td>
<td></td>
<td>Enowetak Atoll, Marshalls Islands. Shallow-water, lagoon sediment rich in carbonate mud and fossils (11.6° N, 162.3° E)</td>
</tr>
<tr>
<td>M14</td>
<td></td>
<td></td>
<td>Enowetak Atoll, Marshalls Islands. Shallow-water, lagoon sediment rich in carbonate mud and fossils (11.6° N, 162.3° E)</td>
</tr>
<tr>
<td>M16</td>
<td></td>
<td></td>
<td>Enowetak Atoll, Marshalls Islands. Shallow-water, lagoon sediment rich in carbonate mud and fossils (11.6° N, 162.3° E)</td>
</tr>
<tr>
<td>O1</td>
<td>Turbinaria</td>
<td>sp.</td>
<td>Aquitane, France (43.8°N, 1.1°W)</td>
</tr>
<tr>
<td>O11</td>
<td>Balanophyllia</td>
<td>irregularis</td>
<td>Siemien, Poland (51.2° N, 22.6° E)</td>
</tr>
<tr>
<td>O12</td>
<td>Balanophyllia</td>
<td>irrorta</td>
<td>Mississippi</td>
</tr>
<tr>
<td>O13</td>
<td>Oculina</td>
<td>vickshurgensis</td>
<td>Byram Fm., Mississippi (32.0° N, 89.4° W)</td>
</tr>
<tr>
<td>O14</td>
<td>Archohelia</td>
<td>vickshurgensis</td>
<td>Byram Fm., Mississippi (32.0° N, 89.4° W)</td>
</tr>
<tr>
<td>O15</td>
<td>Archohelia</td>
<td>vickshurgensis</td>
<td>Byram Fm., Mississippi (32.0° N, 89.4° W)</td>
</tr>
<tr>
<td>O16</td>
<td>Archohelia</td>
<td>vickshurgensis</td>
<td>Byram Fm., Mississippi (32.0° N, 89.4° W)</td>
</tr>
<tr>
<td>E1</td>
<td></td>
<td></td>
<td>Gosport Sand Fm., Alabama (31.5° N, 87.9° W)</td>
</tr>
<tr>
<td>E2</td>
<td>Balanophyllia</td>
<td>irregularis</td>
<td>Siemien, Poland (51.2° N, 22.6° E)</td>
</tr>
<tr>
<td>E3</td>
<td>Balanophyllia</td>
<td>caulifera</td>
<td>Mississippi</td>
</tr>
<tr>
<td>E4</td>
<td>Balanophyllia</td>
<td>desmophyllum</td>
<td>Alabama</td>
</tr>
<tr>
<td>E5</td>
<td>Araeacis</td>
<td>michelini</td>
<td>France</td>
</tr>
<tr>
<td>E6</td>
<td></td>
<td></td>
<td>Ukraine</td>
</tr>
<tr>
<td>E8</td>
<td>Endopachys</td>
<td>maclurii</td>
<td>Moodys Branch Fm., Louisiana (31.5° N, 87.8° W)</td>
</tr>
<tr>
<td>Pa1</td>
<td>Paracyathus</td>
<td>sp.</td>
<td>Monrow Co., North Dakota</td>
</tr>
<tr>
<td>Pa3</td>
<td>Flabellum</td>
<td>conoideum</td>
<td>Wills Point Fm., Colorado River, Caldwell Ranch, Texas (30.3° N, 97.7° W)</td>
</tr>
<tr>
<td>K3</td>
<td>Rennensismilia</td>
<td>complanata</td>
<td>Lower Gosau beds, Gosau, Austria. Sedimentary matrix is dark grey clay (47.6° N, 13.5° E)</td>
</tr>
<tr>
<td>J1</td>
<td>Isastraea</td>
<td>cf. benensis</td>
<td>Ostromice, Poland (53.8° N, 14.8° E)</td>
</tr>
<tr>
<td>J2</td>
<td>Thamnasteria</td>
<td>sp.</td>
<td>Ostromice, Poland (53.8° N, 14.8° E)</td>
</tr>
<tr>
<td>J4</td>
<td>Thamnasteria</td>
<td>gracilis</td>
<td>Hohenferchesar, Germany</td>
</tr>
</tbody>
</table>

