Geochemical Perspectives

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WALLY BROECKER

CO_2: Earth's Climate Driver

Geochemical Perspectives

Each issue of *Geochemical Perspectives* presents a single article with an in-depth view on the past, present and future of a field of geochemistry, seen through the eyes of highly respected members of our community. The articles combine research and history of the field's development and the scientist's opinions about future directions. We welcome personal glimpses into the author's scientific life, how ideas were generated and pitfalls along the way. *Perspectives* articles are intended to appeal to the entire geochemical community, not only to experts. They are not reviews or monographs; they go beyond the current state of the art, providing opinions about future directions and impact in the field.

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About the cover

This issue of *Geochemical Perspectives* presents an overview of the evolution of the Earth's climate in six episodes. This cover illustrates schematically this evolution of our ever changing planet.

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PREFACE

As a scientist, I spend most of my time thinking and writing. After managing a radiocarbon laboratory for a decade and then developing a means to use radon gas as a tracer for gas exchange and eddy mixing, I turned more and more to deciphering how measurements made by my students and postdocs fit into the bigger picture. Also, from the start, I realised that teaching was a learning experience; to teach effectively requires an in-depth understanding of the material.

Recently someone told me that if I had learned to type and to use a computer, I could have accomplished ever so much more. Perhaps, but I'm not convinced. As it turns out, with my pencil and eraser, I can keep up with my thinking. Also, my myriad of hand-plotted graphs has allowed me not only to imbed the information in my brain but also to pay attention to points which appeared to be anomalous.

I suppose that, as a dyslexic, my brain operates somewhat differently than most. It certainly greatly slows my reading rate. Because of this, I depend almost entirely on abstracts, figures, tables and conclusions. I make my own interpretation of the data.

This mini-book is based on material I used in my Carbon Cycle class, taught during the 2017 fall semester to graduate and advanced undergraduate students. It contains my view of the role of CO_2 in six climate episodes extending from the first two billion years of Earth history to this last one hundred years.

As was my 1987 book, "How to Build a Habitable Planet," I hope this one will also be of help to Earth Science students preparing for orals. It is concise, readable, and packed with key information. I like puzzles of any kind. Hence it is what we don't understand about the six episodes discussed here that is of most interest to me. Consequently I speculate; were I to have written this five years ago, it would be quite different; and, of course it would be quite different if written in 2022. Approaching 87, I will not be able to update it but will ponder these questions for the rest of my years.

Morgan Schaller and John Higgins have prominent roles in my book. The reason is that they have made important discoveries which alter thinking regarding the PETM and the Snowball Earth episodes. Further, they both have been extremely generous in sharing their findings with me.

This has been a team effort. Patty Catanzaro drafted and redrafted the figures. Joan Totton transformed my pencil scribbles into manuscript form and then entered my numerous revisions. My wife, Elizabeth Clark, serves as my link to the digital world. We four have worked together smoothly for several decades.

I also much appreciate the reviews by Eric Oelkers and Don Canfield. Finally, I must thank Michael Crow for making it possible for Elizabeth and I to spend our January and February each year at Arizona State University. Much of this book was written there.

In 2001, during a period when I was unable to get support from the National Science Foundation, I was rescued by the late Gary Comer. Puzzled by his successful transit of the Northwest Passage, he came to me for advice about global warming. This led to a collaboration which lasted the rest of Gary's life. He not only 'adopted' me, but also many of those working on abrupt climate change. This brought me out of a sense of lethargy and I've been 'turned on' ever since. Gary's daughter, Stephanie, now carries the torch. Fifty students and scientists meet each fall at the Comer Farm in Soldiers Grove, Wisconsin.

As I write this, I sit in my office in the Comer Geochemistry Laboratory. Lamont has been my scientific home since June 15, 1952 at the age of 20. No, it's not a typo. I've been continuously employed at the Lamont-Doherty Earth Observatory for 66 years. I can think of no other place that could come close to matching this one.

Lastly, I owe ever so much to my "Lizzie." We're together pretty much 24-7. I am a very fortunate man to have such a loving wife.

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CO_2: EARTH'S CLIMATE DRIVER

ABSTRACT

As we struggle to cope with the ongoing buildup of CO_2 produced by burning fossil fuels, can we acquire guidance from the geologic record? Although our ability to reconstruct past atmospheric CO_2 content reliably is currently confined to the last 800 thousand years, we do have compelling evidence that this greenhouse gas played a key role throughout the Earth's history. It certainly compensated for the young Sun's lower luminosity. There is no question that it bailed us out of two snowball episodes or that it led to a brief 5 °C warming at the onset of the Eocene. Less certain is that diminishing atmospheric CO_2 content was responsible for the global cooling that began 50 million years ago when the Indian subcontinent collided with Asia. Finally, it colluded with changing seasonality, ocean circulation re-organisation and iron fertilisation to generate the 100 thousand year glacial cycles that dominated the last half-million years.

1. INTRODUCTION

Averaged across the Earth's surface, the temperature is close to 15 °C. In the absence of reflectors on one hand and greenhouse gases on the other, its temperature would be only ~5 °C. Important to our discussions is that clouds, ice and other reflectors reduce the Earth's temperature by about 25 °C and H_2O vapour, CO_2 and other greenhouse gases increase it by about 35 °C (see Fig. 1.1). As both reflectivity and greenhouse strength have varied over the course of geologic time, so has the Earth's surface temperature.

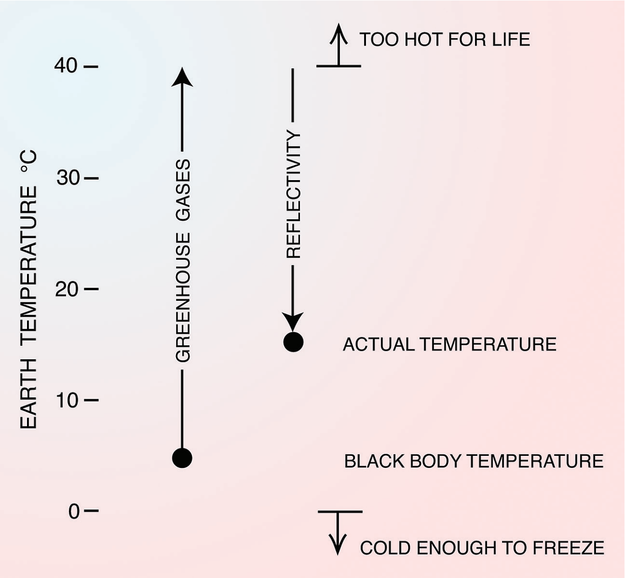


Figure 1.1 If the Earth had no greenhouse gases or reflectivity (*i.e.* were it a "black body"), it would have a surface temperature of about 5 °C. Its present component of greenhouse gases warms it by 35 °C. Its present reflectivity cools it by 25 °C. Clearly variations in either greenhouse gases or reflectivity would lead to temperature changes.

Before delving into the evidence documenting these changes, it is important to understand the control system which regulates the atmosphere's CO_2 and H_2O contents. The situation for water vapour is straight forward as it depends mainly on the temperature of the surface ocean. For each degree centigrade the ocean rises, the vapour pressure of water increases by 7 percent. In contrast, the situation for CO_2 is complex. Although also dictated by the ocean, CO_2 and its backups HCO_3^- and $CO_3^=$ are influenced by life cycles as well as by temperature. As the inputs of carbon from volcanoes (as CO_2) and of calcium from silicate dissolution (as CaO) must be primarily balanced by its removal to marine sediments (as $CaCO_3$), the input of Ca must match that of CO_2 (Fig. 1.2). If, for some reason, this match is disrupted, a feedback system kicks into operation re-establishing the balance. The cycles of these two elements are tightly coupled (see Fig. 1.2).

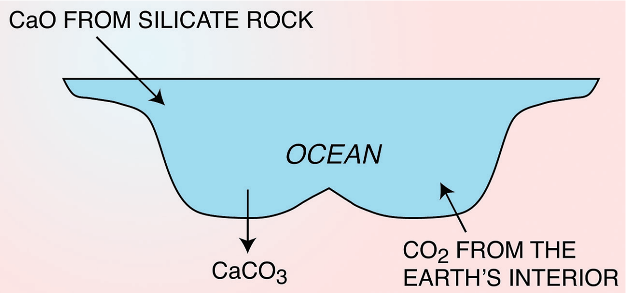


Figure 1.2 Calcium oxide released during chemical weathering of silicate rocks mates with carbon dioxide escaping from the Earth's interior to form calcium carbonate. As there is no other important sink for calcium, the supply of CaO must be matched by that of CO_2. A feedback involving the atmosphere's CO_2 content assures that this match is maintained.

This feedback involves the CO_2 content of the atmosphere (Walker *et al.*, 1981). For example, if some perturbation were to cause the CO_2 supply to exceed that of calcium, the CO_2 content in the atmosphere would be driven up, warming the planet. This extra warmth would increase the rate of chemical weathering of silicate rock and hence the supply of calcium. This would continue until a balance was restored. Were the supply of planetary CO_2 to fall behind the supply of calcium, the reverse would take place. The CO_2 content of the atmosphere would be drawn down causing the Earth to cool and the calcium supply to drop.

At this point one might ask what would cause such perturbations. The answer is many things. For calcium, the first thing that comes to mind is continental elevation. Mountains serve as grinders supplying grist for chemical weathering. Another is that, as basalts weather far more rapidly than granites, continental drift changes the supply of calcium by changing the area of basaltic terrane passing through the tropical rain belt. Further, the advent of rooted plants has likely accelerated chemical weathering. And the list goes on.

Perturbations in the supply of planetary CO_2 are created by changes in the $CaCO_3$ content of the subducted sediment. Also important are disruptions in the rate and pattern of plate motions caused by the collision of continental blocks. Yet another is the CO_2 released during the eruption of volcanoes and mantle plumes. And the list goes on.

In this regard valuable information is provided by what has happened in the aftermath of catastrophes such as extraterrestrial impacts, mega-basalt outpourings and massive extinctions. By adding fossil fuel CO_2 to the atmosphere we are creating yet another such perturbation.

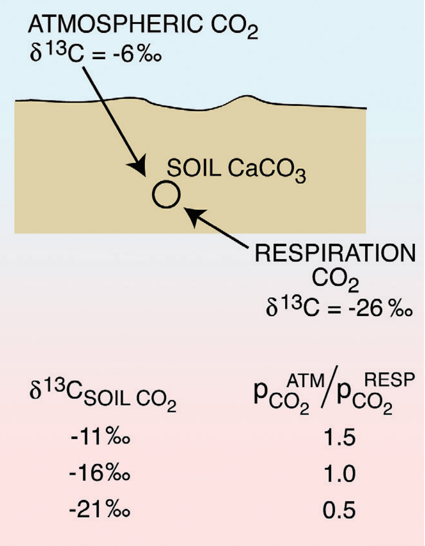
Of course changes in the CO_2 content of the atmosphere are also accompanied by changes in the hydrologic cycle. As the vapour pressure of water changes with temperature, warming or cooling is accompanied by changes in the water vapour's contribution to greenhouse warming. Model simulations suggest that in the case of the ongoing rise of CO_2, the accompanying rise in water vapour amplifies the warming to be about a factor of two.

Not only are there greenhouse side effects, there are also reflectivity side effects. Today clouds reflect back to space about one third of the incoming solar radiation. Hence, changes in the extent of cloud cover alter Earth temperature. The extent of ice and snow cover changes as the Earth warms or cools. Further, as deserts are more reflective than either forests or oceans, changes in the distribution of precipitation alter the Earth's reflectivity.

The greatest impediment to understanding the role of CO_2 in past climate changes is the lack of a reliable proxy for past atmospheric CO_2 contents. Only the air trapped in bubbles in Antarctic ice currently provides a pristine record. However it extends back only 0.8 million years. Existing CO_2 proxies used over longer time scales are unreliable. Except for one, these proxies involve the isotope fractionation that occurs when living organisms produce either organic matter or $CaCO_3$ hard parts. Although ^{13}C decreases with increasing atmospheric CO_2 content, it is not the only thing altering the extent of this depletion. Although each of these CO_2 proxies is based on a sound idea, nature has a way of throwing curve balls which introduce serious biases. Because of this, the proxies which involve photosynthetic fractionation are, in my estimation, not to be trusted.

Fortunately there is one method which is not based on the magnitude of isotope fractionation associated with biologic building blocks. As originally proposed by Thure Cerling (1992), this method involves the ^{13}C to ^{12}C ratio in soil $CaCO_3$ (see Fig. 1.3). The idea is that the $\delta^{13}C$ of soil gas depends on the ratio of atmospheric CO_2 ($\delta^{13}C = -6$ ‰) to respiration CO_2 ($\delta^{13}C = -26$ ‰). For times when atmosphere's CO_2 was higher, the $\delta^{13}C$ of soil CO_2 and hence also of soil $CaCO_3$ would have been less negative. These carbonates are ubiquitous in dry lands. However, Cerling's method suffers from two serious drawbacks. The first is that a 'guess' must be made regarding the respiration CO_2 content of the soil air at the time the soil $CaCO_3$ formed. And, second, the temperature of the soil at that time must be known. Recently, Morgan Schaller, a young scientist at Rensselaer Polytechnic Institute, has proposed a way in which both of these drawbacks might be circumvented. He has demonstrated that soil carbonates contain tiny bubbles filled with soil air. By measuring the CO_2 to N_2 ratio in this trapped air, Schaller avoids the necessity to 'guess' the CO_2 pressure in the soil. Also as the $\delta^{13}C$ Schaller measures is of the CO_2 trapped in these tiny bubbles rather than on the $CaCO_3$, no temperature correction for the isotope fractionation associated with the precipitation of $CaCO_3$ need be made. Further, Schaller uses the ratio of N_2 to Ar to establish the ratio of water to air in these tiny cavities. This is necessary because the ratio of CO_2 to N_2 is different in the water than in the air. He also makes use of the temporal increase in the ^{40}Ar to Ar ratio in the Earth's atmosphere which results from the continuing outgassing of this radiogenic ^{40}Ar from the Earth's interior. Although many tests have yet to be made before Schaller can claim victory, as Cerling's method appears to be the "only game in town," one has to hope that he will be successful.

Figure 1.3 Thure Cerling's soil $CaCO_3$ atmospheric CO_2 proxy (Cerling, 1992): the $\delta^{13}C$ in soil CO_2 depends on the ratio of the partial pressure of CO_2 in the atmosphere to that of respiration CO_2 in the soil. Two problems plague this method. One is that the respiration contribution must be obtained by analogy with that in today's soils and therefore is uncertain. The other is that the fractionation between soil CO_2 and soil $CaCO_3$ is temperature dependent. Soil temperature in the drylands where soil $CaCO_3$ forms can be as much as 10 °C higher than that in the overlying air.



Morgan Schaller proposes to circumvent these problems by measuring both the CO_2 content and the $\delta^{13}C$ of this CO_2 in gas trapped in tiny bubbles in the soil carbonate (Schaller *et al.*, 2016).

One other proxy for CO_2 must be mentioned. It involves the isotopes of the element boron (*i.e.* ^{11}B and ^{10}B). In marine $CaCO_3$ this ratio varies with the pH of the seawater in which it formed. Columbia's Bärbel Hönisch has shown that the $\delta^{11}B$ in planktonic shells reproduces the CO_2 record in ice cores. But the accuracy of these reconstructions is ±15 μatm (compared to ±1 μatm for measurements of CO_2 trapped in ice). But going back in time, a serious problem arises. We know that the $\delta^{11}B$ of seawater has changed with time but not by how much. Until there is a reliable way to reconstruct the ^{11}B to ^{10}B ratio in seawater, the method will be useful for only the last few million years.

With this background in mind, let us turn our attention to examples from Earth history where climate did change and see if a case can be made for the involvement of CO_2 (see Fig. 1.4). The examples I have chosen involve unusual and often catastrophic events in the Earth's past. While it might be preferable to deal with times when the climate was close to steady state, unfortunately our tool kit is not adequate for this task. Rather, we are forced to concentrate on times when the Earth system was involved in some sort of train wreck.

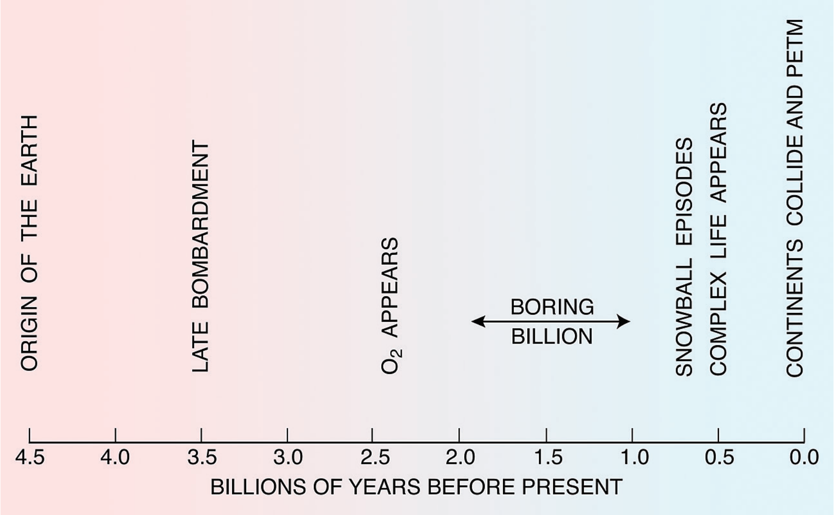


Figure 1.4 Milestones in the Earth's history.

I decided not to include any discussion of mass extinction events. The biggest of these occurred 250 million years ago. Something like 90 percent of the animal species then extant suddenly disappeared. At the same time as the extinctions, the huge Siberian traps were extruded. It is likely that these eruptions were responsible for the kill. The consequent downward spike in ocean $\delta^{13}C$ (see Fig. 1.5) suggests that a substantial rise in atmospheric CO_2 content occurred. But to me it seems more likely that the assassin was sulphur rather than carbon. There is evidence that the assemblage of organisms that came into being at the onset of the Triassic processed carbon in a different way than the Permian assemblage which it replaced. The evidence is a three per mille drop in the $\delta^{13}C$ in the carbon dissolved in the ocean (as recorded by limestones). The likely cause for this was the demise of massive continental forests. Instead of being oxidised entirely by O_2, more of the organic material reached the sea and was oxidised by $SO_4^{=}$.

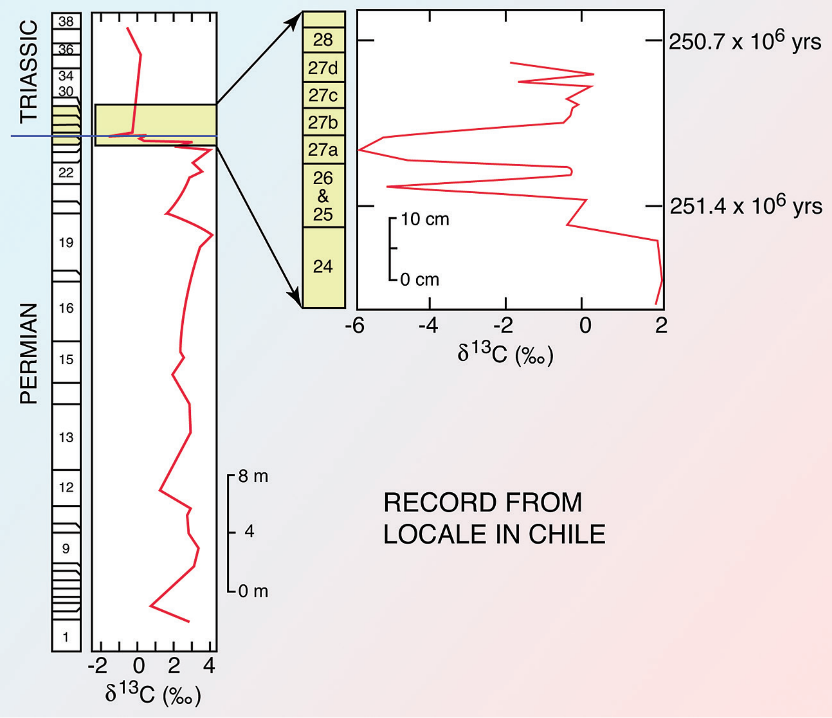


Figure 1.5 The ^{13}C to ^{12}C record kept in limestone reveals two important changes that occurred at the onset of the Triassic (Burgess *et al.*, 2017). The first is a pair of $\delta^{13}C$ spikes that occurred very close to the time of the emplacement of the Siberian traps. As each of these $\delta^{13}C$ drops brought the $\delta^{13}C$ close to that for mantle carbon, the suggestion is that the CO_2 released during the eruptions dominated the atmosphere. The spikes gave way to a longer term 3 per mille decrease. The likely cause is a reduction in the amount of reduced carbon stored in coal beds matched by an increase in the amount of reduced sulphur stored in marine sediments.

I start at the beginning. What was the role of greenhouse gases during the first two billion years when the Sun was faint? Then I will jump forward in time to 800 million years ago when the Earth entered an era of extreme climate instability in which at least two ‘snowball’ episodes occurred. This era came to a close about 520 million years ago when climate stabilised and complex life made its debut.

Next on the list is a short lived but intense global warming (the PETM) which took place 55.8 million years ago. There is no doubt that this sudden 5 °C heat-up was caused by an abrupt release of an amount of CO_2 comparable to that we would produce if we were to burn all of our fossil fuel reserves. Although we suspect that an impact of an extraterrestrial object triggered this event, arguments rage regarding the source of the CO_2.

Fifty million years ago the northward drifting India collided with Asia. This collision changed forever the evolution of the Earth's climate. For 10 or so million years before the event, the Earth had been steadily warming. The collision appears to have terminated the warming and initiated a cooling which continues today. Although decreasing CO_2 is likely responsible for the cooling, only circumstantial evidence supports its role.

The cooling which began 50 million years ago eventually led to glaciation in both of the Earth's polar regions. Antarctica's ice cap appeared about 35 million years ago. Ice caps in Canada and Scandinavia first nucleated about 3 million years ago. An interesting aspect of this partial freeze up is that the glaciers oscillated widely in size. These oscillations were paced by cyclic changes in the Earth's orbit. Of interest is the similarity between the record of atmospheric CO_2 and that of Antarctic temperature. In his movie "An Inconvenient Truth" Al Gore claimed that this correspondence proves that CO_2 drove these glacial cycles. But was he correct in this assessment?

Lastly we will ponder the impact of the CO_2 we have, and will produce, by burning fossil fuels. Clearly it poses an extremely serious threat. In my estimation the outlook for containing it is grim. The seeds of global chaos?

2.

FAINT YOUNG SUN

Astronomers tell us that over the course of its lifetime the Sun has burned ever more brightly. Not only have they been able to make a solid case for this increase in luminosity, but they are also able to tell us by how much. During the last 4.5 billion years the Sun's luminosity has increased by about 25 percent. As there is no palaeo-luminosity proxy, this result is based on how the Sun produces energy.

The Sun's energy is produced by the fusion of four hydrogen nuclei to form one helium nucleus. As the helium nucleus weighs a tiny bit less than four hydrogen nuclei, fusion produces energy (see Fig. 2.1). At the heart of their calculation is the assumption that there must be a balance between the radiation pressure created by our stars' nuclear fire and its self-gravitation. Because hydrogen nuclei are being fused to form helium nuclei, this balance has changed with time.

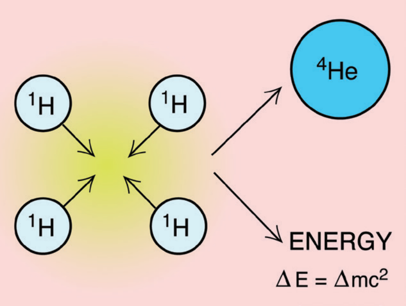


Figure 2.1 Our Sun's energy is produced by the fusion of four hydrogen nuclei into a helium nucleus. The small difference between the mass of the reactants and that of the product is converted to energy.

As the amount of luminous energy leaving the Sun must be close to that produced in its nuclear furnace, astronomers are able to calculate the rate at which the number of nuclear entities in the Sun is decreasing. In order to understand why this allows astronomers to calculate the change of the Sun's luminosity, consider a pair of identical balloons. One is filled with H_2 molecules and the other with the same number of He atoms. If the balloons are at the same temperature, they will be identical in size. The key is that the pressure exerted on the walls of a balloon depends only on the number of molecules bouncing around inside. It is independent of the mass of these molecules. With this in mind, consider what would happen if the hydrogen molecules were by magic merged into helium atoms. The size of the balloon would shrink dramatically. In order to restore the balloon to its original size, it would be necessary to heat it to the point where its helium atoms were moving four times as fast.

In the case of the Sun, this tendency to shrink as hydrogen nuclei are consumed is balanced by an increase in the rate of fusion. This heats the hydrogen and helium nuclei and they bounce more vigorously against the star's gravitation.

Based on the Sun's current luminosity, the rate at which H nuclei are being converted to He nuclei can be calculated. This allows the rate of increase in luminosity to be determined.

This faintness of the young Sun presents a challenge to planetary scientists. The reason is that, based on the sediment record, water was present on the Earth's surface as early as 3.8 billion years ago. At that time the Sun was 20 or so percent less luminous than now, thus the Earth should have been an ice ball. The answer must be that the atmosphere's greenhouse capacity was greater than today's. We know that at these early times CO_2 and H_2O vapour were not the only important greenhouse contributors. As the Earth's interior is highly reducing, the early atmosphere was as well. Hence it would have contained significant amounts of CH_4 and H_2S. And, of course, were this the case there could have been no O_2.

As a matter of fact, there is now firm evidence that during the first two billion years of its history, sulphur gases were a major constituent of the atmosphere and that after that, these gases were absent. The evidence awaited the discovery of what is referred to as mass independent isotope fractionation. To understand this requires an understanding of what is called mass dependent isotope fraction. The element oxygen has three isotopes ^{16}O, ^{17}O and ^{18}O. Over the past 70 years, isotope geochemists have made millions of measurements of the ratio of ^{18}O to ^{16}O. They didn't bother with ^{17}O because it was assumed that ^{17}O fractionation would always be mass dependent, *i.e.* close to half that for ^{18}O. The same is true for the element sulphur. It has three isotopes: ^{32}S, ^{33}S and ^{34}S. Again, only the ^{34}S to ^{32}S ratio are routinely measured. Measuring the ratio of ^{33}S to ^{32}S was thought to be redundant.

It was the University of Chicago's Robert Clayton who first showed that there were deviations from mass dependence. He measured both the ^{18}O to ^{16}O ratio and the ^{17}O to ^{16}O ratio in silicate-bound oxygen from meteorites. To his surprise, the $^{17}O/^{16}O$ results deviated from expectation (*i.e.* $\Delta^{18}O = 2\ \Delta^{17}O$). At first, Clayton proposed that these anomalies were created in the stars during nucleosynthesis. While ^{16}O is made by fusing four ^{4}He nuclei, ^{17}O and ^{18}O are made by side reactions. Clayton postulated that perhaps the ratio of ^{16}O production to that of ^{17}O and ^{18}O differed from star to star.

The breakthrough came when UCSD's Mark Thiemens showed in the laboratory that reactions among gaseous species lead to mass independent fractionation. He showed that $\Delta^{17}O$ was a bit different in atmospheric O_2 than in O_2 made by photosynthesis in the ocean. This small difference is created by reactions among oxygen-bearing gases in the stratosphere.

This led James Farquhar to look for $\Delta^{33}S$ anomalies in ancient sedimentary sulphur minerals. To his delight, he found them and showed that they were present only in samples greater than 2.4 billion years in age (see Fig. 2.2). Measurements on a host of younger samples showed no significant $\Delta^{33}S$ anomalies. He quickly realised that O_2 must have made its appearance in the atmosphere close to 2.4 billion years ago. In the absence of O_2, the atmosphere would have hosted significant quantities of gases containing sulphur. Reactions among these gases would have created $\Delta^{33}S$ anomalies. Sulphur tagged with these anomalies was rained out on the continents where it was mixed with normal sulphur and then deposited in sedimentary sulphur-bearing minerals. Once O_2 appeared, the sulphur-bearing gases would have been purged from the atmosphere. Hence no measurable $\Delta^{33}S$ anomalies could any longer be generated.

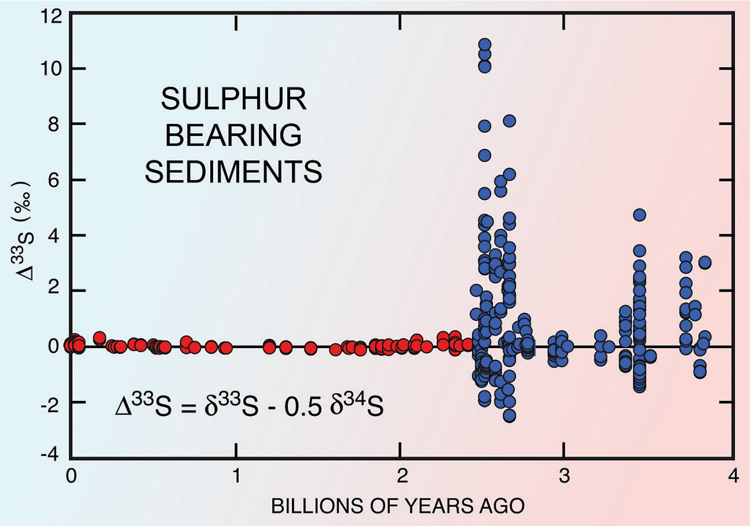


Figure 2.2 Prior to 2.4 billion years ago, sedimentary sulphur contained a component which had been subjected to mass independent fractionation. After that time no such anomalies are found. This tells us that early on H_2S was an important constituent of the atmosphere. Once O_2 appeared, H_2S was rapidly oxidised forming H_2SO_4 aerosols. So even though small amounts of mass independent fractionation currently still take place in the stratosphere, its contribution to sedimentary sulphur is too small to yield a measurable $\Delta^{33}S$ signal (after Farquhar *et al.*, 2007).

This discovery confirmed a long-standing, but much disputed, conclusion based on the disappearance of sedimentary iron formations (see Fig. 2.3) about 2.5 billion years ago. These massive deposits were ubiquitous prior to this time and largely absent thereafter. The controversial explanation was that although iron in its reduced state is soluble in seawater, iron in its oxidised state is insoluble. So, when O_2 appeared in the atmosphere dissolved iron could no longer be a significant constituent of sea salt. And hence there were no more sedimentary iron deposits.

It is of interest that mass independent fractionation of sulphur goes on today, albeit in tiny quantities. Caltech's Andrea Burke and Jess Adkins seeking to create a record of volcanic eruptions turned to the sulphate-rich layers present in long ice cores from Greenland's ice cap. Although volcanic ash doesn't get very far from the source, the SO_2 gas can travel great distances before being converted to H_2SO_4 aerosols and rained out. As interest centred around the largest eruptions, a means of distinction was needed to determine whether a given layer rich in SO_4 was from a far-away large eruption or a nearby small eruption. It turns out that the clouds produced by large volcanic eruptions penetrate into the stratosphere. As there are no raindrops or snowflakes up there, the sulphur remains aloft for several years. During this time it undergoes mass independent fractionation generating $\Delta^{33}S$ anomalies. This signal is preserved in the ice allowing mega eruptions to be distinguished from run-of-the-mill eruptions.

Figure 2.3 Example of an iron-rich sediment. Prior to 2.4 billion years ago, so called "banded iron formations" were common. After that time, they are largely absent. The explanation for their demise is the appearance of O_2. In its absence, iron was in its reduced state (*i.e.* valence +2). As such, it is highly soluble and, as is calcium today, it was deposited in thick sedimentary deposits. The appearance of O_2 changed things. Iron was oxidised to its +3 valence state. In this state it is highly insoluble. During weathering oxidised iron tends to remain behind in soils. That which gets to the sea is rapidly absorbed onto particulates (photo credit: Stefan Lalonde).

Two other events of importance took place during the first two billion years of Earth history. The first was what is termed by the planetary scientists as the late bombardment. It occurred about 3.5 billion years ago and is believed by some to have delivered volatile constituents (CO_2, H_2O, noble gases…) thought to have been sparse in the proto Earth. If so, this might explain why the Earth is so well-endowed with H_2O and CO_2. As its surface is continually reworked by erosion, no evidence for these impacts is to be found on Earth. Rather, the evidence comes from the Moon.

The second event involved the formation of granitic cratons which constitute the core of each continent. Their formation was centred at about 2.8 billion years ago and they are still around. They dominate much of the landscape in Canada, Scandinavia, Brazil and Australia. As granitic rocks are unusually rich in incompatible elements (*i.e.* potassium, rubidium, uranium, thorium, rare earths…) their emplacement was likely accompanied by the release of CO_2 and H_2O contained in the Earth's interior. It is tempting to speculate that the delivery of volatile elements to the Earth's surface at both 3.5 and 2.8 billion years ago played a role in fostering life on our planet.

Back to the "faint young Sun." The answer to why early Earth wasn't a snowball appears to be that extra greenhouse gases, including CO_2 and water, compensated for the deficit in illumination. The absence of O_2 likely played a key role for it allowed CH_4, H_2S and other reduced gases to enhance the atmosphere's greenhouse strength.

The conversion of H to He will continue into the future. Eventually Earth will become so hot that life will be extinguished. This will happen roughly two billion years from now (see Fig. 2.4). In this case, there will be no compensation. Rather, the warming will be amplified; more water vapour and less ice. Even if the CO_2 content of the atmosphere were to decrease, the consequent cooling would be overwhelmed.

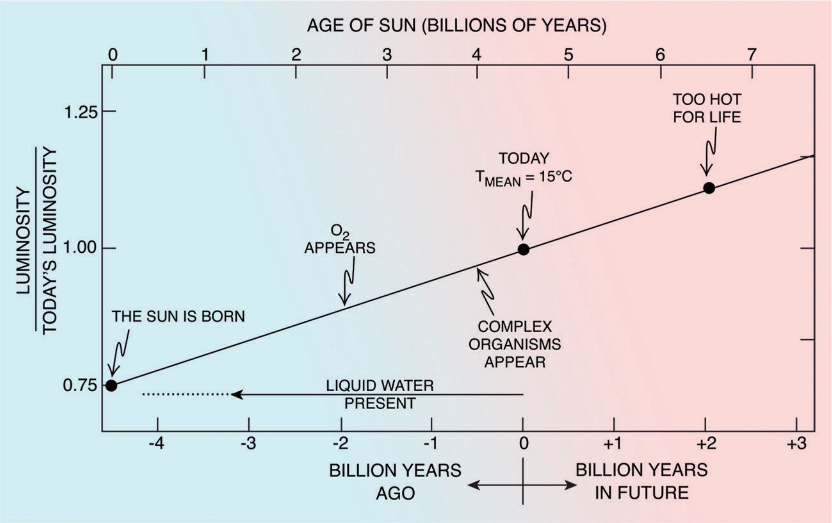


Figure 2.4 The Sun's luminosity as a function of time as calculated by astrophysicists. The presence of water as early as three billion years ago requires that greenhouse warming was far larger than today's.

3. SNOWBALL EARTH

Much of what we know about environmental changes that occurred during the Precambrian comes from the carbon isotope record kept in limestone (see Fig. 3.1). This record is relatively featureless except for two 0.3 billion year time intervals during which large variations occur. The first of these took place between 2.3 and 2.0 billion years ago – a time interval following the appearance of O_2 in our atmosphere. The second occurred between 0.8 and 0.5 billion years ago – a time interval during which the Earth underwent two total freeze-ups. As the carbon isotope record quietened down between these two noisy episodes, it is referred to as the boring billion. This chapter focuses on the second of the two noisy eras.

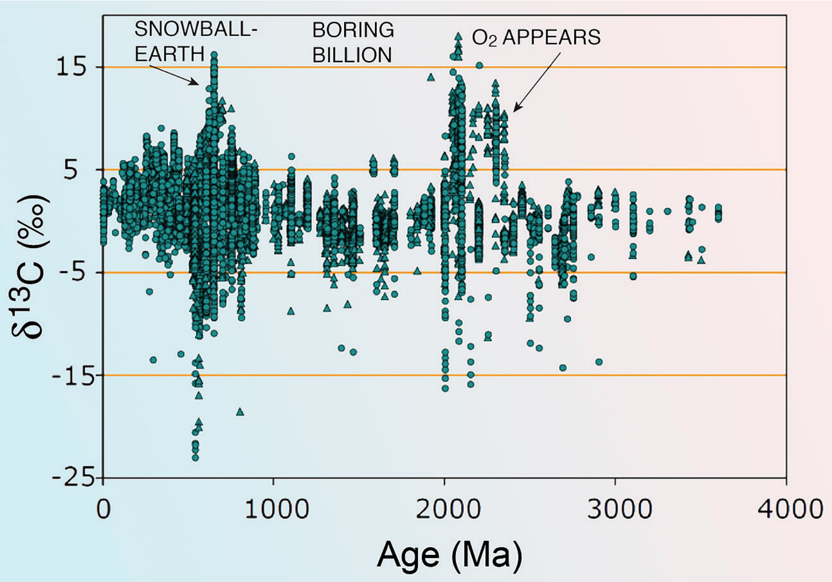


Figure 3.1 Summary of carbon isotope measurements on marine limestones and dolomites put together by Shields and Veizer (2002). It spans the last 3.6 billion years. As can be seen, except for two time intervals, the $\delta^{13}C$ values fall mainly within the permissible range. One of these anomalous periods spans the 2.4 to 2.0 billion year time interval which immediately followed the appearance of O_2 in our atmosphere. The second spans the time interval 0.8 to 0.5 billion years which includes the snowball episodes (modified by John Higgins from Shields and Veizer, 2002).

During quiet intervals, ^{13}C to ^{12}C ratios in limestone are confined to what might be referred to as the expected range. Based on measurements on diamonds, carbonatites and CO_2 trapped in ridge-crest basalts, the consensus is that mantle carbon has a δ^{13}C averaging about –5 ‰. This sets a lower limit on the isotope ratio in marine carbonates. This limit can be achieved only if all the carbon supplied from the Earth's interior is removed as carbonate minerals. To the extent that it is buried as organic matter, the δ^{13}C for marine carbonates is shifted toward more positive values. For example, if half were deposited as organic matter with a δ^{13}C averaging –26 ‰, then the marine carbonates would have a δ^{13}C of +16 ‰ $\left(\frac{+16}{2} + \frac{-26}{2} = -5\right)$.

Much of the limestone deposited during the last 0.5 billion years has a δ^{13}C value close to zero. This translates to a 20-80 mix of organic matter and $CaCO_3$. It should be mentioned that this way of interpreting the carbon isotope ratios in marine carbonates is biased by the failure to include the contribution of recycled marine carbonate. To the extent that it is important, it shifts the –5 ‰ input value toward zero.

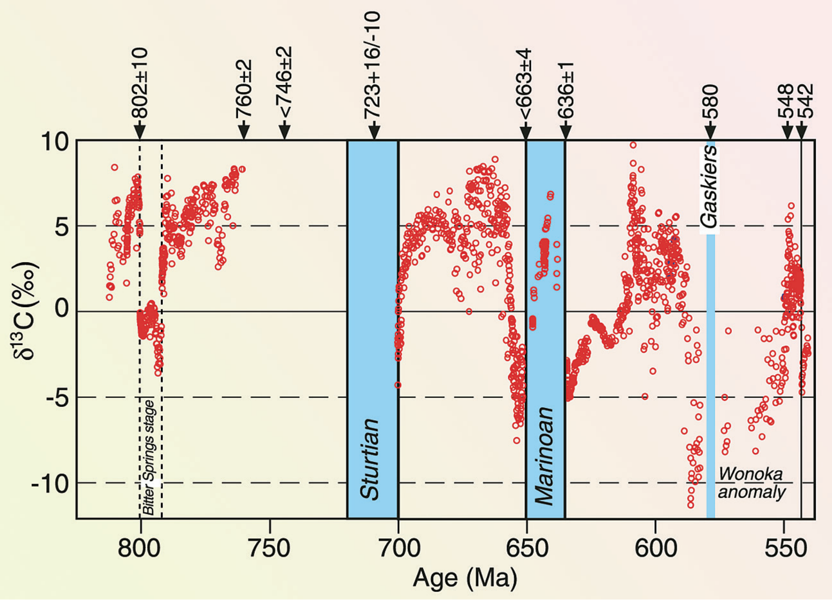


Figure 3.2 Carbon isotope record for limestones and dolomites formed during the time interval 0.81 to 0.54 billion years. The shaded bands represent the time intervals when ice covered the entire planet. Also shown are 9 highly precise ages based on uranium-lead ratio measurements on zircons. Note that the very low δ^{13}C values in carbonates formed just before and just after the freeze ups. Similar drops characterise the Bitter Springs event for which there was no snowball (from Halverson *et al.*, 2005 with permission from the Geological Society of America).

With this background in mind, let us ponder the ^{13}C record for the time period 0.8 to 0.5 billion years ago (see Fig. 3.2). During this time period there were four major negative excursions of $\delta^{13}C$. Two of these culminated in snowball Earth episodes (the Sturtian and the Marinoan). During the Bitter Springs $\delta^{13}C$ dip at 0.8 billion years ago snowball conditions didn't materialise. The Wonoka excursion, centred at 0.57 billion years ago, differs from the other three in that the $\delta^{13}C$ dips well below the permissible range. But no snowball.

Before delving into what the $\delta^{13}C$ records might be telling us, it is important to define what is meant by Snowball Earth episodes. As the name implies, they are times when both land and ocean were ice bound. Sediments containing a jumble of entities ranging in size from angular cobbles to fine clays are found at a dozen or so locales. These diamictites were deposited by glaciers. A number are in contact with marine sediments suggesting that the glaciers which produced them extended to sea level.

Key to the conclusion that these freeze-ups were global in extent are reconstructions of the latitudes at which the diamictites formed (see Fig. 3.3). This is done by measuring the direction of magnetic fields built in at the time of their deposition. As the Earth's lines of magnetic force are near vertical at high latitudes and near horizontal in the tropics, these magnetic field directions can be used to reconstruct palaeo-latitudes. At seven of the diamictite locales, the reconstructions are judged to be sufficiently firm to declare that the glacier extended to sea level somewhere between 10 °N and 10 °S latitude. As today's tropical snowlines are at about five kilometres elevation, in order to have had mountain glaciers at sea level, the temperature must have been at least 25 °C colder than today's.

For many years, there were disagreements regarding whether there were two snowball episodes or only one. The problem was that there was no way to put these geographically diamictites in stratigraphic order. The breakthrough came when it was shown that zircons present in volcanic ash deposits yield precise radiometric ages. These ages are based on measurements of both the ^{206}Pb generated by the decay of ^{238}U and the ^{207}Pb generated by the decay of ^{235}U. Shown in Figure 3.2 are 9 such ages for the period of interest. These ages make it possible to create an approximate time scale for the rise in the ^{87}Sr to ^{86}Sr recorded in limestones formed during this time interval (see Fig. 3.4). With this in hand, it was possible to place in stratigraphic order locales where there are no radiometric ages. Based on this time scale, it is clear that there were two snowball episodes separated by about 70 million years (see Fig. 3.2).

Now back to the carbon isotope record. An ongoing controversy rages regarding its interpretation. At one extreme are those who believe these carbonates have been so thoroughly metamorphosed that the carbon isotope ratios are meaningless. Others contend that, although altered, the record retains a valuable message. A breakthrough in this regard awaited new evidence which narrows the controversy. Princeton University's John Higgins stepped up to the plate and delivered just what was needed. He supplemented the carbon isotope record with that for calcium isotopes and that for Sr to Ca ratios.