Table 5.4 Fossil coral identification and provenance
Calculation of ancient seawater [Ca] and Δ(Coral-Farkaš) used in Fig. 5.3:

Records of ancient seawater [Ca] are derived from the composition of fluid inclusions in halite (e.g. Lowenstein et al., 2001, 2003, 2005; Brennan et al., 2013). To allow for direct comparison between fossil coral δ⁴⁴Ca and seawater [Ca] at the time of coral growth, we linearly interpolate between the results of seawater [Ca] reconstructions given in Lowenstein et al., (2003). Brennan et al. (2013) reconstruct a range of [Ca] concentrations for each of their samples. We take the average [Ca] from this range, but note that the uncertainty on these averages is ~ ±4 mmol/kg [Ca] (Lowenstein et al., 2003; Fig. 3B of the main text). To calculate Δ(Coral-Farkaš) we assume that the Farkaš et al. (2007) represents seawater δ⁴⁴Ca and we linearly interpolate between data to obtain a value for seawater δ⁴⁴Ca in 1 Myr intervals. Where multiple samples exist for a given 1 Myr interval, we average the data. The apparent isotope discrimination for our fossil corals is then calculated by taking the difference between our coral sample and the isotopic composition interpolated from the Farkaš et al. (2007) record at the same geologic age as our sample.

Rayleigh equations used to generate Fig. 5.4:

\[ \frac{R_{\text{coral}}^{44/40}}{R_{\text{sw}}^{44/40}} = \alpha f^{(\alpha-1)} \]

\( R_{\text{coral}}^{44/40} / R_{\text{sw}}^{44/40} = (f^\alpha - 1) / (f - 1) \)

\( R_{\text{coral}}^{44/40} / R_{\text{sw}}^{44/40} = \alpha f^{(\alpha-1)} \)

\( R_{\text{coral}}^{44/40} / R_{\text{sw}}^{44/40} = (f^\alpha - 1) / (f - 1) \)

\( R_{\text{coral}}^{44/40} / R_{\text{sw}}^{44/40} = \alpha f^{(\alpha-1)} \)

\( R_{\text{coral}}^{44/40} / R_{\text{sw}}^{44/40} = (f^\alpha - 1) / (f - 1) \)
Figure 5.6 (a) Relationship between growth rate and culture solution [Ca]. (b) Relationship between $\delta^{44}\text{Ca}$ of cultured corals grown under varying [Ca] conditions and their measured growth rates. There is no apparent relationship between $\delta^{44}\text{Ca}$ and growth rate for our experiments.
Figure 5.7 $\delta^{44}$Ca of cultured corals vs. culture solution [Mg]. Each panel represents a different culture solution [Ca] scenario. The y-axis scales for each panel are the same. There does not appear to be a relationship between coral $\delta^{44}$Ca and solution [Mg]. The blue arrow corresponds to the one culture solution in which [Mg] was not elevated, [Ca] was not elevated, but [Sr] was 2x modern concentrations.
CHAPTER 5. CALCIUM ISOTOPE IN SCLERACTIAN FOSSIL CORALS SINCE THE MESOZOIC: IMPLICATIONS FOR VITAL EFFECTS AND BIOMINERALIZATION THROUGH TIME

References


Proc. ODP, Initial Reports, Ocean Drilling Program, 497-537.