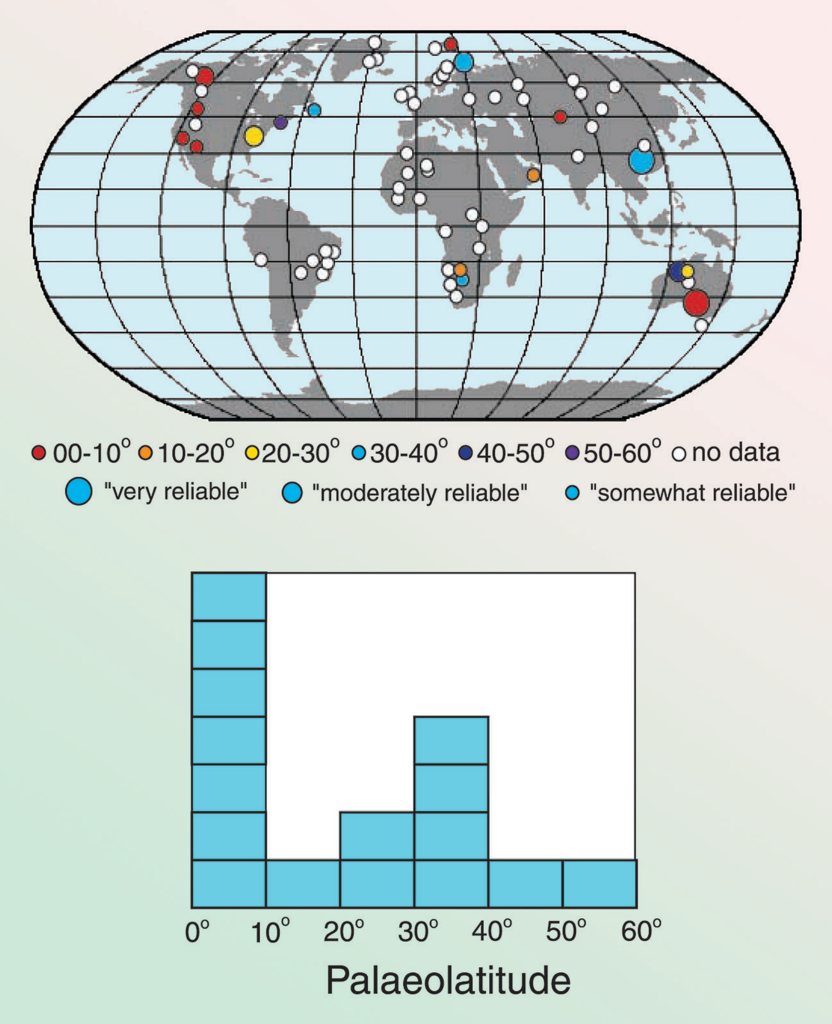


Figure 3.3 Shown in the upper panel are the fifty or so locations where snowball earth's glacial deposits have been found. Seven of these sites have been shown to lie within the latitude range 10 °S to 10 °N. As in each case there is an association with marine sediment, it appears that glaciers in the tropics reached sea level (after Schrag *et al.*, 2002).

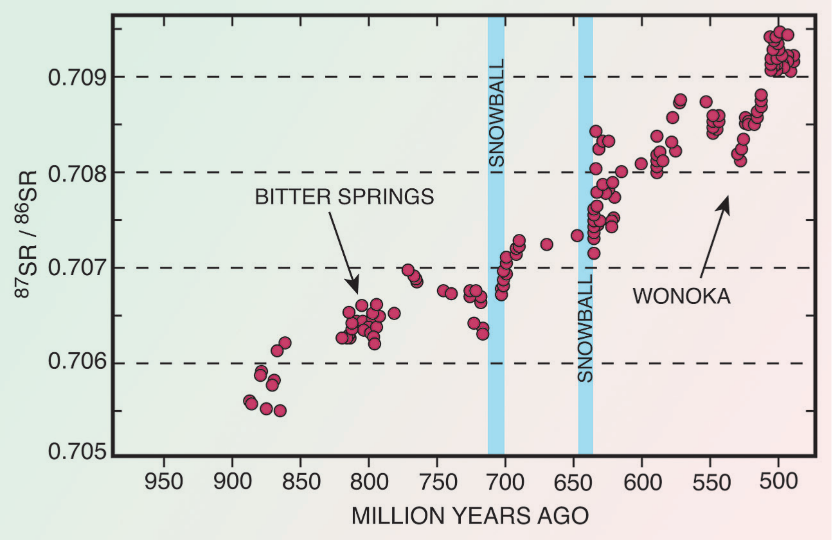


Figure 3.4 Complementing the sparse radiometric ages are ^{87}Sr to ^{86}Sr measurements on limestones. During the time interval 0.9 to 0.5 billion years ago, this ratio steadily increased. Even though there is considerable structure superimposed in this rise, there is no overlap between the values for the Sturtian and Marinoan Snowball events (shown in blue). This allows the two to be distinguished at locales where no radiometric dates have been obtained (after Halverson *et al.*, 2009).

Higgins and his colleagues developed a routine for making large numbers of highly precise measurements of the ^{44}Ca to ^{40}Ca ratio in marine carbonates. They documented that planetary calcium has a δ^{44}Ca of –1 ‰. This is also the ratio they found in limestones ranging in age from 3.0 to 0.5 billion years in age (see Fig. 3.5). This match makes sense; as the calcium added to the ocean is removed almost entirely as carbonate sediment.

What Higgins *et al.* found was that some of the limestone and dolomite samples have δ^{44}Ca values less than –1 ‰ and that these samples had Sr to Ca ratios up to an order of magnitude larger than those with planetary ^{44}Ca to ^{40}Ca ratios (see Fig. 3.6). Further, these samples often had δ^{13}C values more negative than the -5 ‰ limit. It must be noted, however, that not all the samples with anomalously low δ^{13}C values have anomalous δ^{44}Ca and Sr to Ca ratios. For example, samples from the Wonoka event with δ^{13}C values ranging down to –12 ‰ have no significant calcium isotope or strontium anomalies. But based on their very high manganese content, he suggests that they experienced metamorphism similar to that experienced by the Monterey Formation (see Blättler *et al.*, 2015).

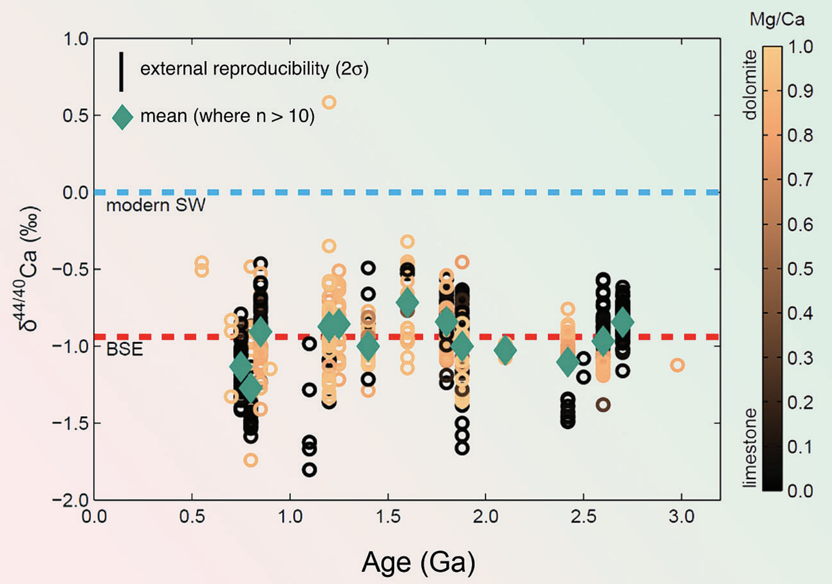


Figure 3.5 Calcium isotope measurements obtained by Blättler and Higgins on carbonate sediments with ages in the range 2.7 to 0.5 billon years. Most of these fall within the two sigma reproducibility range of the planetary δ^{44}Ca value of –1.0 ‰ (after Blättler and Higgins, 2017).

Higgins has found what appears to be a modern analogue for the anomalous Precambrian carbonates. It is sedimentary carbonate deposited on the Bahama Banks. Cores drilled into these sediments encountered a jumble of mineral types: aragonite, low Mg calcite, high Mg calcite and dolomite. These rocks were initially primarily deposited as aragonite and subsequently were diagenetically altered. As shown in Figure 3.7, a scatter plot of δ^{44}Ca against Sr to Ca obtained for the Bahama carbonates is similar to that for the Precambrian carbonates. In both cases samples with δ^{44}Ca of less than –1 ‰ have elevated Sr to Ca ratios.

It should be noted that coralline aragonite has a higher initial Sr to Ca ratio than other marine carbonates. Also aragonite has a half per mille lower δ^{44}Ca than limestone (*i.e.* –1.5 ‰ instead of –1.0 ‰). The latter is presumably the result of calcium isotope fractionation associated with aragonite formation. Similarities between the geochemical fingerprints (δ^{44}Ca *vs.* Sr/Ca) of Precambrian and Bahamian carbonates convinced the Higgins' team that both datasets reflected aragonite that was diagenetically recrystallised to calcite and dolomite by a seawater-like fluid. Samples with negative δ^{44}Ca values and high Sr were from recrystallisation that took place under closed conditions that appears to preserve the primary sediment chemistry.

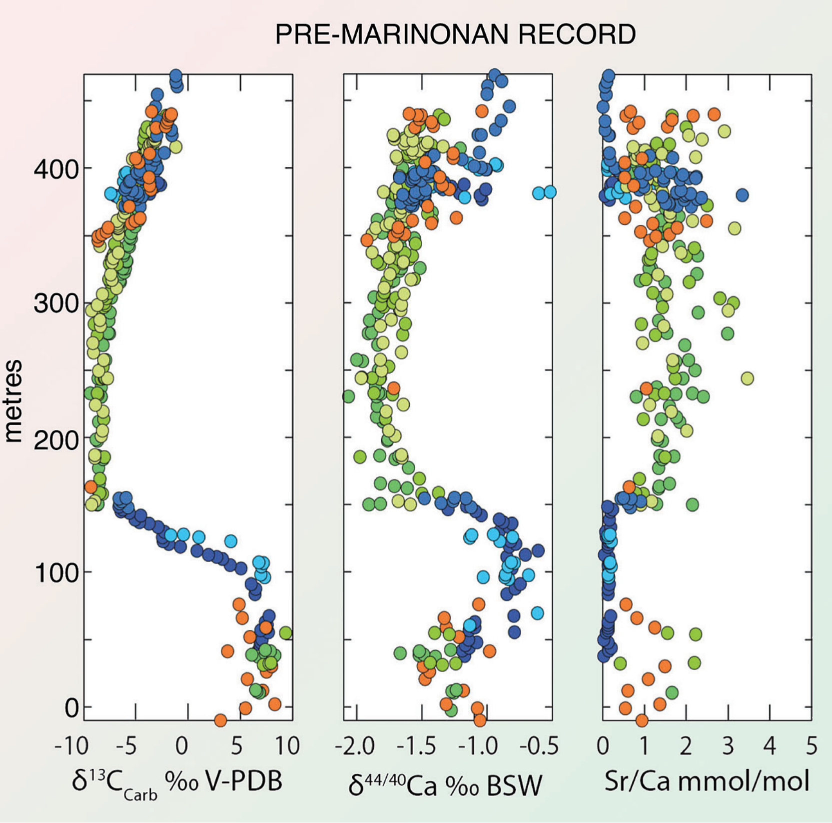


Figure 3.6 Records for δ^{13}C, δ^{44}Ca, and Sr to Ca for the time period leading up to the Marinoan Snowball event. Note that major drop in δ^{13}C (from +7 ‰ to –9 ‰) is accompanied by a decrease in δ^{44}Ca and an increase in Sr to Ca. These anomalous values match those for δ^{13}C (Ahm *et al.*, unpublished).

Precambrian rocks that contain anomalous δ^{13}C values – both positive and negative – tend to be characterised by low δ^{44}Ca values and elevated Sr contents (Fig. 3.7). In other words, the anomalous carbon isotope values occur predominantly in rocks in which the chemistry of the primary aragonite was preserved. In the Bahamas, this aragonite is characterised by carbon isotope values that are 3 to 4 per mille higher than open ocean carbonate. The Higgins' group interprets these C isotopic compositions to the environments where the aragonite was metamorphosed. If this interpretation is correct, it begs at least two important questions; 1) what processes drive the δ^{13}C of shallow-water aragonite to both extremely positive and negative values and 2) how does this interpretation explain the apparent synchronicity of these excursions on different continents?

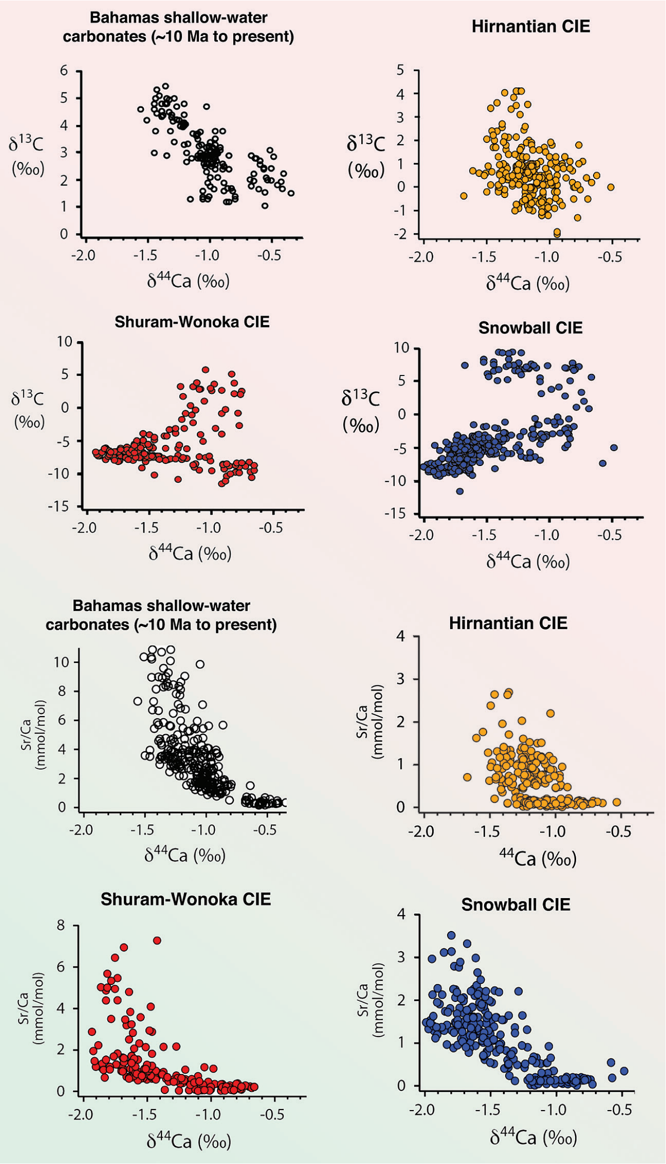


Figure 3.7 The Higgins team were pleased to discover that the trend of Sr to Ca and the calcium isotope ratios in a core taken on the Bahama Banks are quite similar to that for the Snowball Earth carbonates. This match is particularly interesting because the carbonates in the Bahamas core were originally deposited as

aragonite with a δ^{44}C of –1.3 ‰ and a Sr to Ca ratio of 10 millimoles/mole. During recrystallisation to calcite, the δ^{44}Ca increases by about 0.5 per mille and the Sr to Ca ratio drops by more than a factor of 10. Note that the trend for δ^{13}C *versus* δ^{44}Ca for the Bahama samples does not match that for those from Precambrian (Higgins group, personal communication).

Higgins proposes a possible mechanism for the range in δ^{13}C values during Precambrian carbon isotope excursions. Methane oxidation accounts for low δ^{13}C values and methane escape for high δ^{13}C values.

Although Higgins *et al.* make a convincing case that metamorphism has biased the snowball era carbon isotope record, he also creates what to me is an enigma. If the carbon isotope composition of these shallow water carbonates was produced in isolated environments, one would expect that the δ^{13}C record for a given event would differ from place to place. As much of the diagenesis is likely to have taken place well below the sediment–water interface, it is hard to imagine how diagenetic offsets from different locales would be the same. Yet despite their anomalous δ^{44}Ca and Sr to Ca ratios, δ^{13}C records from different places are remarkably similar.

Two examples are shown. The first is the Bitter Springs event (see Fig. 3.8). As can be seen, records from Australia and Svalbard are nearly the same in both amplitude and shape. The second is the Wonoka event (see Fig. 3.9). Partial records from four continents follow the same pattern. Also, the large negative Wonoka δ^{13}C spike is recorded on two continents.

The enigma is that, as these anomalous carbonates cannot have formed in open ocean water, some global link other than ocean chemistry must be called upon in order to explain the near identical records from widely separated places. The global link that comes to mind is sea level. When large ice sheets are present, the Earth's orbital cycles cause them to oscillate in size. These oscillations drive sea level up and down. This subjects shallow banks to alternating times of submergence and emergence. As is well documented, when subjected to fresh water, marine aragonites rapidly recrystallise. Although sea level oscillations provide a global link, they do not explain why diagenesis experienced at different locales produces similar δ^{13}C anomalies. This is especially puzzling for sediments whose diagenesis occurred deep enough to be out of contact with the overlying seawater. So, although the Higgins team has made huge strides, there remains more to be learned.

It must be mentioned that during the Ordovician there was a glaciation and associated with it were both ^{13}C and ^{44}Ca anomalies (see Fig. 3.10). In this case, the δ^{13}C shift was toward more positive values. As proposed by Higgins, the high values might be generated if the ^{13}C-deficient CH_4 escapes and the co-produced ^{13}C-enriched CO_2 reacts with the carbonates.

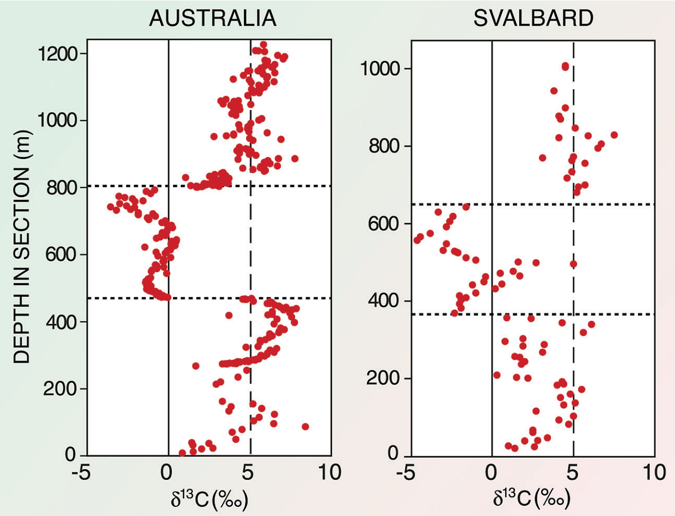


Figure 3.8 Comparison of the carbon isotope records for the Bitter Springs event in Australia and Svalbard. The similarity is so striking that it's difficult to believe that either was subjected to diagenesis. It will be interesting to see the calcium isotope and Sr to Ca ratio results when they become available (modified from Halverson *et al.*, 2005).

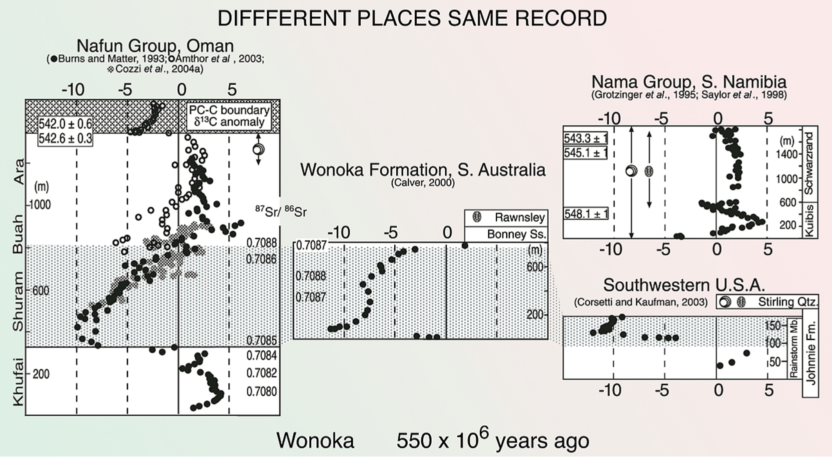


Figure 3.9 Comparison between the complete carbon isotope record obtained in Oman for the Wonoka and partial records in Australia, Africa and North America. Radiometric ages for the Namibia section nicely match those for Oman. Strontium isotope measurements for the Australian section nicely match those for Oman. Note that the shapes and amplitudes match quite well (from Halverson *et al.*, 2005 with permission from the Geological Society of America).

So, did CO_2 play a role in all this? Only in the case of the terminations of the snowball events can a firm case be made. The scenario is as follows. Even though frozen at its surface, the Earth's interior would have remained hot. Volcanoes would have continued to belch out CO_2. But on a frozen Earth, there would be no generation of either $CaCO_3$ or organic matter. Hence, this CO_2 would have accumulated in the atmosphere increasing the Earth's greenhouse strength and, as a result, its temperature. Eventually (*i.e.* in a few million years) the buildup of CO_2 would become large enough to cause the ice to melt. This would reduce the Earth's reflectivity and thereby amplify the warming. Once the ice was gone, heated by the excess CO_2 (and H_2O vapour), the planet would have been quite hot. Further, acidified with CO_2, ocean water and rain water would have attacked basaltic rocks releasing calcium oxide. The calcium oxide would have combined with excess CO_2 to make limestone and eventually the Earth would have cooled to its pre-snowball state.

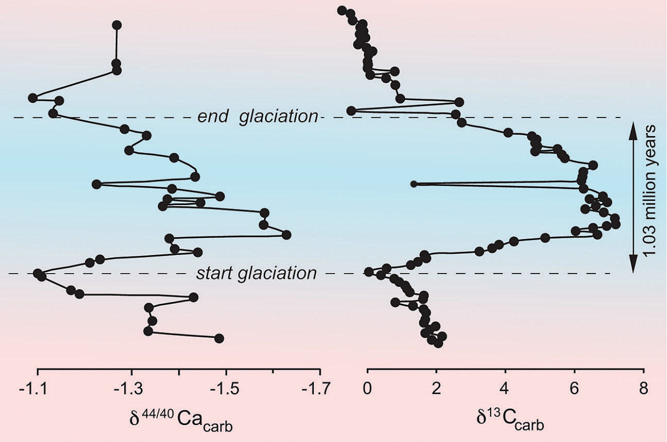


Figure 3.10 Calcium and carbon isotope shifts during the Ordovician glaciation (after Holmden *et al.*, 2012).

Evidence supporting this scenario is contained in what are referred to as 'cap carbonates' which overlie the diamictites. They are unlike any other limestone. Instead of horizontal layering, cap carbonates often consist of large vertically oriented blades. The sea level rise associated with the ice melt allowed the cap carbonates to be deposited on top of the glacial diamictites. So one might say that CO_2 saved our planet from remaining forever frozen.

Although declining atmospheric CO_2 content likely played a role in cooling the planet to its freezing point, it is not clear what caused the plunge. My suspicion is that photosynthesis somehow got the upper hand over respiration drawing down the atmosphere's CO_2 content. The answer will likely come from an improved understanding of the chemical cycles that took place in the algal mats which dominated Precambrian life.

It is tempting to postulate that the decreases in $\delta^{13}C$ which characterised the onset of the Bitter Springs, Marinoan, Sturtian and Wonoka events record times of cooling and hence of atmospheric CO_2 drawdown. Perhaps photosynthetic organisms became so adept at packing away carbon in organic matter that the atmospheric CO_2 content was drawn way down. If so, one might ask why the Bitter Springs drawdown did not culminate in a snowball. Perhaps a point was reached where decline was stemmed by low CO_2 availability to the point where respiration could keep pace with photosynthesis. This balance persisted for a few million years before things returned to their pre-Bitter Springs state value. It seems to me that understanding the Bitter Springs event is key to understanding the subsequent snowball episodes.

4. A COLLISION CHANGES EVERYTHING

About 100 million years ago the breakup of a super continent centred over the South Pole initiated the northward drift of Africa, Australia and India (see Fig. 4.1). Of particular interest is India for its drift was terminated by a head-on collision with Asia. Such a collision between continental blocks is geologically rare. That between India and Asia is the only one in the last 200 million years. A continent-continent collision is quite different than that involving ocean crust and continental crust. In such cases the ocean crust is subducted intact into the mantle beneath the continent. Hence it is more a sideswipe than a collision. But, when two 30 kilometre thick granitic blocks run smack into one another, they are mashed into a single 60 kilometre thick mass.

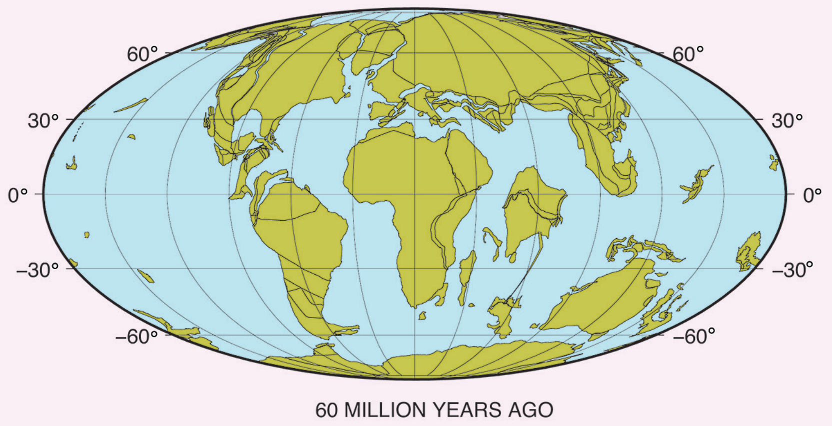


Figure 4.1 180 million years ago a super continent consisting of what is now Antarctica, Africa, India and Australia broke up. The pieces drifted apart. Of interest here is India which drifted to the north eventually colliding with Asia.

Based on studies of rock formations in the Himalayas, geologists have proposed a wide range of ages for the onset of this collision. As outlined below I suspect that the main blow was struck close to 51 ± 2 million years ago. Indeed, according to one author (Bouilhol *et al.*, 2013), India struck an island arc 50.2 ± 1.5 million years ago (see Fig. 4.2). Two additional sets of observations point to 50 million years as the key time. One is based on changes in plate motions and the other on observations on marine sediments.

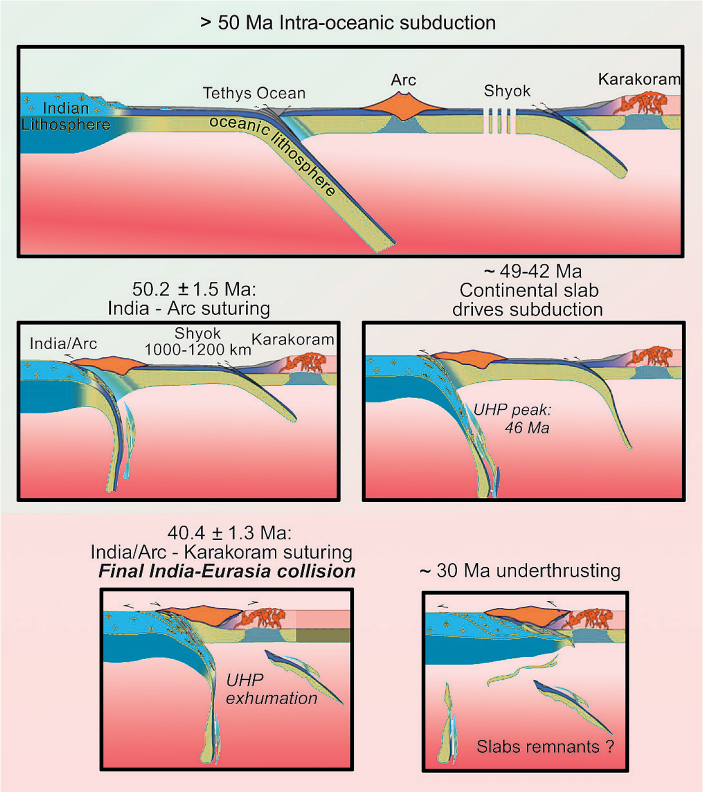
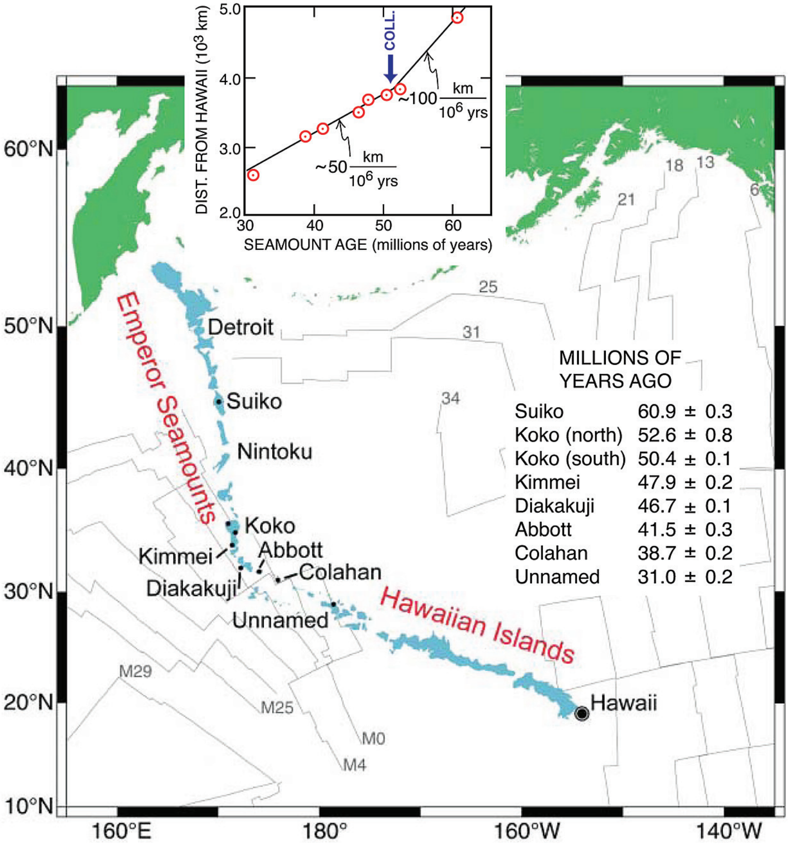


Figure 4.2 One view of the sequence of events associated with the collision of India with Asia (modified from Bouilhol *et al.*, 2013).

Earth's plates must normally move harmoniously across the planet. However, just as highway wrecks disrupt traffic patterns, continental plate wrecks disrupt plate movements. Indeed there is striking evidence that plate motions were disrupted close to 50 million years ago. The record is kept by a chain of islands and sea mounts in the northern Pacific (see Fig. 4.3). This chain was produced by the drift of the ocean crust over a plume of molten basalt thought to be rising from the boundary zone separating the Earth's iron core from its silicate mantle. If the position of the plume is assumed to have remained fixed, then this chain records both the direction of drift and its speed. The head of the plume is currently located beneath the island of Hawaii. To the northwest is a chain of islands which make up the Hawaiian group. Farther away, the chain consists of seamounts. Slow cooling of the 10 km thick ocean crust caused it to shrink and the islands it supported to slowly sink. Once they have descended beneath the sea surface they are called sea mounts. Our interest here lies in the sharp kink in the chain's path which took place close to 50 million years ago. Prior to this time the Pacific plate was moving to the north. Then its path abruptly shifted to the northwest. Further, at that time the average rate of plate drift decreased by a factor of two. Of additional interest is that the Pacific plates push to the west had initiated the Mariana, Tonga, Tzu, and Aleutian arcs.



Suiko	60.9 ± 0.3
Koko (north)	52.6 ± 0.8
Koko (south)	50.4 ± 0.1
Kimmei	47.9 ± 0.2
Diakakuji	46.7 ± 0.1
Abbott	41.5 ± 0.3
Colahan	38.7 ± 0.2
Unnamed	31.0 ± 0.2

Figure 4.3 The trace of volcanoes left behind as the Pacific plate moved over a mantle plume; the K-Ar ages of some of these volcanoes are listed on the right. Prior to 50 million years ago the Pacific plate was headed north. After this time it has been moving WNW. It currently underlies Hawaii. As can be seen in the insert, the rate of movement of the plate slowed by roughly a factor of two at the time of the collision (modified from Sharp and Clague, 2006).

The ^{18}O to ^{16}O ratio in the calcitic shells of bottom-dwelling (*i.e.* benthic) foraminifera changes with time for two reasons. First, the isotopic fractionation between dissolved inorganic carbon and solid $CaCO_3$ is temperature dependent. It increases by about 0.23 ‰ for each °C of cooling. Second is that the snow which falls accumulates on the Antarctic ice cap and is depleted in ^{18}O by several percent. The missing ^{18}O is left behind in the ocean. Shown in Figure 4.4 is the $\delta^{18}O$ record for benthic foraminifera extending back 63 million years. Two aspects of the record are of particular interest. First, prior to 50 million years ago the deep ocean was warming and since that time it has steadily cooled. This can be stated with confidence because, between 60 and 40 million years ago, the polar regions were too warm to host ice caps. Hence the change in ^{18}O must have been driven entirely by temperature. It is thought that Antarctica was ice free until about 33 million years ago. Glaciation of the northern polar region started about three million years ago. Second, the 'scatter' of the ^{18}O record is quite small before 33 million years and increases progressively thereafter. For the last million or so years this scatter has become extremely large. This variability in $\delta^{18}O$ is, at least in part, related to the variability in the extent of ice cover driven by the Earth's orbital cycles. We know for sure that this is the case for the last million or so years.

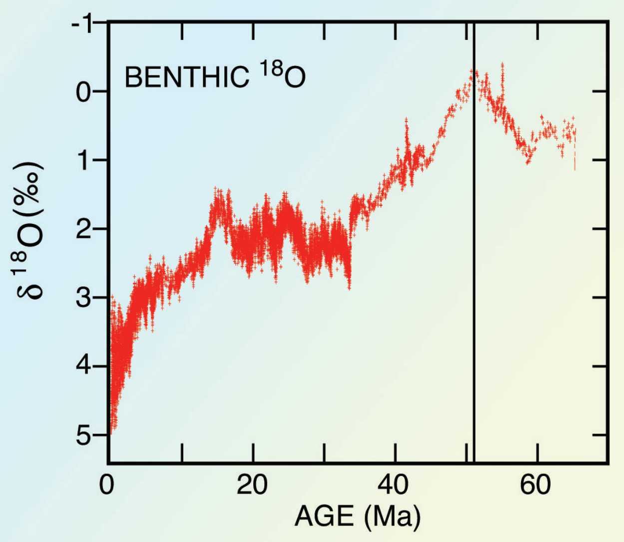


Figure 4.4 Record of the ^{18}O to ^{16}O ratio in calcitic benthic foraminifera shells. Two aspects are important to us. First, a change in trend from a warming to cooling took place close to 50 million years ago. Second, although a pause in the cooling took place between 33 and 15 million years ago, it continues right up to the present. At least some of the scatter is the result of changes in size of the polar ice caps driven by orbital cycles (Zachos *et al.*, 2001) (from Broecker, 2015a).

The difference in $\delta^{18}O$ between today (3.2 ‰) and that 50 million years ago (–0.2 ‰) is 3.4 ‰. The ^{18}O ice depleted on Antarctica accounts for about 1.0 ‰ leaving 2.4 ‰ for deep ocean cooling. Hence during the last 50 million years the deep sea has cooled by about 10 °C. The transition from a warming deep ocean to a cooling deep ocean occurred at very close to the same time as the kink in the Pacific plate's path. This suggests that this change is related to the collision of India with Asia.

So what is the connection between deep ocean temperature and plate tectonics? I would like to believe that it is a drop in the atmospheric CO_2 content. Both the reconstruction of the ^{13}C to ^{12}C ratio in alkenones and that in ocean-sediment organics show shifts with time to the ever more positive values expected if atmospheric CO_2 content were declining (see Fig. 4.5). Further, the planet-wide switch in horse diet from C-3 to C-4 grasses which took place about 8 million years ago is best explained by a drop in atmospheric CO_2 content. While this evidence suggests that atmospheric CO_2 has decreased, both the magnitude and shape of this decline remain highly uncertain. Hopefully, Morgan Schaller will come to the rescue with his improved soil $CaCO_3$ proxy.

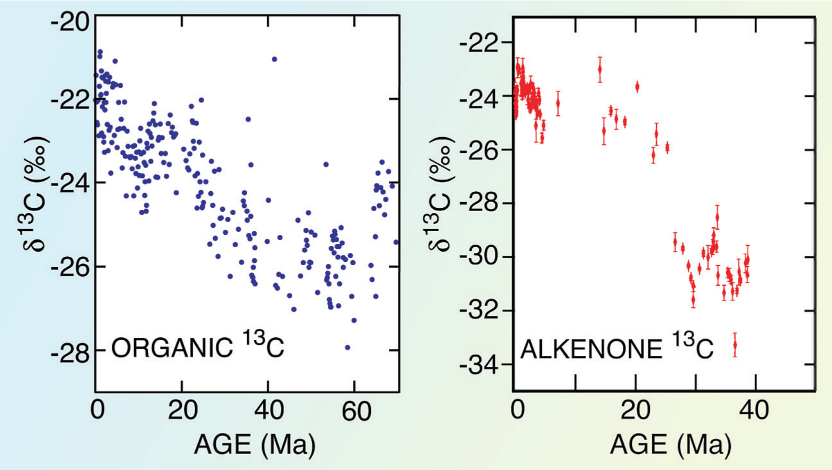


Figure 4.5 Two carbon isotope-based reconstructions of the $\delta^{13}C$ in marine organic matter. On the left is the record for traces of organic carbon preserved in deep sea sediments (Falkowski *et al.*, 2004). On the right is the record for alkenones contained in the $CaCO_3$ coccolith tests produced by Emiliania Huxleyi (Zhang *et al.*, 2013). As can be seen, both records show that $\delta^{13}C$ has increased with time as would be expected if the CO_2 content of the surface ocean has been decreasing. But, as can also be seen, the two records have different amplitudes and shapes. Also it is not clear how to convert $\delta^{13}C$ to CO_2 content.

In addition to the evidence for deep sea cooling kept in benthic foraminifera, several lines of evidence make it clear that the chemical and isotope composition of sea salt has changed over the last 50 million years. Most striking is the steady increase in the ratio of ^{7}Li to ^{6}Li recorded in the shells of planktonic foraminifera (see Fig. 4.6). Another is a sharp 4 ‰ jump in the ratio of ^{34}S to ^{32}S in marine barite which occurred 50 million years ago (see Fig. 4.8). A third is a five-fold increase in the magnesium-to-calcium ratio of sea salt as recorded in aragonitic coral. A fourth is a two-fold decrease in calcium content as inferred from the increase in the uranium content of aragonitic corals. Although it is tempting to attribute these changes solely to the creation of the Himalaya Mountain chain, the great rivers draining this geomorphic feature currently account for only 16 percent of global input to the ocean. Hence the cause of these changes must be on a global scale rather than a local one.

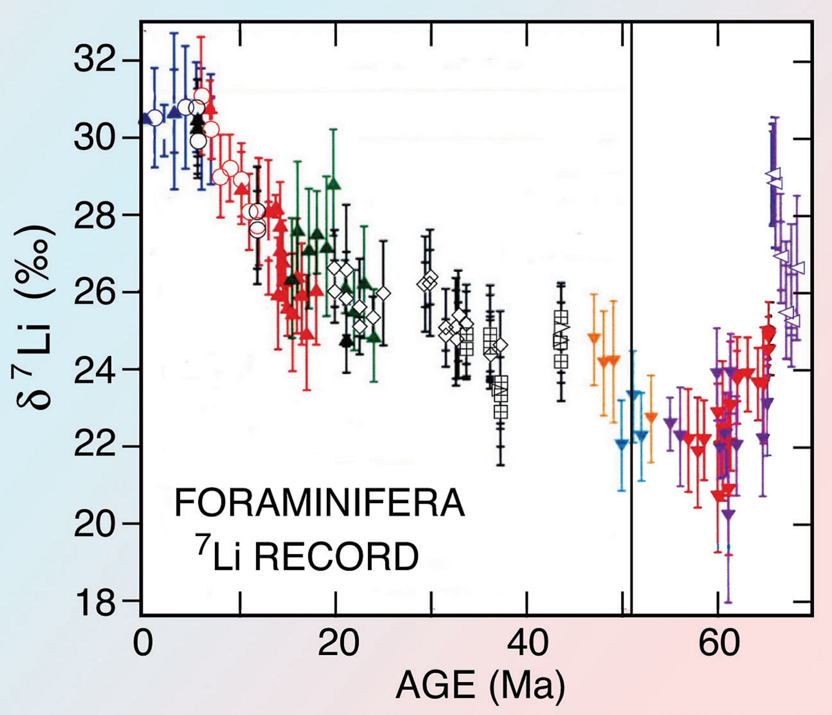


Figure 4.6 The isotopic composition of seawater lithium as recorded in planktonic foraminifera shells (Misra and Froelich, 2012); as can be seen, starting about 50 million years ago, the δ^7Li began an increase which continues today. Note that, as is the case for the ^{16}O record kept in benthic foraminifera shells, there appears to be a 15 million year pause centred about 25 million years ago (from Broecker, 2015a).

Of the records in hand, that for lithium isotopes kept in planktonic shells is the most detailed and the least noisy (see Fig. 4.6). The δ^7Li for planetary lithium is +5 ‰. Fifty million years ago the δ^7Li in sea water was about +18 ‰. Since then, it has steadily risen. It is now +28 ‰. Riverine lithium is enriched in its heavy isotope. The reason for this is clear. Some of the lithium released during the weathering of primary igneous minerals is built into clay minerals in soils. During this process, the light lithium isotope (^{6}Li) is preferentially taken up leaving behind the heavy isotope. Hence the lithium in rivers is enriched in ^{7}Li.

As of this writing, there is no current consensus regarding the cause of this very large increase in the δ^7Li in seawater. As the magnitude of isotope fractionation increases as temperature falls, it is tempting to attribute it to planetary cooling. However a ten per mille increase in δ^7Li for a tropical cooling of only about 3 °C is clearly unreasonable. Although the cause of this large δ^7Li change remains unclear, of importance here is that the increase began close to the time of the India-Asia collision.

A second isotope record, *i.e.* that for the ratio of ^{87}Sr to ^{86}Sr in marine $CaCO_3$ (see Fig. 4.7) has been a source of considerable controversy. The problem is that although its shape resembles that of the lithium isotope record, its rise began some 10 million years later. Geologists who favour a younger date for the collision often point to the ^{87}Sr record in support of this choice. However, unlike ^{18}O and ^{7}Li which record things going on at the Earth's surface as first pointed out by the late John Edmond, ^{87}Sr likely records metamorphism which took place 50 or so kilometres beneath the Earth's surface. Edmond attributed the 10 million year delay to time required to bring the product of this metamorphism to the surface exposing it to chemical weathering.