208


CHAPTER 5. CALCIUM ISOTOPE IN SCLERACTIAN FOSSIL CORALS SINCE THE MESOZOIC: IMPLICATIONS FOR VITAL EFFECTS AND BIOMINERALIZATION THROUGH TIME


CHAPTER 5. CALCIUM ISOTOPE IN SCLERACTIAN FOSSIL CORALS SINCE THE MESOZOIC: IMPLICATIONS FOR VITAL EFFECTS AND BIOMINERALIZATION THROUGH TIME

_Cosmochimica Acta_ 67, 1375-1382.


Heuser, A., Eisenhauer, A., 2008. The Calcium Isotope Composition ($\delta^{44/40}$Ca) of NIST SRM 915b and NIST SRM 1486. _Geostandards and Geoanalytical Research_ 32, 311-315.


CHAPTER 5. CALCIUM ISOTOPE IN SCLERACTIAN FOSSIL CORALS SINCE THE MESOZOIC:
IMPLICATIONS FOR VITAL EFFECTS AND BIOMINERALIZATION THROUGH TIME

*Cosmochimica Acta* 66, 3733-3756.


McConnaughey, T., 1989. ¹³C and ¹⁸O isotopic disequilibrium in biological carbonates: II. In


Mertz-Kraus, R., Brachert, T.C., Reuter, M., Galer, S.J.G., Fassoulas, C., Iliopoulous, G., 2009. Late Miocene sea surface salinity variability and paleoclimate conditions in the Eastern
Mediterranean inferred from coral aragonite $\delta^{18}O$. Chemical Geology 262, 202-216.


Chapter 5. Calcium Isotope in Scleractian Fossil Corals since the Mesozoic: Implications for Vital Effects and Biomineralization Through Time

Schmitt, A.-D., P. Stille, and T. Vennemann, 2003. Variations of the $^{44}\text{Ca}/^{40}\text{Ca}$ ration in seawater during the past 24 million years: Evidence from $\delta^{44}\text{Ca}$ and $\delta^{18}\text{O}$ values of Miocene phosphates. *Geochimica et Cosmochimica Acta* 67, 2607-2614.


Tang, J., Dietzel, M., Bohm, A., Kohler, P., Eisenhauer, A., 2008. \(\text{Sr}^{2+}/\text{Ca}^{2+}\) and \(\text{Ca}^{44}/\text{Ca}^{40}\) fractioning during inorganic calcite formation: II. Ca isotopes. *Geochimica et Cosmochimica Acta* 72, 3733-3745.


Tyrrell, T., Zeebe, R.E., 2004. History of carbonate ion concentration over the last 100 million

doi: 10.3334/CDIAC/otg.CO2SYS_MATLAB_v1.1


Appendix

A.1 Introduction

Studies of lithium and its isotopes (\(^{7}\text{Li}\) and \(^{6}\text{Li}\)) have the potential to yield important information about Earth’s surface environment. Because of the large relative mass difference between the two isotopes (16\%), sizeable Li isotope fractionations are expressed in nature. In fact, the range of measured Li isotope compositions in natural samples is > 50 \(\text{‰}\) (Tomascak et al., 2004). These fractionations have been observed to occur during weathering of rocks on land, magmatic processes, mantle processes, hydrothermal processes, and the biogenic and inorganic formation of minerals such as calcium carbonate (Tomascak et al. 2004; Huh et al. 1998; James et al., 1999; Pistiner and Henderson, 2003; Chan et al. 2002; Vigier et al. 2008; Vigier et al. 2015; Marriot et al., 2004).