Unlike the variations in the isotopic composition of oxygen and lithium which are created by the tendency of light isotopes to react faster than the heavy isotopes, those for radiogenic strontium are the result of the production of ^{87}Sr by the radioactive decay of the long lived ^{87}Rb ($t_{1/2}$ = 50 billion years). This production is of interest because the ratio of Rb to Sr varies widely among Earth reservoirs. In Earth's mantle strontium is far more abundant than rubidium. So large is the difference that the ^{87}Sr produced there over geologic time has generated only a very small increase in the mantle's ratio of ^{87}Sr to ^{86}Sr. The same is true for basalts produced by melting of mantle rock. At the other end of the scale are granites which have unusually high ratios of Rb to Sr. The reason is that Rb is a highly enriched relative to Sr during partial melting. As granites are the ultimate product of partial melting, they have a much higher Rb to Sr ratio than do basalts. This difference is amplified by their large mean age (averaging two or so billion years).

Although rich in ^{87}Sr, granites are loath to give it up during chemical weathering. Not only are granites more resistant to weathering than basalts, the K (and Rb) feldspar and K mica rich in rubidium are particularly resistant. Along with quartz, these two minerals tend to end up in detritus. One only has to take a look at beach sand to realise this.

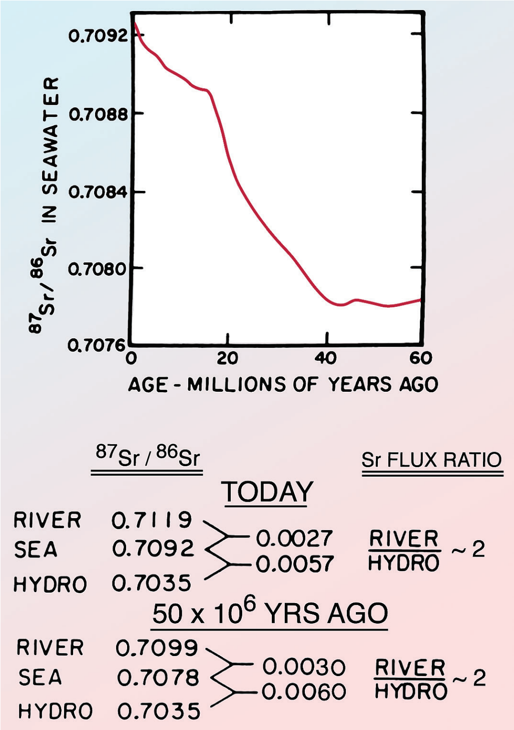


Figure 4.7 The graph shows the record for the ^{87}Sr to ^{86}Sr ratio in seawater as recorded in the shells of planktonic foraminifera. Note that the rise begins 10 million years after that for δ^7Li. Shown below is Edmonds' scenario regarding the cause of the rise. He envisioned that it was the result of high ^{87}Sr to ^{86}Sr ratio in Himalayan Rivers (Edmond *et al.*, 1992).

John Edmond sought to explain why the ^{87}Sr to ^{86}Sr ratio in limestones has steadily increased over the last 40 million years. He envisioned that the lower portion of the 60 kilometre thick granitic crust created by the collision of India with Asia was geothermally heated to the point where the high ^{87}Sr strontium in potassium-bearing minerals was mixed with the low ^{87}Sr strontium present in calcium-bearing minerals. Tens of millions of years later these metamorphosed granites were unroofed and exposed to weathering. Unlike the situation for their un-metamorphosed brothers, the dissolution of Ca feldspar released strontium rich in ^{87}Sr. This un-roofing continues today as the Himalaya is sculptured by glaciers.

Edmond's idea is confirmed by the unusually high ^{87}Sr to ^{86}Sr in rivers draining the Himalaya. As these rivers are also rich in strontium, their contribution to the ocean has steadily increased its ^{87}Sr to ^{86}Sr ratio. So unlike the

^{18}O and ^{7}Li signals which reflect things happening planet-wide, the ^{87}Sr signal comes from the Himalayas. Further, the 10 million year lag in its appearance in the limestone record is a measure of the time required to un-roof rock metamorphosed at a depth of 50 or so km.

The sulphur isotope record preserved in marine $BaSO_4$ has a different shape than those for oxygen and lithium. Close to 50 million years ago, the ratio underwent a 4 ‰ upward jump and then remains at this new level all the way to the present (see Fig. 4.8). Jess Adkins, puzzled by this record, set out to duplicate it. Rather than employing marine barite, he turned to traces of SO_4 present in the shells of planktonic foraminifera. He reproduced both the four per mille jump and the post-jump constancy (Rennie *et al.*, 2018).

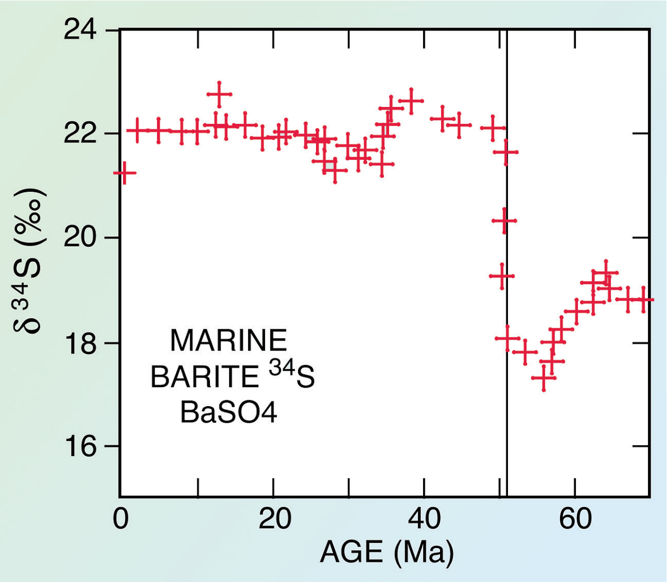


Figure 4.8 The record for the ratio of ^{34}S to ^{32}S kept in marine barite has a quite different shape than that for ^{7}Li to ^{6}Li. It undergoes an abrupt 4 ‰ jump 50 million years ago and remains constant thereafter (Paytan *et al.*, 2004) (from Broecker, 2015a).

Although the results for $\delta^{7}Li$ and $\delta^{34}S$ tell us that a change in ocean chemistry occurred at the time of the collision, they don't tell us anything about the actual changes in the ionic composition of seawater. In particular, how did the concentrations of Mg^{++}, Ca^{++}, and $SO_4^{=}$ change? Three archives offer information in this regard: fluid inclusions in marine halite, the magnesium content of ridge-crest calcites and the magnesium and uranium contents of aragonitic corals.

Halite inclusions offer information regarding the evolution of the magnesium content of seawater but not that of Ca^{++} and of $SO_4^{=}$. The reason is that gypsum (*i.e.* $CaSO_4$) is less soluble than halite. Hence fluid inclusions in halite formed 5, 17 and 36 million years ago contain little calcium. The reason is that precipitation of gypsum removed nearly all of it prior to the formation of halite. And, of course, it also removed part of the sulphate. Fortunately, there is no magnesium mineral that is less soluble than halite. Hence, water trapped in the fluid inclusions should contain all the original magnesium. However, in order to reconstruct the original concentration, the inclusion magnesium content must be ratioed to that of a constituent which remained unchanged with time. The choice of those conducting this research is potassium. Based on this assumption the answer turns out to be that over the last 37 million years the magnesium content of seawater has increased by roughly a factor of two.

Recently Anne Gothmann, as part of her thesis research at Princeton University, measured the magnesium content of well-preserved aragonitic corals extending in age back 200 million years. She demonstrated the integrity of these corals by demonstrating that their uranium-helium ages agreed with their geologic ages. Her results are consistent with the halite-based factor of two increases in magnesium.

Gothmann also picked up on a means to reconstruct the calcium content of seawater based on the uranium content of her corals. Decades ago, I proposed this approach. It involved three assumptions.

1. The U to Ca ratio in corals was close to that in seawater.
2. The U content of seawater was proportioned to its ΣCO_2 content.
3. The product of $Ca^{++} \times CO_3^{=}$ in the ocean has remained constant.

The defense for these assumptions is as follows:

1. Holocene and modern corals have U to Ca ratios within ±15 percent that for seawater.
2. Both the U content and ΣCO_2 content of Mono Lake water are two orders of magnitude higher than that in seawater. Gothmann located a paper documenting that a lake in Mongolia has U and ΣCO_2 contents similar to those in Mono Lake.
3. The depth of the calcite lysocline in the ocean has remained constant to within about one kilometre. Hence its Ca to $CO_3^{=}$ has varied by no more than 20 percent.

To the extent that these assumptions are correct:

$$\frac{Ca^{seawater\ then}}{Ca^{seawater\ now}} \sim \sqrt{\frac{U\ coral\ now}{U\ coral\ then}}$$

Gothmann found that the uranium content of her corals was about four times lower 35 million years ago than it is today. Based on the above set of assumptions, this suggests that the calcium content of sea salt decreased by a factor of two over this time period.

Taken together, these reconstructions suggest that the Mg to Ca ratio in seawater has risen by at least a factor of four since India collided with Asia. Magnesium has gone up by roughly a factor of two and calcium has gone down by roughly a factor of two. So, what could account for this large change? The answer that first comes to mind is that the formation of dolomite has steadily decreased as shallow inland seas disappeared. This would have increased the residence time of magnesium in the sea and decreased that of calcium. But, while this reduction has certainly taken place, Higgins and Gothmann have shown that the shift of Mg isotope ratios expected to accompany the demise of dolomite formation is not seen in their aragonitic corals. It is expected because there is a small separation between ^{26}Mg and ^{24}Mg during the formation of dolomite (see Fig. 4.9 caption).

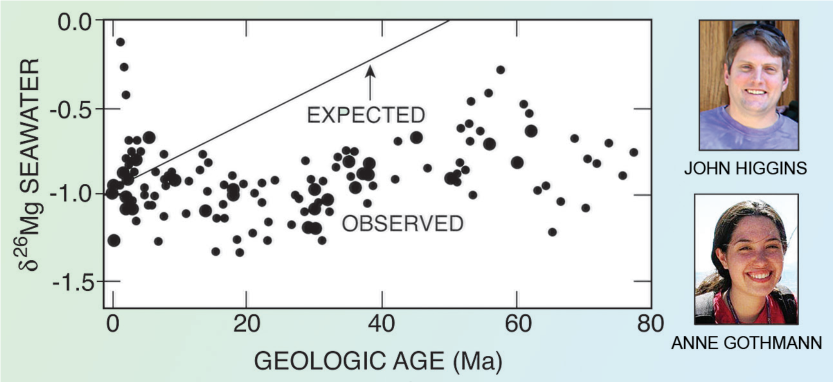


Figure 4.9 Magnesium isotope composition of seawater over the last 80 million years as reconstructed from aragonitic corals (large dots) and other carbonates (small dots). Were the increase in Mg to Ca ratios in sea salt driven by the demise of dolomite formation, then over the last 50 million years there should have been a 1 ‰ drop in δ^{26}Mg. Based on this record, Higgins and Gothmann conclude that dolomite formation 50 million years ago accounted for no more than 15 percent of the Mg budget (Higgins and Schrag, 2015; Gothmann *et al.*, 2017).

Although I know of no satisfactory explanation for the rise in the ratio of Mg to Ca, I suspect that something happened at the time of the collision which set the world on a new environmental track. The deep ocean has been cooling, the enrichment of heavy lithium has become ever larger, and the Mg to Ca ratio in sea salt has risen. I suspect that behind it all is a reshaping of the continents and ocean basins. One way to bring the atmosphere's CO_2 content down is to make the continents more mountainous. Mountains serve as crunchers and grinders creating material that is subject to rapid chemical weathering. Increased weathering would lead to an increase in the supply rate of silicate-bound calcium to the ocean. This would create a mismatch between the inputs of Ca and CO_2 (see Fig. 4.10) leading to a drawdown of atmospheric CO_2. The cooling produced in this way would decrease weathering rates, restoring the CaO – CO_2 balance.

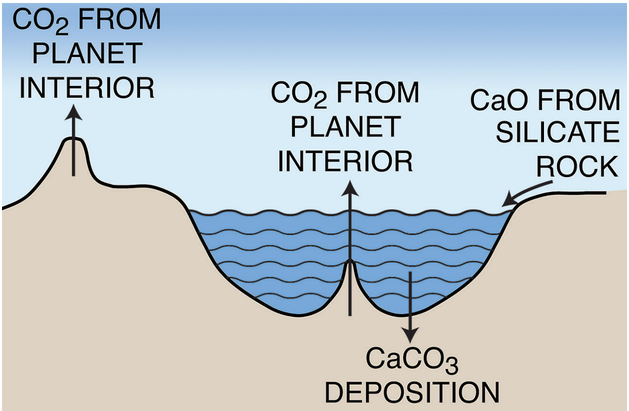


Figure 4.10 As almost all the calcium entering the ocean is removed as $CaCO_3$, for each calcium atom added by silicate weathering, there must be a matching molecule of planetary CO_2. If this balance is disrupted, a feedback will drive the CO_2 content of the atmosphere up or down restoring the Ca-CO_2 match.

How long will this cooling trend continue? If it is tectonic as proposed here, then one might guess it will continue until another continent-continent collision occurs putting us on a new course. In its absence, the Earth will continue to cool. As the deep sea is already close to its freezing point, it can't get much colder. But the sea ice surrounding the polar land masses will become ever more extensive. The Laurentian and Scandinavian ice sheets will join Antarctica as permanent features. Eventually the Earth would once again become a snowball (see Fig. 4.11). But, as it will take several tens of millions of years for this scenario to play out, chances are something will intervene and Earth's environment will go on a different track.

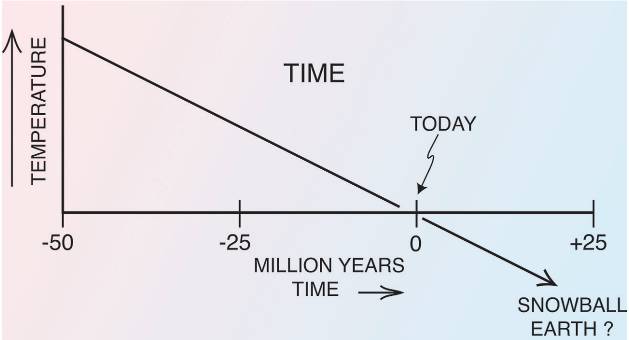


Figure 4.11 Expectation if the Earth's temperature continues along the trend experienced during the last 50 million years (from Broecker, 2015a).

5.

A SHORT-LIVED HOT SPELL

Five million years before India collided with Asia, the Earth experienced a sharp warming. It is known as the PETM (Palaeocene-Eocene Thermal Maximum). Over a time span of no more than four thousand years, the Earth's surface temperature jumped up by about 5 °C. This abrupt hot spell lasted for about 20 thousand years, after which the temperature slowly returned to its pre- PETM level.

This event was discovered by Jim Kennett and Lowell Stott in 1991. At a depth of 170 metres in a sediment core from the Southern Ocean, they encountered puzzling anomalies in the $\delta^{18}O$ and in the $\delta^{13}C$ recorded in foraminifera shells. The ^{18}O dropped by about 1.4 per mille suggesting that the Southern Ocean warmed by about 5 °C (see Fig. 5.1). When placed on the long term benthic record, this anomaly stands out like a sore thumb (see Fig. 5.2).

It was, however, the carbon isotope record that came as the biggest surprise. The $\delta^{13}C$ for both the upper and the deep Southern Ocean plunged by about 2.6 per mille. In order to create such a drop in today's ocean would require adding 3500 gigatons of carbon with a $\delta^{13}C$ of –26 per mille (*i.e.* that for terrestrial organic material). This is roughly the amount of carbon contained in our entire fossil fuel reserve.

This finding triggered a debate regarding the source of this carbon, and the debate continues 25 years after the PETM discovery. Attention was initially focused on methane clathrates stored in continental margin sediment. The idea was that they were destabilised by a precursory warm event releasing the trapped methane. This CH_4 was (as it is now) promptly oxidised to CO_2. A problem plagues this explanation. As only about 1500 gigatons of carbon are thought to be stored in today's methane clathrates, in order to get enough CO_2 all the clathrates present at the end of the Palaeocene would have to have been released in less than 4000 years. This global release would require some sort of precursory heating. But there is no evidence for such a precursor.

At the other extreme is a hypothesis put forth by Dennis Kent in 2003. He postulated that the carbon was delivered by a comet. As carbon-bearing gases are thought to make up about 10 percent of a comet's mass, in order to bring in even one thousand gigatons of carbon, the comet would have to have been a whopping 10 or so kilometres in diameter. The impact of such an object would have been catastrophic. Yet, the only extinctions which occurred were those of a few species of benthic foraminifera. Also, no PETM-related tsunami deposits have been found.

Kent's idea supported a claim by Jim Wright that the PETM-age Marlboro clay present on New Jersey's coastal plain was deposited at the huge rate of two or so centimetres per year. Measurements of $\delta^{13}C$ in bulk $CaCO_3$ indicated that the entire ^{13}C drop occurred in the first 15 of these annual layers. If correct, this would mean that the PETM carbon must have been added during a period of 10 or so years. Only Kent's comet could deliver the carbon this rapidly.

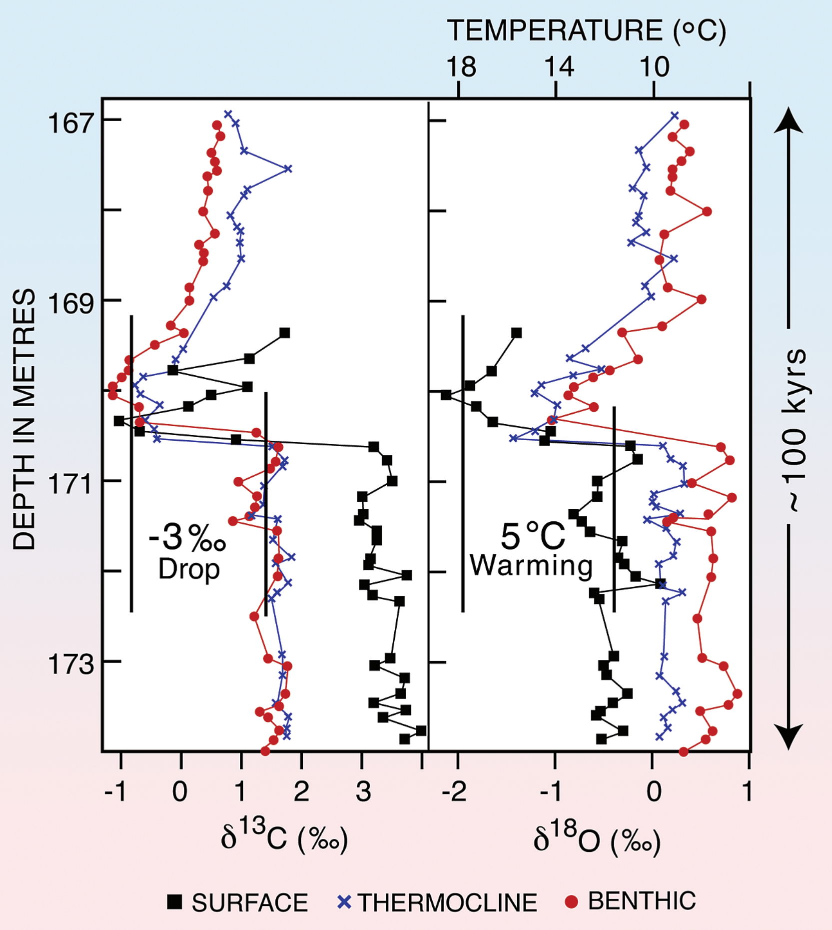


Figure 5.1 Carbon and oxygen isotope records for a Southern Ocean sediment core. It was this record that tipped off Kennett and Stott to the existence of the brief warming event now referred to as the PETM. Surface, thermocline and bottom-dwelling foraminifera record abrupt decreases in $\delta^{13}C$ and in $\delta^{18}O$. The ^{13}C drop requires the addition of roughly 3500 billion tons of ^{13}C-depleted carbon ($\delta^{13}C$ = –26 ‰) and the ^{18}O drop a 5 °C warming of the entire ocean (Kennett and Stott, 1991).

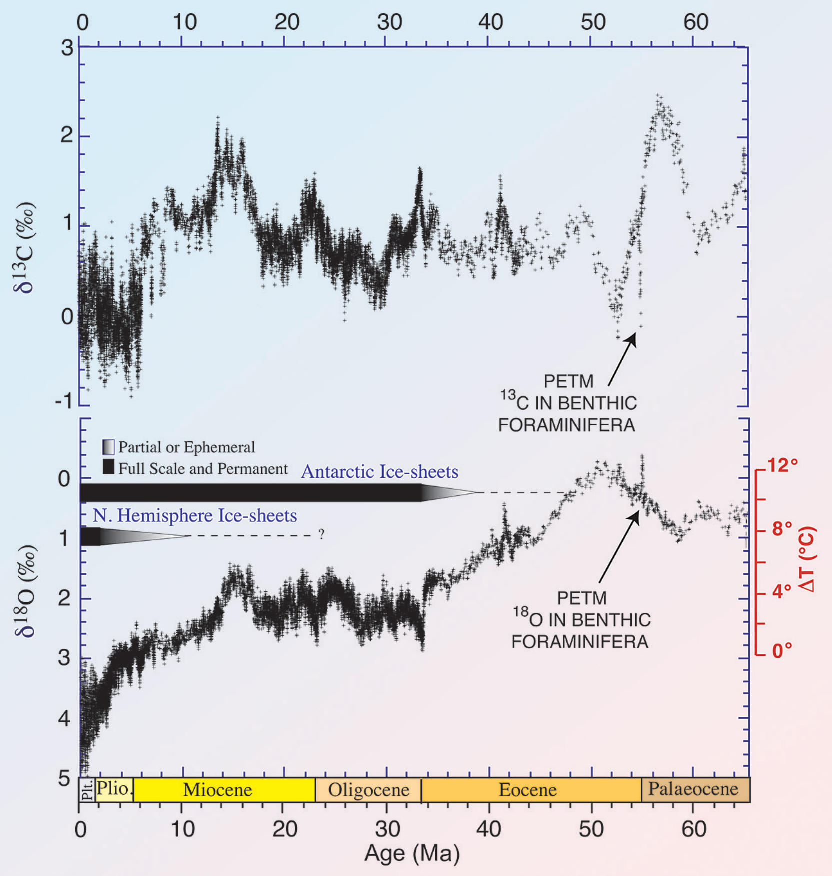


Figure 5.2 When placed on Zachos' composite benthic $\delta^{13}C$ and $\delta^{18}O$ records for the last 60 million years, the PETM is unique. Although excursions of similar amplitude are present, they were long lived compared to that for the PETM (Zachos *et al.*, 2001).