Because of the prevalence of lithium in silicate minerals, Li and its isotopes are particularly good candidates for tracing of changes in cycling of silicate rocks over time (Tomascak et al. 2004). Such changes can be tracked by reconstructing histories of the Li isotope composition of seawater, which is also strongly influenced by silicate-related geologic processes (Tomascak et al. 2004; Huh et al. 1998; James et al., 1999; Chan et al. 2002; Pogge von Strandmann et al. 2010; Misra and Froelich, 2012). The two main sources of Li to seawater are silicate weathering on the continents and high-temperature hydrothermal alteration of basalt (Huh et al. 1998; Elderfield and Schultz, 1996; Chan et al. 2002; Huh et al. 2001; Pistiner and Henderson, 2003; Pogge von Strandmann et al., 2010). The main sinks of lithium from seawater are low-temperature hydrothermal alteration and uptake in clay minerals (Chan et al. 2002; James et al. 1999; Vigier et al. 2008). Accordingly, and considering the relatively long residence
time of Li in seawater (~1.2 My; Sarmiento and Gruber, 2006), records of seawater δ^{7}Li can provide insight into geologic processes that play a role in the geological carbon cycle on million-year timescales (e.g., silicate weathering, hydrothermal alteration, clay authigenesis).

A recent record of the Li isotope composition of seawater, reconstructed from planktonic foraminifera, shows a ~9 ‰ increase in seawater δ^{7}Li between 60 Ma and today (Misra and Froelich, 2012). This result suggests significant changes in the sources and/or sinks of Li to seawater since the Early Cenozoic. A record of seawater δ^{7}Li from the fossil coral samples presented in this dissertation could supplement the existing record and extend it back into the Mesozoic. In the following sections of this Appendix, Li isotope sample preparation and measurement methods are described, and initial results are presented.

**A.2 Li isotope methods**

*A.2.1 Sample preparation for coral carbonate samples*

In preparation for Li chemistry, ~30 mg of coral carbonate was cut using a dremel tool and powdered (using a mortar and pestle), or was drilled from hand samples. This powder was then dissolved in ~10 mL of 1 N HNO₃, and subsequently centrifuged for ~30 minutes in order to separate any insoluble residue. Although insoluble residue in fossil corals was rare, some bulk powders did contain small amounts of clay minerals that were not possible to avoid during powder sampling. The dissolved sample was poured off from the insoluble residues into ~10 mL Teflon® vials and dried down on a hot plate overnight.
Appendix

Figure A.1 Lithium gravity column calibrations. (a) Calibration with JCP-1B, which is a recent coral. (b) Calibration with LSVEC doped with Ca, Mg, and Na to resemble aragonite matrix. Mass of Li loaded was ~20 ng.

A.2.2 Li isotope separation

Due, in part, to the tendency for Li isotopes to fractionate, measurements of Li isotopes in natural samples have historically been a challenge. In order to make robust measurements of Li isotopes, Li must be separated from the matrix in which it exists, and so it is processed through ion exchange columns for purification. Because there are only two isotopes of Li, it is not possible to use a double spike during sample processing, and high Li yields for samples processed by ion chromatography are critical for robust measurements. We use a two-step Li separation in order to separate Li from CaCO₃ matrix. The first step consists of a traditional gravimetric ion exchange column, during which Li is separated from >80% of the Ca matrix. This step is designed to be a rough separation with a wide collection window in order to ensure complete recovery of Li. The second step consists of two passes of the sample through a Thermo Dionex DCS5000+ Ion Chromatograph (IC) system fit with an IonPack CS16 column (9mm by 250mm). The IC system offers an automated means by which to separate cations for isotopic analysis. One of the main advantages of the IC purification for Li isotopes is that separation of Li from cations like Na and K – along with Li yields – can be monitored by
measurements of sample conductivity. As a result, it is possible to screen samples for poor yields prior to isotopic analysis, and for the presence of matrix.