Then Paul Pearson dropped a bomb. When he examined the New Jersey margin cores, he concluded that the layers were not seasonal. Rather, they are 'biscuits' produced by rotary drilling. Pearson's explanation has received wide acceptance. Wright's claim fell to the wayside.

Jim Wright's work, however, did focus attention on the PETM record kept in the Marlboro clay present on much of the coastal plain of eastern North America. This fine clay is very different from the silty sediment which underlies and overlies it. The Marlboro contains little kaolinite whereas the silty sediments are rich in it. Something quite unusual must be responsible for the deposition of this 8 metre thick package of fine sediment.

Then it was Morgan Schaller's turn to drop bombs. His first was the discovery of tektites in a centimetre thick layer located at the base of the Marlboro clay (see Fig. 5.3). These tektites contained an unusually large amount of calcium suggesting that the impact which created them occurred in $CaCO_3$-rich sediment or rock. Argon-argon ages confirm that the tektites formed about 55 ± 3 million years ago. Until the size of the strewn field for these objects has been established, little can be said about the size of the impactor which produced them. But the tektites do suggest that PETM was triggered by the impact of an extra-terrestrial object.

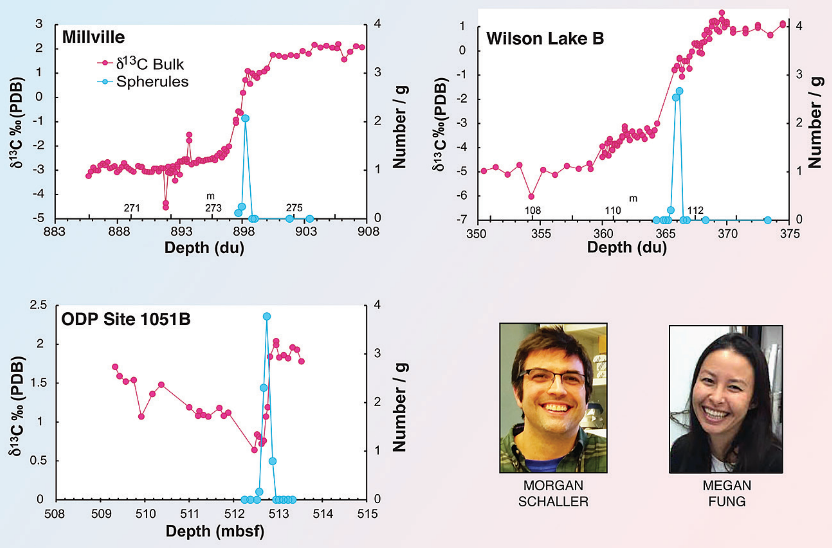


Figure 5.3 Abundance of glass spherules (*i.e.* tektites) in two sediment cores from New Jersey's coastal plain (above) and in a core from the continental margin off the Carolinas (below). In all three, the sharp peak is located at the base of the Marlboro clay. The widths of these peaks can be explained by bioturbation. The $\delta^{13}C$ records for bulk $CaCO_3$ records are also shown (from Schaller *et al.*, 2016).

Schaller's second bomb dropped when he identified a charcoal peak a few centimetres above the tektite peak (see Fig. 5.4). To explain this separation Schaller (personal communication) proposes the following scenario: the impact generated wildfires which extended over much of New Jersey's coastal plain. Charcoal produced by these fires was sluiced into the sea by the first large PETM rain event. In support of this scenario, Schaller points out that the ^{13}C to ^{12}C ratio in the charcoal is the same as that in pre-PETM organic material. Hence, the wildfires must have consumed Palaeocene organic matter. He also shows that the peak temperature (550 °C) experienced by this charcoal produced by this massive fire was larger than that of 250 °C to 325 °C experienced by traces of charcoal produced in ordinary forest fires from above and below the PETM peak. Finally, the magnetic properties of the Marlboro clay are markedly different than those in the underlying Palaeocene silt, likely due to the wildfire's heat. Schaller concludes that the Marlboro clay consists of the fire-modified soil sluiced off the New Jersey coastal plain.

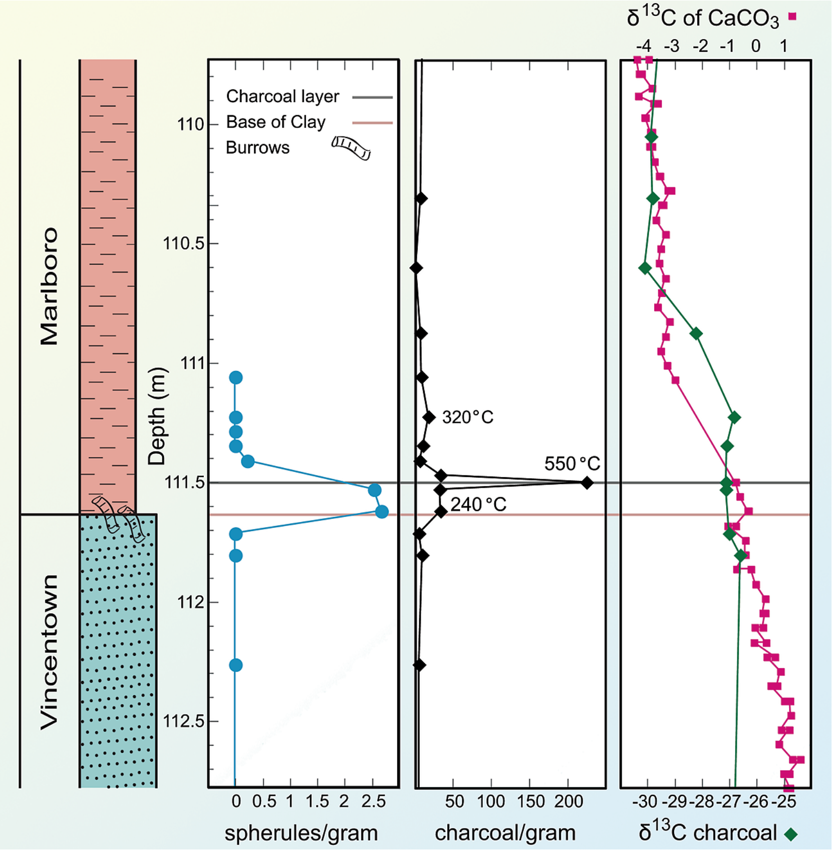


Figure 5.4 Relationship between the charcoal and tektite peaks in a core from New Jersey's coastal plain established by Megan Fung and Morgan Schaller. Note that the charcoal peak is located about 13 cm above the base of the Marlboro clay. Also shown are the $\delta^{13}C$ records for bulk $CaCO_3$ and for charcoal. Note that the PETM $\delta^{13}C$ shift for charcoal is delayed relative to that for bulk $CaCO_3$. The $\delta^{13}C$ for the charcoal peak is the same as that for Palaeocene organics. Note that the charcoal at the peak formed at a higher temperature than that above and below the peak (Schaller personal communication).

Schaller's hypothesis can only be correct if the Marlboro clay was deposited at a rate at least as high as that proposed by Wright for it is difficult to accept even a decade delay between the tektite fall and the precipitation event responsible for the charcoal. I'll come back to Schaller's third bomb, but first one other piece of the puzzle needs to be discussed.

As pointed out by Michael Storey at the PETM meeting held in January 2016 at Arizona State University, the Skaergaard sill, which was injected into North Sea sediments, has an age within the half percent uncertainty of that for the onset of the PETM. Further, the heat released as this sill cooled appears to be responsible for 100 or so mud volcanoes identified in seismic surveys (see Fig. 5.5). Svensen *et al.* suggest that the organic matter in the sediment was 'cooked' producing CO_2 and CH_4. They calculate that something like 1500 gigatons of carbon could have been released over a period of about 4000 years.

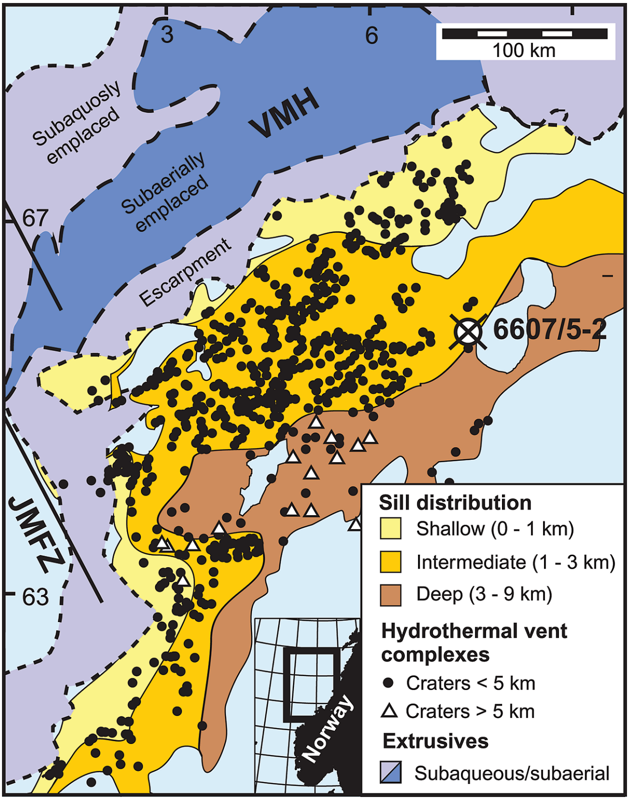


Figure 5.5 The Skaergaard intrusion cooked the overlying Norwegian Sea sediments releasing both CO_2 and CH_4. Seismic surveys suggest that this gas created mud volcanoes (see black dots). This intrusion outcrops along the margins of

Greenland's ice sheet. Its age is identical to that for the onset of the PETM. Model calculations by Svensen *et al*. suggest that the amount of carbon released over a time period of about 4 kyr was on the order of 1500 billion tons (from Svensen *et al*., 2010).

So we have an enigma. Two additions of CO_2 are needed. One is wildfires which generated a three per mille drop in $\delta^{13}C$ in less than a decade in the shallow waters bathing New Jersey's coastal plain. However, it must be stressed that to get the 150 or so gigatons of carbon necessary to produce a 3 per mille drop in $\delta^{13}C$ in the atmosphere and ocean mixed layer would require a far larger burn area than the New Jersey coastal plain. The other is the Skaergaard sill which released enough ^{13}C-deficient carbon to create a comparable drop in $\delta^{13}C$ of the entire ocean on the time scale of a few thousand years. One way to explain this would be to say that the CO_2 released by the wildfires was initially confined to the atmosphere and upper ocean. Then over a period of some decades it mixed into the ocean interior. The dilution created in this way reduced its amplitude to a few tenths per mille (*i.e.* undetectable). Only after this dilution had occurred did the $\delta^{13}C$ lowering caused by the release of CO_2 and CH_4 from the Norwegian Sea sediment become detectable. Further, by this time, accumulation of the Marlboro clay would have ceased.

While a feasible scenario, it involves a bothersome coincidence. The amplitude of the $\delta^{13}C$ drop created by both the brief wild-fire event and by the long lived cooking event are close to the same. The ^{13}C drop recorded in foraminifera shells from the Marlboro clay persists from its base to its top (see Fig. 5.6). Even if the Marlboro accumulated at the rate of 2 cm/year, to deposit the 8 metres would require about 400 years. By analogy with the present ocean, the ^{13}C-deficient wildfire CO_2 would have mixed into much of the ocean.

Only if all the carbon were delivered by a comet which struck the open ocean could a $\delta^{13}C$ large overshoot be avoided. For example, had the CO_2 been added to the atmosphere, the initial $\Delta\delta^{13}C$ would have been about 10 times larger than after it had mixed with the entire ocean. The comet impact could have spread the carbon throughout the entire ocean. But this explanation makes no sense for the huge impact itself would have heated up the atmosphere far more than 5 °C. It should show up in the $\delta^{18}O$ record. But it doesn't.

The ^{18}O record contained in the New Jersey margin cores (see Fig. 5.6) adds to the mystery. Like that for $\delta^{13}C$, the amplitude of the abrupt $\delta^{18}O$ drop at the onset of Marlboro clay deposition is comparable to that recorded in deep sea sediments. Also, the reduced $\delta^{18}O$ persists during the entire duration period of Marlboro deposition. Important to this discussion is the cause of the $\delta^{18}O$ drop. If it was the result of a warming, then it had to be global. If it was ^{18}O-deficient fresh water, then it could have been local. But if the latter, then the similarity in amplitude of the New Jersey margin and the deep sea $\Delta\delta^{18}O$ has to be attributed to yet another coincidence.

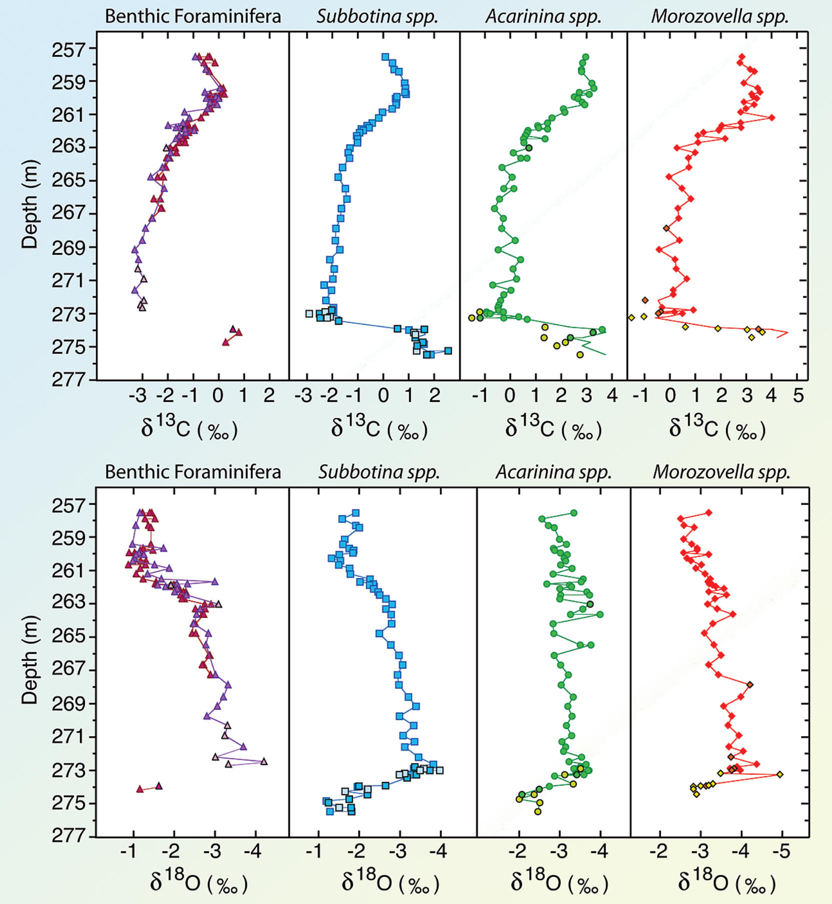


Figure 5.6 Records of $\delta^{13}C$ and $\delta^{18}O$ for foraminifera shells from one of the New Jersey margin cores. These results replace the earlier less reliable ones on bulk $CaCO_3$. Two aspects of the $\delta^{13}C$ and $\delta^{18}O$ records merit mention. One is the very sharp drop at the onset of Marlboro deposition. The other is the near constancy during the course of Marlboro. The interpretation depends on whether the sedimentation rate is several centimetres *per* kyr as claimed by Wright's detractors or centimetres per year as proposed by Schaller (modified from Makarova *et al.*, 2017).

If the ultra-rapid accumulation scenario is correct, then in the persistence of the isotope shifts requires that the deposition of the Marlboro took place in less than the time it took to mix the upper ocean with its interior. It must be kept in mind that a sudden 5 °C warming would likely greatly strengthen the stratification of the upper ocean and hence retard the rate of vertical mixing.

So we are left with an enigma. The charcoal peak convinces me that the 8 metre thick Marlboro clay accumulated extremely rapidly. But I can't generate a satisfactory consistent isotope scenario.

The question becomes how rapidly did the Marlboro clay accumulate? Schaller's third bomb was to come up with an accumulation proxy. He found one. It involves the rain of so-called cosmic spherules. Based on their composition, these objects are thought to be created in space by collisions between small asteroids. Schaller has identified these objects in the Marlboro clay and in the Palaeocene sediment beneath it. The important observation is that their concentration in the Marlboro is 70 times lower than that in the Palaeocene sediment. Although this observation strongly supports a far faster Marlboro accumulation rate, quantifying this rate remains problematic. The reason is that the proximity to a terrestrial source raises the question regarding the contribution of laterally reworked cosmic spherules. If, for example, the rare spherules present in the Marlboro clay were reworked from the coastal plain, then the contrast in spherule concentration would be even larger than a factor of 70.

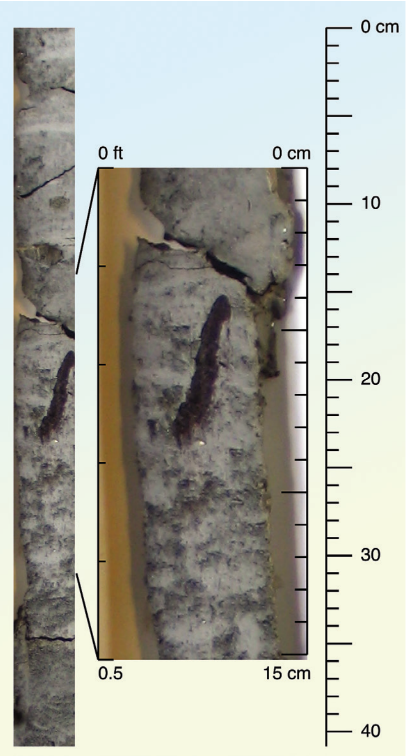


Figure 5.7 Photo of a 5 cm long stick in vertical position in one of Wright's New Jersey coastal plain cores. It is difficult to believe that this twig could have survived if the sedimentation were on the order of 5 cm per kyr. Rather, it speaks to a very high sedimentation rate (courtesy of Jim Wright).

Jim Wright reported an interesting observation which speaks to a high accumulation rate. It is a one cm thick, five cm long stick of wood standing close to vertical in one of the New Jersey margin cores (see Fig. 5.7). Were the accumulation rate of the Marlboro clay only about five cm per kyr as suggested by Zachos and the other Wright detractors, it would have stood in place for a millennium before being fully buried.

If the PETM is to be used as an analogue for the ongoing global warming, then it will be necessary to establish the atmosphere's pCO_2 before and during this warming event. Hence one might ask whether the information in hand makes it possible to calculate the increase in atmospheric CO_2 content during the PETM. The answer is a qualified no. But there are two pieces of information which constitute small steps toward this goal. The first of these is the record of $CaCO_3$ dissolution. As shown in Figures 5.8 and 5.9, five cores taken by Zachos at various water depths on Atlantic's Walvis Ridge offer an insight into how much the ocean's carbonate ion content dropped. However, there is a problem associated with quantifying this observation. It is that the $CaCO_3$ content drops

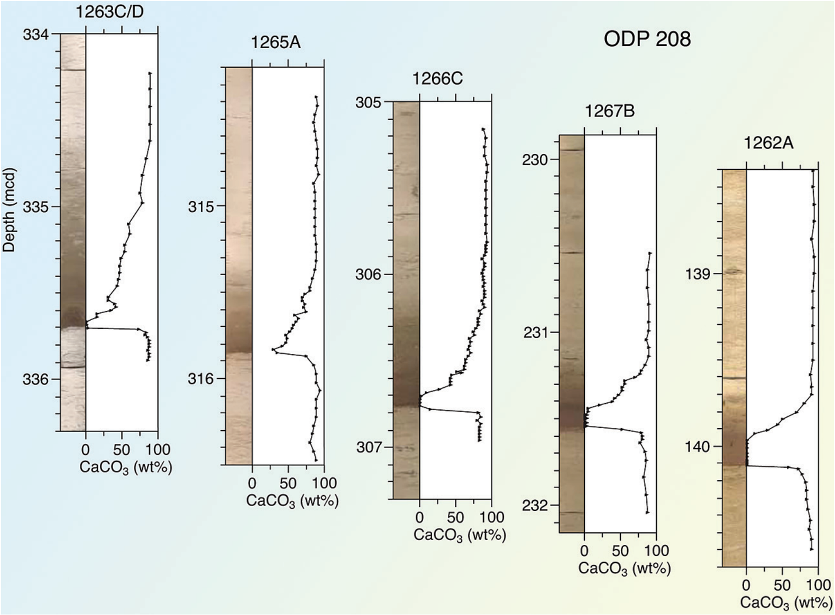


Figure 5.8 Plots of $CaCO_3$ content *versus* depth in sediment cores from the South Atlantic. The PETM is recorded in each core by a drop to zero (or in one core near zero). This drop shows up in photos. The $CaCO_3$-rich sediment above and below the PETM is light in colour and the $CaCO_3$-free PETM is dark. Note that the thickness of the dark layer increases with water depth (see Fig. 5.9 for explanation) (from Zachos *et al.*, 2005 with permission from the American Association for the Advancement of Science).