For the gravity column separation, dried down samples of dissolved carbonate were re-dissolved in 0.4 mL 1N HNO₃. Similar to Misra and Froelich (2009), Teflon® gravity columns with 10mL reservoirs were packed with a BioRad® X12 resin such that the height of the resin was ~250mm. The resin-filled columns were then cleaned with 15 mL 5N HNO₃ and 10 mL 1N HNO₃. Prior to loading samples, columns were conditioned with 4 mL 1N HNO₃, after which dissolved carbonate samples were loaded in 0.4 mL 1N HNO₃. Lithium was eluted with 14 mL 1N HNO₃, and some Na and Mg co-eluted with Li during these steps. Subsequently, 10 mL of 5N HNO₃ was added to columns to elute remaining Na, Mg, Ca, and Sr. Along with samples, LSVEC standard (spiked with Ca, Mg, and Na) was processed through gravity columns to check for fractionation. Results of column calibrations for Li and Na are shown in Fig. A.1.

Collections of Li from gravity column separations were dried down and re-dissolved in 200 µL 0.2% HNO₃ in preparation for IC separation. Samples were injected and eluted using methanesulfonic acid (MSA). Li fractions were collected using a Dionex AS-AP autosampler. Along with samples, seawaters and pure LSVEC standards were processed through the IC. Typical conductivity chromatograms for a carbonate IC run and for a seawater IC run, are shown in Fig. A.2. After IC separation, samples were dried down once more in preparation for mass spectrometry.
Figure A.2 Chromatograms showing measurements of sample conductivity from Li IC separation. (a) A typical chromatogram showing the 1\textsuperscript{st} IC pass for a modern coral, which was already separated by gravity column. The green shaded area corresponds to the collection window for Li. The Li peak is difficult to see because of its small size relative
to the Na peak. (b) A zoom in of the green shaded area and the Li peak from the same sample shown in (a). (c) A representative chromatogram showing the 1\textsuperscript{st} IC pass for a seawater sample. The double-humped Li peak shows co-elution with small amounts of Na along with Li. (c) A representative chromatogram showing the 2\textsuperscript{nd} IC pass for a seawater sample, in which the double-humped peak has disappeared.

Eluent taken from the 5N HNO\textsubscript{3} wash step for gravity columns was collected to check for yields. In addition, blanks were monitored for both gravity column and IC separation. While there was no significant blank (<0.1\%) associated with the gravity columns, there was a significant blank associated with IC separation (0.2-6 \% of sample mass). It is unclear whether this blank derived from buildup of Li on the column, or from Li blank in the MSA used to elute cations. To better understand the contribution of blank, LSVEC standards were processed through the IC at different concentrations. Column processed LSVEC standards with > 30 ng Li gave Li isotope compositions within uncertainty of 0 when measured relative to unprocessed LSVEC. However, LSVEC standards processed through the IC with Li masses < 30 ng were shifted toward heavy values (see Section A.3 for more details). Fig. A.3 shows results of $\delta^7\text{Li}$ measurements of the separated LSVEC standards relative to pure (unprocessed) LSVEC, which appear to fall along a mixing trend when plotted as $\delta^7\text{Li}$ analyzed vs. $1/\text{Li}$. Due to small sample sizes, the mass of Li (to plot $1/\text{Li}$) was not analyzed directly. Instead, estimates of were made based on results of sample intensity measurements used to dilute samples to the same concentrations as standards (for isotopic analysis), and from conductivity measurements on the IC. The effect of leftover Na on our samples, was also quantified. Fig. A.4 shows results of Li doping experiments, where Na was added to pure Li\textsubscript{2}CO\textsubscript{3} standard. We observe up to a 2 \‰
enrichment in the heavy isotopes of Li for levels of Na ~100 times greater than expected for our samples.

**Figure A.3** Mixing trend between $\delta^7\text{Li}$ of LSVEC vs. $1/\text{Li}$ from samples of different Li mass which were processed through the IC only.

**Figure A.4** Isotopic composition of Li in pure lithium standards doped with Na.
A.2.3 Mass Spectrometry

Dried Li samples were re-dissolved in 2% HNO₃ for mass spectrometry. Li was analyzed using a ThermoFinnegan Neptune Plus multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) with an ESI Apex-IR sample introduction system (no membrane module). The isotopes ⁷Li and ⁶Li were measured in faraday cups H4 and L4, respectively with 10¹¹ Ω resistors. Samples were concentration matched to standards and were analyzed at a concentration of 10 ppb. This concentration typically yielded a ~7 V signal for ⁷Li. To achieve this sensitivity, jet sample and X-skimmer cones were used.

Measurements were made in low resolution using cold plasma (RF 800 W). Cold plasma uses a more gentle ionization and effectively helps to increase sensitivity of samples relative to machine blanks, which have been observed to be problematic for Li isotope measurements (Jeffcoate et al., 2004; Choi et al., 2013). In addition, cold plasma has been found to help eliminate interferences by ¹²C²⁺ and ¹⁴N²⁺ on ⁶Li and ⁷Li (Misra and Froelich, 2009; Jeffcoate et al., 2004). As seen by other workers (Jeffcoate et al. 2004; Choi et al. 2013; Huang et al. 2013), the Li machine blank typically increases during an analysis (see Fig. A.5), perhaps due to deposition on the cones. This blank does not wash out between samples even when using relatively long washout times (~5 minutes for measurements presented here). Between analytical sessions, cones were cleaned using 2% HNO₃, which reduces the blank by about a factor of 5. Machine blanks during our analytical sessions were typically ~1%. Because this blank is estimated to have a very light isotopic composition (~200 ‰; Jeffcoate et al. 2004), we correct for its presence on-line using a sampling sequence of blank-standard-blank-sample-blank-standard-blank. Sample standard bracketing also accounts for the large mass discrimination
imparted by the mass spectrometer during sample ionization. Total measurement time for each sample or standard, including the pre-sample wash step, was ~7 minutes.

![Figure A.5](image)

**Figure A.5** Increase in the intensity of the Li blank over the course of an analytical session.

### A.3 Results

During each analytical session, we measured three isotopically distinct Li standards for quality control: LSVEC, High Purity Standards (HPS) Li, and $^6$Li enriched HPS (HPS spiked with $^6$Li$_2$CO$_3$). As listed in Table A.1, the average measured Li isotope composition of LSVEC relative to HPS Li is $-12.11 \pm 0.33$ ‰ ($2\sigma$ S.D., n=30). The composition of the $^6$Li enriched HPS relative to pure HPS Li is $-32.74 \pm 0.91$ ‰ ($2\sigma$ S.D., n=19).

Table A.1 also shows results of Li samples and standards passed through chemistry (LSVEC, Bermuda seawater, modern corals, and fossil corals). An LSVEC standard that was...
only passed through gravity column chemistry and measured relative to unseparated LSVEC gave a $\delta^7\text{Li}$ value of -0.5 ‰ (n=1). This value is slightly lighter than the expected value (0 ‰), but considering the reproducibility of our standards, there does not seem to be any measurable fractionation of Li occurring on the gravity column. Likewise, this result suggests the absence of a measurable gravity column blank. In contrast, LSVEC standards with Li masses <30 ng and separated only by the IC are shifted toward heavy $\delta^7\text{Li}$ (1.52 ± 0.34 ‰; 2σ S.D., n=8). LSVEC standards processed with Li masses >30 ng give values close to 0 (see Table A.1). Together, these results suggest the presence of an isotopically heavy Li blank associated with the IC, as discussed briefly in Section A.2.2 and shown in Fig. A.3. In order to improve this Li isotope methodology, the presence of this IC blank must either be corrected for, or greater masses of Li must be processed to avoid shifts in $\delta^7\text{Li}$ as a result of mixing with the blank. Additional mixing experiments conducted by running different masses of Li through the IC (for LSVEC, carbonate samples, and seawaters) may help better quantify the IC blank.