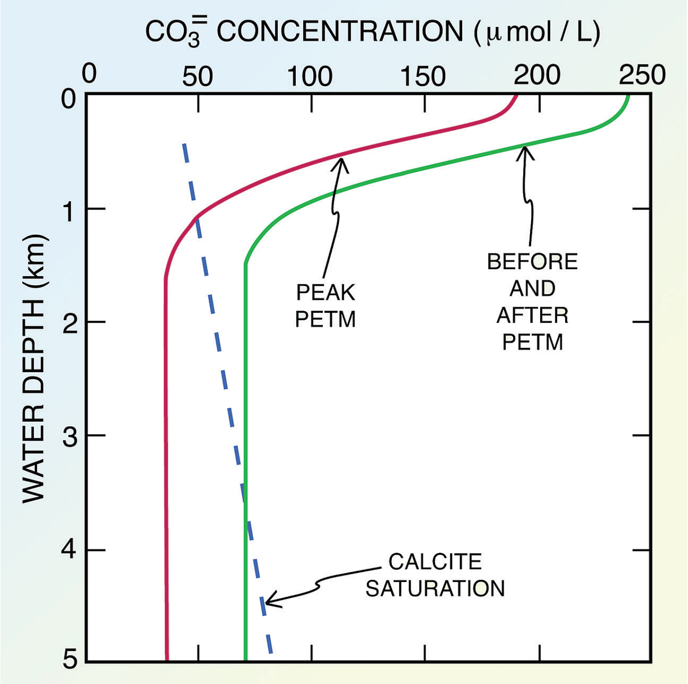


Figure 5.9 Shown here is the relationship between the water-depth profile of carbonate ion concentration (solid lines) and the solubility of calcite (dashed line). The depth at which these lines cross marks the boundary between waters supersaturated with respect to calcite and waters undersaturated with respect to calcite. Prior to the PETM, this cross-over occurred at about 3.5 km. Most of the extra CO_2 added to the ocean at the onset of the PETM mated with $CO_3^=$ (and H_2O) to form two HCO_3^- ions. The consequent lowering of the ocean's carbonate ion content caused the cross-over to shift up water column to a depth of about one kilometre. The water overlying all five of Zachos' core sites became undersaturated. The resulting dissolution of sea-floor calcite slowly raised the $CO_3^=$ content of the water back to its pre-PETM state.

to zero. Hence any estimate of the drop in $CO_3^=$ ion would be a minimum (*i.e.* that required to dissolve away the $CaCO_3$). So while this record makes it clear that the PETM CO_2 acidified the deep ocean, it places only a lower limit on drawdown of the PETM atmospheric pCO_2.

More promising is the boron isotope record. It is well established that the ratio of ^{11}B to ^{10}Be in the boron contained in foraminifera shells depends on the pH of the water in which they formed. This ratio has now been measured across the PETM in several deep sea cores. In each the $\delta^{11}B$ drops sharply by about one per mille and then recovers slowly (see example in Fig. 5.10). Unfortunately, this

$\Delta\delta^{11}$B cannot be converted to a ΔpH. The reason is that at the time of the PETM the ^{11}B to ^{10}B ratio for the borate dissolved in the ocean must have been lower than today's. But so far no one has come up with a way to determine by how much.

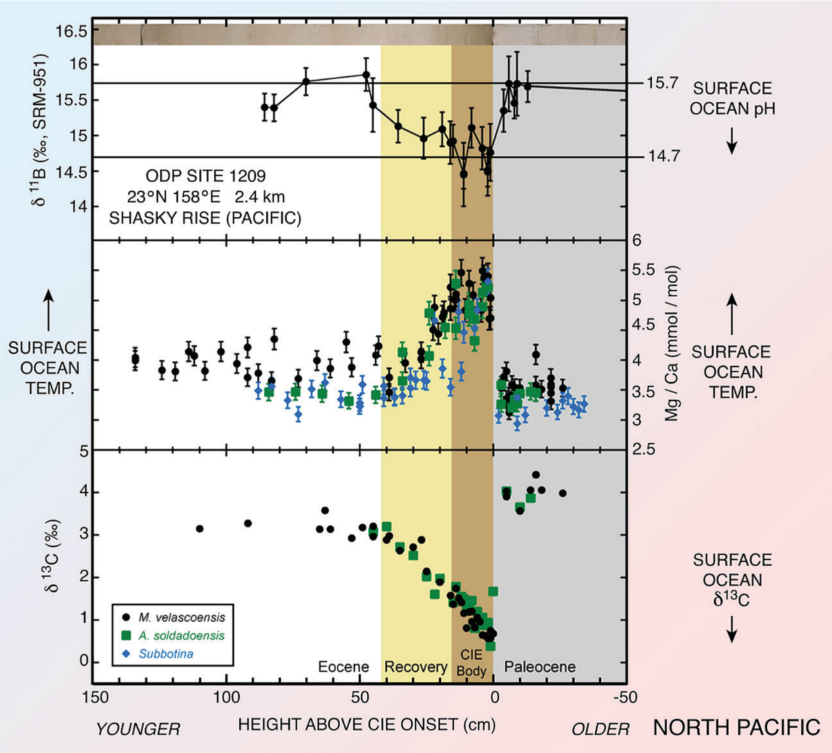


Figure 5.10 PETM records for δ^{11}B, Mg/Ca and δ^{13}C for a sediment core from the deep Pacific Ocean; all three properties underwent abrupt changes at the Palaeocene-Eocene boundary. The drop in δ^{11}B records the decrease in surface ocean pH created by the extra CO_2. The sharp rise in Mg to Ca ratio is the result of surface ocean warming (from Penman *et al.*, 2014 with permission from John Wiley and Sons).

As outlined in Figure 5.11, I believe that the impact of an extraterrestrial object created wildfires and also triggered the intrusion of the Skaergaard sill. The intrusion cooked Norwegian Sea sediments releasing the CO_2 (and CH_4) which warmed the planet by about 5 °C. Perhaps the PETM heat caused the release of CH_4 stored in continental-rise sediment extending the duration of the warming (as suggested by Richard Zeebe).

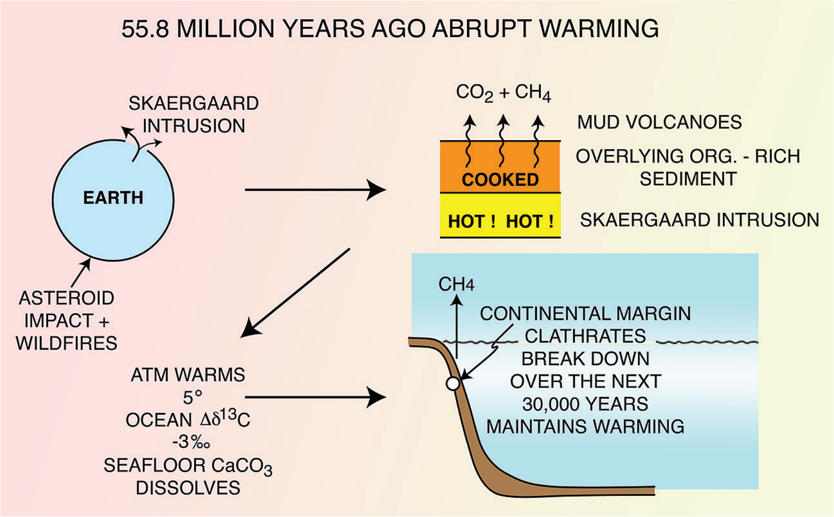


Figure 5.11 A possible scenario linking the impact which produced the tektites to the release of the CO_2 which generated the PETM warming. It must be kept in mind that CH_4 released from Norwegian Sea sediments would then, as now, have been rapidly oxidised to produce CO_2 and H_2O. Of importance to the ongoing production of CO_2 by fossil fuel burning is whether the warming of the ocean will lead to the breakdown of the methane clathrates present in continental margin sediments. Modelling by Richard Zeebe suggests that the duration of the PETM warming required such a release.

If we are to get to an answer to what caused the PETM and how much the atmosphere's pCO_2 changed, it will be necessary to:

1. Establish the global debris footprint related to the PETM impact.
2. Create a better understanding of what controls the accumulation rate of cosmic spherules in coastal sediments.
3. Find a proxy for the ^{11}B to ^{10}B ratio in seawater 55 million years ago.
4. Establish the atmosphere's CO_2 partial pressure in the late Palaeocene.

Special acknowledgement: I am indebted to Morgan Schaller for allowing me to make use of this as yet unpublished material.

6. GLACIAL CYCLES

For the last 800 thousand years we have a precise record of atmosphere CO_2 content. It is based on the analysis of air trapped in small bubbles in Antarctic ice. During the sintering process which converts snow into ice, air is trapped in small bubbles which occupy about 10 percent of the volume. The trapped air is pristine. It preserves the original composition including that for the trace gases CO_2 and CH_4.

As shown in Figure 6.1, this CO_2 record is similar to that for Antarctic air temperature. This led Al Gore, in his movie "An Inconvenient Truth", to claim that changes in atmospheric CO_2 content drove glaciation. Based on this he concluded that the CO_2 produced by burning fossil fuels would certainly have important climatic consequences. However, as correlation need not involve causation, a closer look must be taken before accepting this claim. Although CO_2 is the obvious candidate for the change in temperature, it is not the only one. Others must be considered, including Milankovitch changes in summer insolation driven by cycles in the Earth's orbit, variations in atmosphere's dustiness and re-organisations of the ocean's thermohaline circulation.

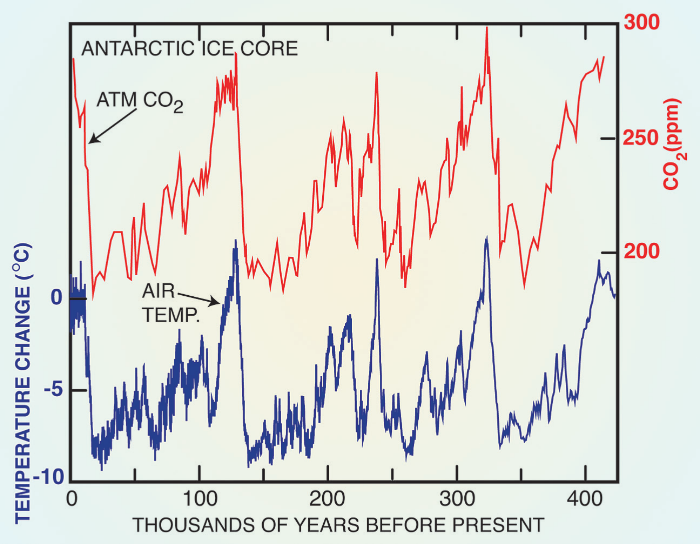


Figure 6.1 Record for the last 420 kyr of the CO_2 content of air trapped in Antarctic ice and of the extent of Antarctic cooling (based on the ^{18}O to ^{16}O in ice). Note that while similar in shape, the match between Antarctic cooling and CO_2 is not perfect. For example, the interglacial CO_2 peaks are wider than those for air temperature (from Broecker, 2015b).

The elements of the Earth's orbit are precession, ellipticity and axial tilt. Of importance here is that the Earth's precession which gives rise to a 20 kyr cycle that produces summer insolation changes in the Southern Hemisphere which are anti-phased with those in the Northern Hemisphere. The reason is that when the Southern Hemisphere is having its summers closest to the Sun, the Northern Hemisphere is having them when it is furthest from the Sun and vice versa (see Fig. 6.2). This anti-phasing of distance seasonality provides a way to distinguish between the influences of forcing by summer insolation and CO_2. Were it CO_2, then glaciation in the Southern Hemisphere should be synchronous with that in the Northern Hemisphere. On the other hand, were it summer insolation, they should be anti-phased.

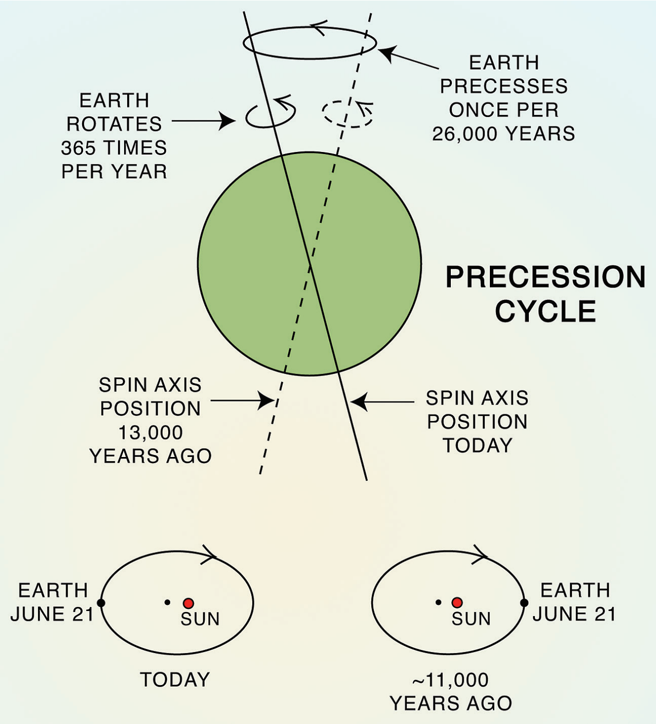


Figure 6.2 The gravitational pull of the moon on the Earth's equatorial bulge causes our planet to precess. It does so once every 26 kyr. As the Sun occupies one of the foci of the Earth's elliptical orbit, precession creates a seasonal distance cycle. Further, it generates an out-of-phase relationship between summer insolation in the Northern and Southern Hemispheres. Note that time between the peak of summer insolation in the north and that in the south is 11 kyr rather than 13 kyr. The reason is that the Earth's orbit 'hula-hoops' around the Sun shortening the repeat times.

When precession is put together with variations in the Earth's tilt and eccentricity, these motions generate a complex record of summer insolation (see Fig. 6.3). Even so, the 20 kyr precession cycle stands out. As can be seen, its amplitude changes following the 100 kyr eccentricity cycle. Although the tilt seasonality changes are latitude dependent, those associated with distance are not. This accounts for the difference in shape of insolation changes from latitude to latitude.

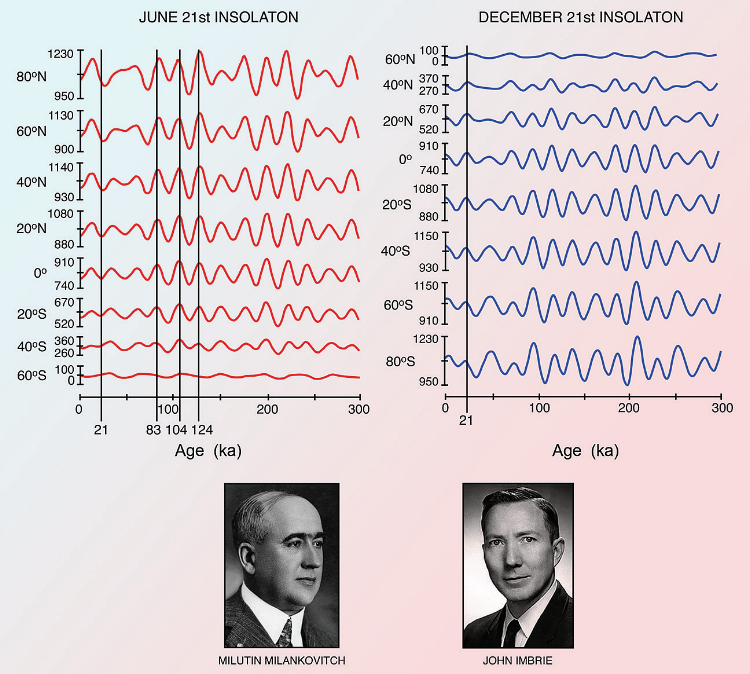


Figure 6.3 Summer insolation changes at various latitudes. Northern summer is on the left and southern summer is on the right. Note the prominence of the 21 kyr precession cycle and its anti-phasing between the hemispheres. Also note that insolation has no ramp. Finally, note the summer insolation peak at 103 ka in the Northern Hemisphere. Curiously it shows up in the sea level and monsoon records but not in those for CO_2 and iron and manganese release from the ridge crests. Milankovitch was the first to make these calculations. Imbrie was the first to show that orbital frequencies showed up in climate records.

It has long been clear that the Laurentide Ice Sheet which once covered Canada and the northern part of the USA reached its maximum extent close to 21 kyr ago. The timing is based on radiocarbon measurements on wood associated with the outermost moraines in Ohio, Indiana and Illinois. This is also the time when sea level stood at its lowest level. As the Antarctic ice sheet did not change very much in size, sea level records are dominated by the size of the great northern ice sheets.

Following up on a single radiocarbon age obtained in 1972 by John Mercer which suggested that mountain glaciers in the southern Andes reached their maximum extent at the same time as the North American ice sheet, George Denton decided to do a thorough job of establishing the chronology for Southern Hemisphere mountain glaciation. He started by collecting samples for radiocarbon dating from peats associated with glacial moraines in Chile. Then, joining forces with Joerg Schaefer, he obtained a host of ^{10}Be exposure ages on massive boulders from the outermost moraines located in the eastern side of New Zealand's Alps. Once the job was completed, no doubt remained that in both Chile and New Zealand glaciers stood at their maximum extent about 21 kyr ago. Mercer had it right, there wasn't a half-precession cycle offset between the hemispheres.

Ages for the outermost last glacial mountain moraines have now been established at 10 widely spread locales (see Fig. 6.4). For each the answer comes back 21 ± 1 ka. As shown by Meredith Kelly, this includes equatorial East Africa. As the minimum in atmospheric CO_2 also occurred at this time, these results appeared to confirm that Gore was correct in his judgement. CO_2 was more important than summer insolation.

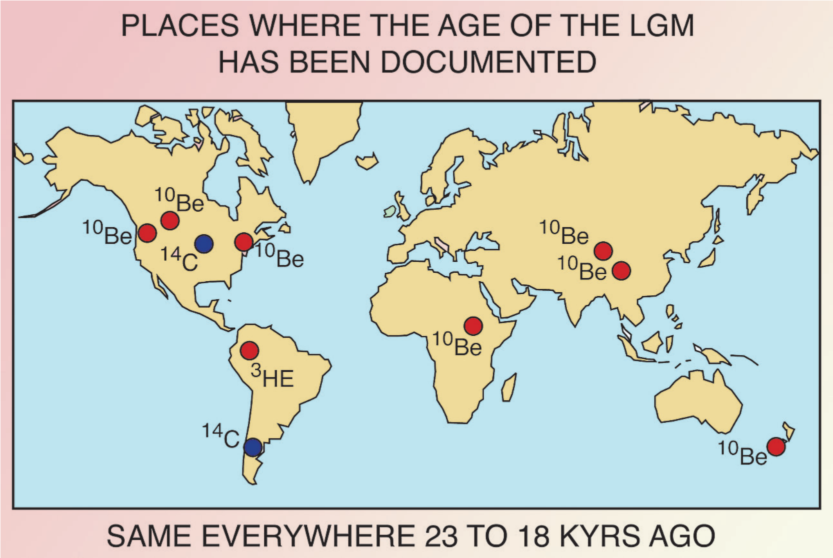


Figure 6.4 Locations where the time of the maximum extent of mountain glaciation has been precisely determined. Note that these ages were obtained using three cosmogenic isotopes: ^{14}C, ^{10}Be and ^{3}He. The planet-wide synchronicity of these advances suggest that they were driven by CO_2 rather than summer insolation.

The Denton group also established that the rapid demise of New Zealand's mountain glaciers, which commenced 18 kyr ago, broadly paralleled the rise in atmospheric CO_2 content (see Fig. 6.5). I say, 'broadly' because both the rate of retreat of the glaciers and the rate of rise in Antarctic air temperature appear to have outstripped the rate of CO_2 rise.

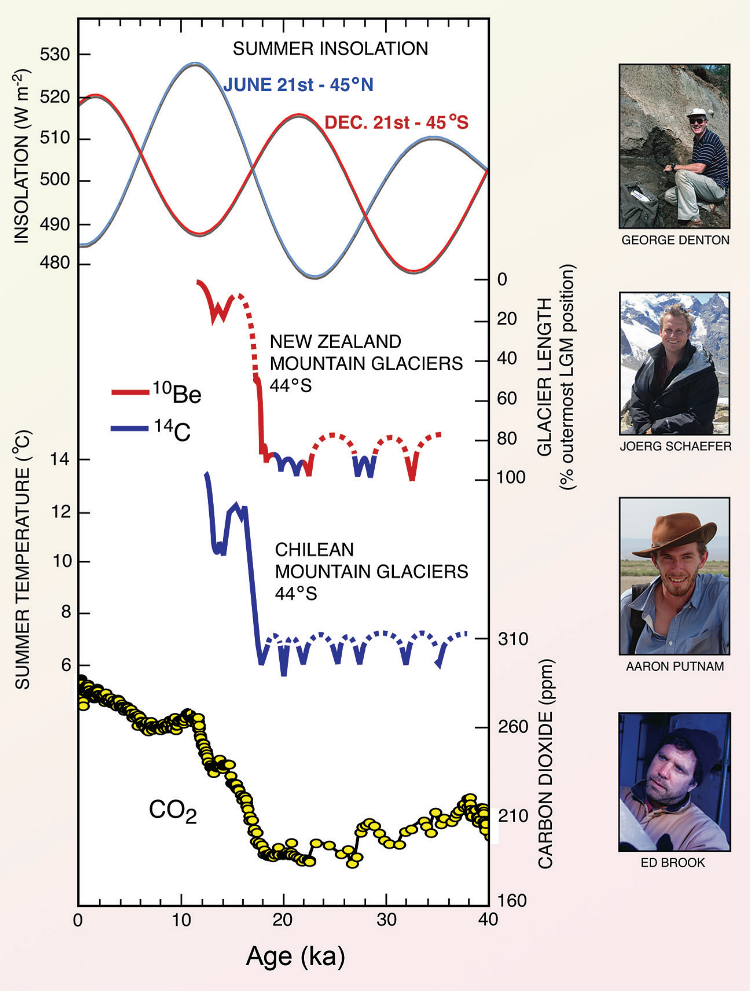


Figure 6.5 The maximum extent of mountain glaciers in the Southern Hemisphere occurred at the time of a summer insolation maximum. This suggests that these glaciers responded to CO_2 rather than summer insolation. Note that the retreat of these glaciers commenced at the same time as CO_2 started to

increase (*i.e.* 18 kyr ago). Also note that this retreat was steeper than the rise in CO_2. The 'heroes' of this effort are shown on the right. Ed Brook is included because he is responsible for the very precise CO_2 record (from Broecker, 2015b).