The measured $\delta^7\text{Li}$ composition for modern seawaters is 31.28 ± 1.15 ‰ (2σ S.D., n=9). This value is within uncertainty of the range measured by others using MC-ICP-MS (Jeffcoate et al. 2004; Tomascak et al. 1999; Nishio and Nakai, 2002; Rosner et al. 2007; Huang et al. 2010; Choi et al. 2013). Modern corals passed through chemistry also fall within the range of other modern corals measured by MC-ICP-MS and SIMS (see Table A.1; Rollion-Bard et al. 2009; Marriot et al. 2004). However, the JCp-1 coral standard is different from the value reported in Huang et al. (2010). This may be due to contribution of a blank for low Li masses processed through the IC, but additional work is still needed to understand why our measured JCp-1 value is distinct from previous work. A measured Oligocene age coral (~30 million years old) gives a Li isotope value 3-4 ‰ lighter than modern corals (see Table A.1). This difference is
broadly consistent with the change between Oligocene-age planktonic foraminifera $\delta^7$Li and modern planktonic foraminifera $\delta^7$Li as measured by Misra and Froelich (2012). All seawater and carbonate samples measured to date have Li masses <30 ng, but have not yet been corrected for blank. Finally, we note that we have not yet measured existing basalt standards (e.g., BHVO-2) for Li isotopes, but measurements of these materials would further help assess the accuracy and reproducibility of our method.

Table A.1 Summary of Li isotope results from this work, and summary of previously published standards for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^7$Li (%)</th>
<th>2$\sigma$</th>
<th>n</th>
<th>STD</th>
<th>notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Study</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unprocessed (no gravity column/IC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSVEC</td>
<td>-12.11</td>
<td>0.33</td>
<td>30</td>
<td>HPS Li</td>
<td></td>
</tr>
<tr>
<td>6Li HPS SPIKE</td>
<td>-32.74</td>
<td>0.91</td>
<td>19</td>
<td>HPS Li</td>
<td></td>
</tr>
<tr>
<td>IC separated only</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSVEC mass &lt;30ng</td>
<td>1.52</td>
<td>0.34</td>
<td>8</td>
<td>LSVEC</td>
<td></td>
</tr>
<tr>
<td>LSVEC mass &gt;30ng</td>
<td>0.04</td>
<td>0.37</td>
<td>4</td>
<td>LSVEC</td>
<td></td>
</tr>
<tr>
<td>Seawater (Bermuda)</td>
<td>31.28</td>
<td>1.15</td>
<td>9</td>
<td>LSVEC</td>
<td></td>
</tr>
<tr>
<td>Gravity column separated only</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSVEC</td>
<td>-0.50</td>
<td>NA</td>
<td>1</td>
<td>LSVEC</td>
<td></td>
</tr>
<tr>
<td>Gravity column and IC separated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSVEC &lt;30 ng</td>
<td>1.78</td>
<td>0.88</td>
<td>3</td>
<td>LSVEC</td>
<td></td>
</tr>
<tr>
<td>ERP modern coral (~30 mg CaCO$_3$)</td>
<td>18.7</td>
<td>2</td>
<td>2</td>
<td>LSVEC</td>
<td></td>
</tr>
<tr>
<td>JCp-1B coral (~30 mg CaCO$_3$)</td>
<td>18.86</td>
<td>NA</td>
<td>1</td>
<td>LSVEC</td>
<td></td>
</tr>
<tr>
<td>JCp-1 coral standard (~30 mg CaCO$_3$)</td>
<td>17.14</td>
<td>1.6</td>
<td>2</td>
<td>LSVEC</td>
<td></td>
</tr>
<tr>
<td>Oligocene coral</td>
<td>14.41</td>
<td>NA</td>
<td>1</td>
<td>LSVEC</td>
<td></td>
</tr>
<tr>
<td>Other Studies</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seawaters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atlantic (NASS-5)</td>
<td>30.55</td>
<td>0.45</td>
<td>15</td>
<td>LSVEC</td>
<td>Choi et al. (2013)</td>
</tr>
<tr>
<td>Atlantic (NASS-5)</td>
<td>30.73</td>
<td>0.15</td>
<td>10</td>
<td>LSVEC</td>
<td>Huang et al. (2010)</td>
</tr>
<tr>
<td>Atlantic (NASS-5)</td>
<td>30.64</td>
<td>0.44</td>
<td>3</td>
<td>LSVEC</td>
<td>Rosner et al. (2007)</td>
</tr>
<tr>
<td>Region</td>
<td>Latitude</td>
<td>Altitude</td>
<td><strong>n</strong></td>
<td>Technique</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------</td>
<td>----------</td>
<td>-------</td>
<td>-----------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>Atlantic (IAPSO)</td>
<td>30.88</td>
<td>0.12</td>
<td>10</td>
<td>LSVEC</td>
<td>Huang et al. (2010)</td>
</tr>
<tr>
<td>Atlantic (IAPSO)</td>
<td>30.84</td>
<td>0.19</td>
<td>3</td>
<td>LSVEC</td>
<td>Rosner et al. (2007)</td>
</tr>
<tr>
<td>Pacific (North)</td>
<td>29.3</td>
<td>0.92</td>
<td>3</td>
<td>LSVEC</td>
<td>Nishio and Nakai (2002)</td>
</tr>
<tr>
<td>Pacific (South)</td>
<td>31.8</td>
<td>1.9</td>
<td>15</td>
<td>LSVEC</td>
<td>Tomascak et al. (1999)</td>
</tr>
<tr>
<td>Multiple sites</td>
<td>31.1</td>
<td>0.2</td>
<td>9</td>
<td>LSVEC</td>
<td>Jeffcoate et al. (2004)</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>LSVEC</strong></td>
<td></td>
</tr>
<tr>
<td><strong>All sites</strong></td>
<td></td>
<td></td>
<td>31.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modern corals (MC-ICP-MS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average of Porites sp. subsamples</td>
<td>18.84</td>
<td>0.44</td>
<td>8</td>
<td>LSVEC</td>
<td>Marriot et al. (2004)</td>
</tr>
<tr>
<td>Acropora sp.</td>
<td>21</td>
<td>0.4</td>
<td>-</td>
<td>LSVEC</td>
<td>Marriot et al. (2004)</td>
</tr>
<tr>
<td>JCP-1 coral standard</td>
<td>20.16</td>
<td>2</td>
<td>5</td>
<td>LSVEC</td>
<td>Huang et al. (2010)</td>
</tr>
<tr>
<td>Modern corals (SIMS)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lophelia pertusa</td>
<td>18.90</td>
<td>2.31</td>
<td>40</td>
<td>LSVEC</td>
<td>Rollion-Bard et al. (2009)</td>
</tr>
<tr>
<td>Lophelia pertusa</td>
<td>18.98</td>
<td>2.42</td>
<td>17</td>
<td>LSVEC</td>
<td>Rollion-Bard et al. (2009)</td>
</tr>
<tr>
<td>Desmophyllum cristagalli</td>
<td>19.07</td>
<td>1.46</td>
<td>7</td>
<td>LSVEC</td>
<td>Rollion-Bard et al. (2009)</td>
</tr>
<tr>
<td>Porites lutea</td>
<td>22.75</td>
<td>1.67</td>
<td>14</td>
<td>LSVEC</td>
<td>Rollion-Bard et al. (2009)</td>
</tr>
<tr>
<td>Cladocora caespitosa (cultured)</td>
<td>21.45</td>
<td>2.02</td>
<td>15</td>
<td>LSVEC</td>
<td>Rollion-Bard et al. (2009)</td>
</tr>
<tr>
<td>Cladocora caespitosa (cultured)</td>
<td>23.05</td>
<td>2.33</td>
<td>10</td>
<td>LSVEC</td>
<td>Rollion-Bard et al. (2009)</td>
</tr>
</tbody>
</table>
References