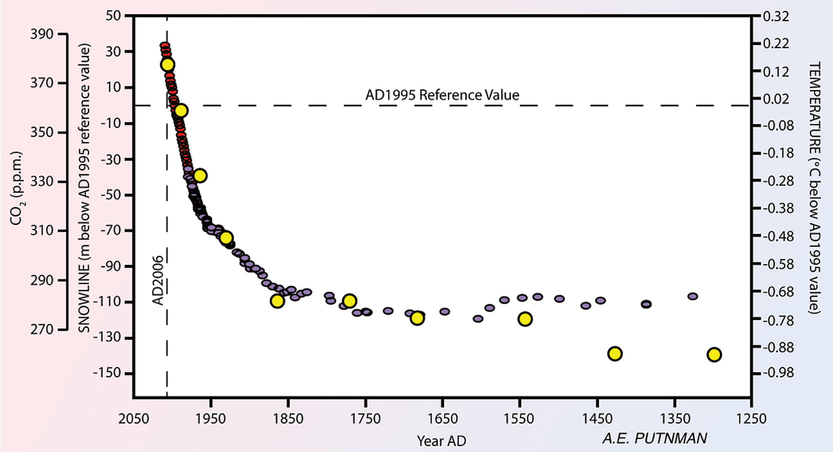


Figure 6.6 Snowline elevation for the last 800 years as recorded by New Zealand's Camero Glacier (yellow dots). Also shown is the atmosphere's CO_2 content (red dots). The nearly perfect match in shape provides evidence that CO_2 drives summer warming and hence the extent of glaciers. Further, the warming required to produce this rise in snowline (~0.8 °C) matches that recorded by thermometers. Note that this does not mean that other forcings are unimportant. Rather, none were in play during the last several hundred years (data from Putnam *et al.*, 2012).

Additional evidence in support of the role of CO_2 comes from a detailed study made by Aaron Putnam on the historic retreat of New Zealand's Cameron Glacier. As shown in Figure 6.6, he found a match between the rate of this retreat and the CO_2 content of the atmosphere. Further, the extent of the retreat following the Little Ice Age requires a warming of about 0.8 °C in agreement with that recorded by thermometers.

But it turns out that CO_2 cannot have been the only player in glacial cycles. In particular, it did not initiate each 100 kyr cycle. Evidence for this comes from the record kept in Antarctic ice. As can be seen in Figure 6.1, the width of the interglacial CO_2 peak centred at 125 ka is larger than that for Antarctic air temperature. So either the temperature rise at the onset of the interglacial lagged the CO_2 rise or the CO_2 drop at its end lagged the temperature drop. The choice between these scenarios proved elusive. The reason is that the CO_2 record kept in bubbles is displaced up core from that for air temperature kept in ice. Bubble closure occurs at 70 or so metres depth in the firn. As the cores from the Antarctic interior which provide these long records accumulate at only two or so cm per year, the bubbles are several thousand years younger than the ice which contains them. Further, the actual age difference has a large uncertainty. Because of this the answer has to come from ice cores taken at the margin of the Antarctic ice sheet where accumulation rates are ten times higher and the ice age – gas age difference is correspondingly far smaller. These cores made it clear that for the last deglaciation which started 18 kyr ago, there was no significant lag between CO_2 and temperature. While it would be comforting to demonstrate this for earlier interglacials, the high accumulation rate margin cores reach only to the latter part of the penultimate glaciation. Based on these records, it appears that the CO_2 decline at the end of the peak interglacial lagged the temperature decline by several thousand years. If so, something other than CO_2 triggered the onset of glacial cycles. I believe that the 'something' was a re-organisation of the ocean's thermohaline circulation.

The tipoff that the ocean's circulation is subject to global scale re-organisations came from the record kept in Greenland's ice (see Fig. 6.7). During the last glacial period, the ^{18}O to ^{16}O ratio in the ice underwent a series of abrupt back and forth jumps. These jumps were accompanied by abrupt changes in both the dust content of the ice and the methane content of the air bubbles. These shifts were caused by abrupt changes in the amount of deep water produced in the northern

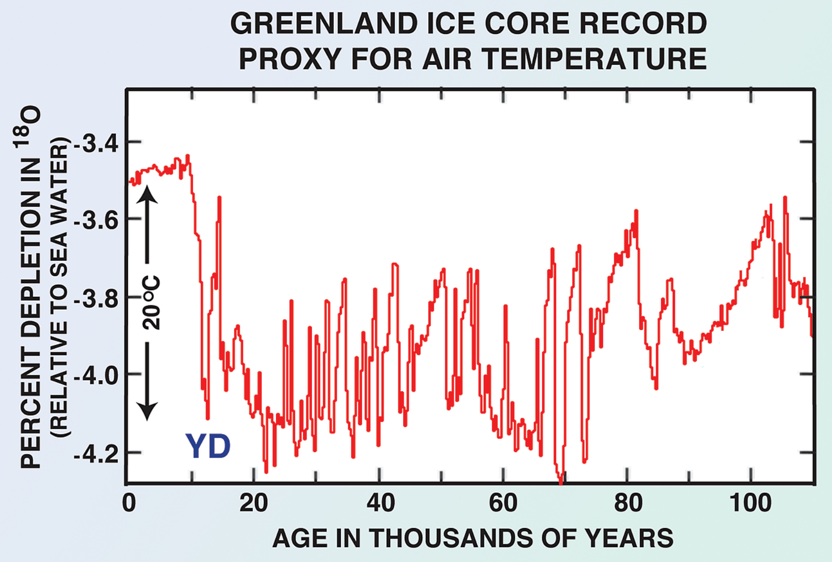


Figure 6.7 The ^{18}O to ^{16}O record kept in Greenland ice serves as a stand-in for air temperature. Important here are the abrupt back and forth jumps which characterise the last glacial period. They record 8 to 10 °C up and down jumps in air temperature caused by the sudden expansions and retractions of the winter sea ice cover in the northern Atlantic. The sea ice cover expanded when the production of deep water in the northern Atlantic was reduced.

Atlantic. When smaller than now, the winter sea ice cover expanded from the Arctic into the northern Atlantic. The consequent cooling of the northern polar cap caused a freeze-up of the marshes and ponds responsible for the production of a sizable fraction of the Earth's methane. It also increased the pole to equator temperature gradient and hence the atmosphere's gustiness. Extra gustiness led to extra dustiness.

Of particular interest here is the very large ^{18}O to ^{16}O shift which took place at the end of the last glacial period (*i.e.* 11.4 kyr ago). It is twice as large as the other jumps. The extra height is the result of a deep sea temperature change. So sea level is responsible for one half and ocean temperature for the other half. The smaller jumps in ^{18}O correspond to temperature changes of 8 to 10 °C. The large jump at 11.4 ka in age corresponded to ~20 °C warming. The reason is that deep water production in the northern Atlantic jumped from its glacial low to its interglacial high.

It should be mentioned that the methane record in ice cores allows the air temperature record for Antarctica to be tightly correlated with that for Greenland. It turns out that the abrupt events in Greenland have correlatives in Antarctica. Sharp warmings in the north are followed by slow coolings in the south and vice versa. Further, taken together, the CH_4 correlation and annual layer counting demonstrate that there was a 200 year delay between the sharp warming in the north and the onset of the cooling in the south. The delay suggests that the message was carried to the south by slow transport through the ocean rather than by rapid transport through the atmosphere. In today's ocean, deep waters formed in the north Atlantic take on the average about 200 years to reach the Southern Ocean.

Comparison of the benthic ^{18}O record with the sea level record for the last interglacial (*i.e.* 130 to 75 ka) makes clear that deep sea temperature changes accompanied those of sea level (see Fig. 6.8). Note that the amplitude of the ^{18}O peak at 124 ka is about twice that for sea level. This extra magnitude suggests that the deep ocean warmed by 2 °C or so at the abrupt onset of deglaciation and cooled by 2 °C or so at the end of the peak interglacial. The conclusion is that the cooling which initiated the last glacial period was primarily the result of re-organisation of the ocean's thermohaline circulation. CO_2 had no role!

CO_2 and thermohaline circulation are not the only drivers of glaciation. This can be seen by comparing the CO_2 record for the last glacial cycle with that for sea level (see Fig. 6.8). An important difference is seen at 103 kyr. The peak in sea level at that time has no correlative in the CO_2 record. But there is a peak in summer insolation at 103 ka (see Fig. 6.3), which suggests that summer insolation modulated the size of the Northern Hemisphere's ice sheets. Another difference is that the small bumps in CO_2 content between 60 to 30 kyr ago are not present in the benthic ^{18}O record. This suggests that each Heinrich ice armada somehow impacted the atmosphere's CO_2 content. So, while Gore was correct that CO_2 played a major role in glaciation, it did not act alone.

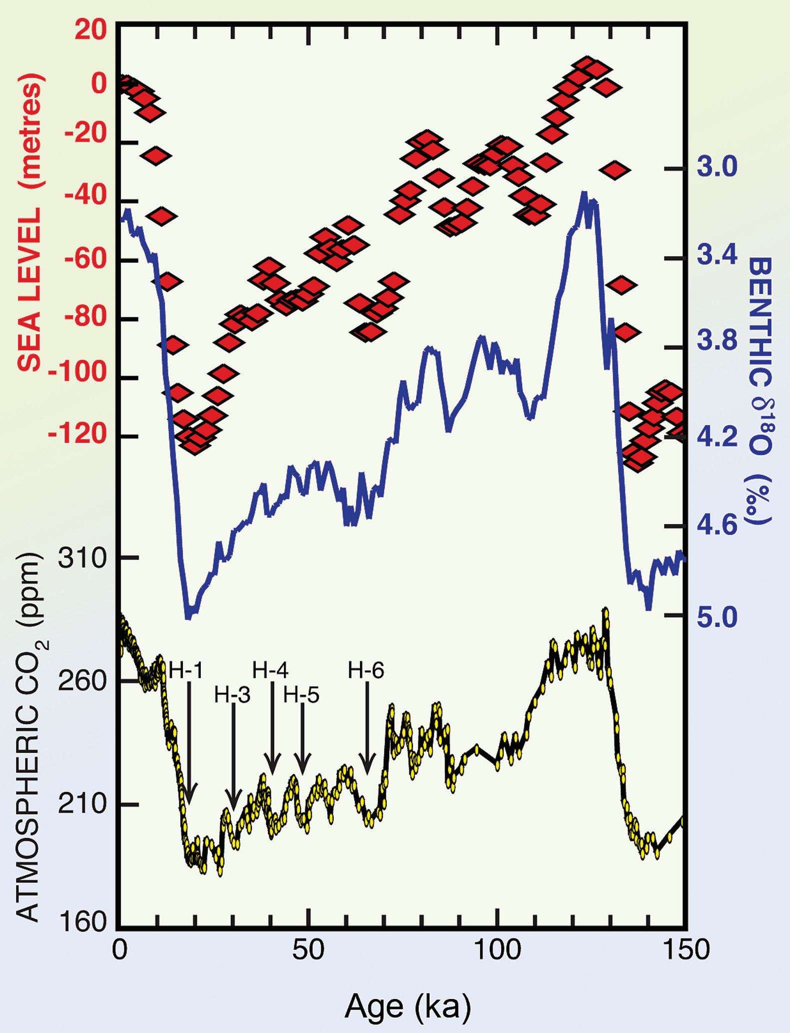


Figure 6.8 Comparison between the records for sea level (red diamonds) and atmospheric CO_2 (yellow curve) for the last 150,000 years. Although the ups and downs of sea level track CO_2 reasonably well, there are certainly significant mismatches. Also shown is the well documented ^{18}O record for benthic foraminifera (blue curve). It records some combination of ice volume and deep ocean temperature. Eelco Rohling is largely responsible for the sea level record, Maureen Raymo for the ^{18}O record and Ed Brook for the CO_2 record (from Broecker *et al.*, 2015, with permission from Elsevier).

But what caused the atmosphere's CO_2 content to change? Five contributors can be identified.

1. Surface ocean cooling: The CO_2 partial pressure in surface ocean water drops by 10 μatm for each °C of cooling. At the time of the glacier maximum, the surface ocean was 4 ± 1 °C colder than now. Hence it reduced pCO_2 by 40 ± 10 μatm.
2. Surface ocean salinification: At the time of the glacial maximum, sea level was about 120 metres lower than now. As the salt remained behind, the ocean's salinity was about three percent higher. This raised the pCO_2 of surface water by 10 μatm.
3. Reduction of terrestrial biomass: Measurements of the $\delta^{13}C$ in benthic foraminifera suggest that at the time of the glacial maximum the $\delta^{13}C$ of dissolved inorganic carbon was 0.3 per mille lower than now. If the decrease is attributed to the reduction of terrestrial biomass, then the glacial ocean must have contained about 500 more gigatons of carbon than it does now. Once this extra CO_2 had been buffered by the dissolution of $CaCO_3$ in deep sea sediments, it would have increased the atmosphere's CO_2 by about 15 μatm.
4. Increased storage of respiration CO_2 in the ocean's interior: This led to a decrease of CO_2 in surface water and hence also in the atmosphere. This increase appears to have been driven by a combination of Southern Ocean iron fertilisation and stratification of the deep sea. However, the magnitude of the extra CO_2 storage remains uncertain.
5. Pulsing of the input of CO_2 from the Earth's interior: Ice loading of the continents suppressed eruptions of terrestrial volcanoes. But the drop in sea level could also have modulated the release of CO_2 from the ridge crests. In any case, the magnitude of this mode of CO_2 reduction remains uncertain.

Taken together, the pCO_2 changes resulting from deforestation, cooling and salinification account for a 15 ± 10 μatm CO_2 reduction. If so, the remaining 80 ± 10 μatm must have been the result of some combination of deep ocean storage and starvation of mantle CO_2 input. Although both storage in the deep sea and reduction of planetary 'leakage' contributed, it is as yet not possible to quantify either one. In the case of storage in the deep sea, we do know that nutrient utilisation in the Southern Ocean increased (see Fig. 6.9) and that, at times, the deep Atlantic was stratified (see Fig. 6.10). In the case of the input of planetary CO_2, we do know that terrestrial volcanoes adjacent to ice masses shutdown during peak glacial time and that they were rejuvenated between 13.5 kyr and 7.5 kyr ago (see Fig. 6.11). We also know that the release of iron and manganese from hydrothermal vents at mid-ocean ridge crests appeared to have peaked during times of deglaciation but have no confirmation that the release of CO_2 accompanied that of Fe and Mn (see Fig. 6.12).

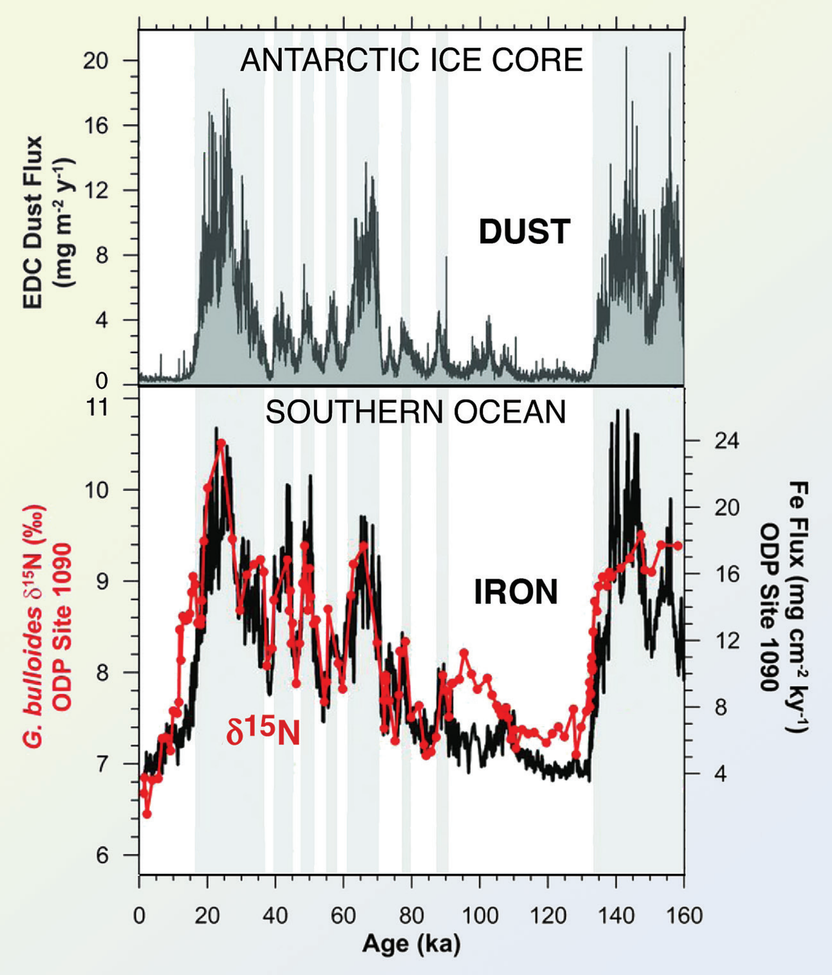


Figure 6.9 Records for the last 160 kyr of the dust rain onto the Antarctic ice cap and of iron accumulation in the Southern Ocean. Also shown is the record of the ^{15}N to ^{14}N ratio of NO_3 in foraminifera shells obtained by Alfredo Martínez-García and Daniel Sigman. This ratio serves as a proxy for nutrient utilisation. The larger the $\delta^{15}N$, the greater its extent. Clearly iron fertilisation drove nutrient utilisation in the Southern Ocean. Further, the extra iron was delivered by dust (Martinez-Garcia *et al.*, 2014).

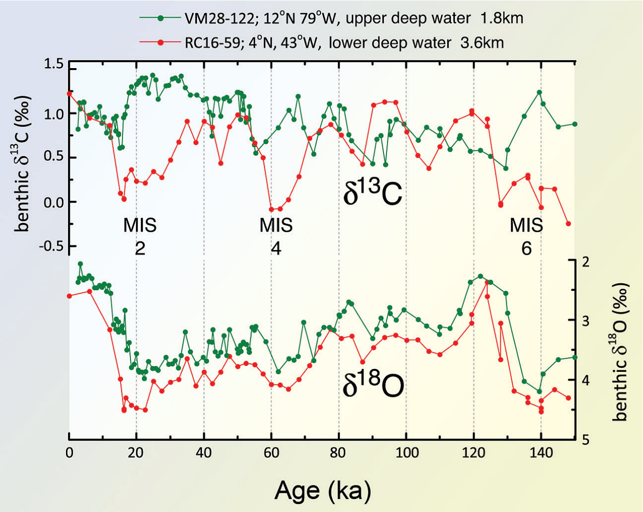


Figure 6.10 Records obtained by Jimin Yu of $\delta^{13}C$ and $\delta^{18}O$ for benthic foraminifera shells from two tropical Atlantic sediment cores. One records the water spilling over a 1.8 km depth sill into the deep Caribbean Sea and the other water at a depth of 3.6 km on the Ceara Rise. The ^{18}O record allows a time scale to be placed on these $\delta^{13}C$ records. The variations in $\delta^{13}C$ serve as a proxy for respiration CO_2. As can be seen, during marine isotope stages 2, 4 and 6, the equatorial Atlantic was strongly stratified. There was more respiration CO_2 than now at 3.6 km and less at 1.8 km. Note that while the ^{18}O record has a distinct ramp, the ^{13}C does not (Broecker *et al.*, 2015).

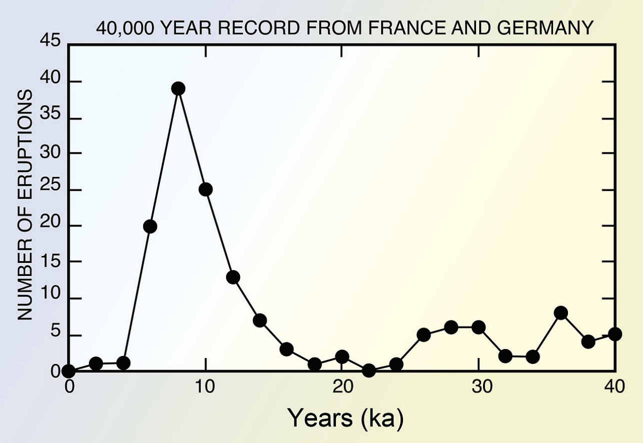


Figure 6.11 Number of volcanic eruptions evident in each 2 kyr interval back to 40 ka (Nowell *et al.*, 2006). Note that between 24 ka and 18 ka (*i.e.* the LGM), there were very few. Then during the time of deglaciation and the early Holocene

there were many. During the last 4 kyr, there have been only 2. The volcanoes which produced these ash layers were not overlain by ice. Rather they are located north of the Alps and south of the Scandinavian ice sheet (prepared by Charles Langmuir based on data from Nowell *et al.*, 2006).

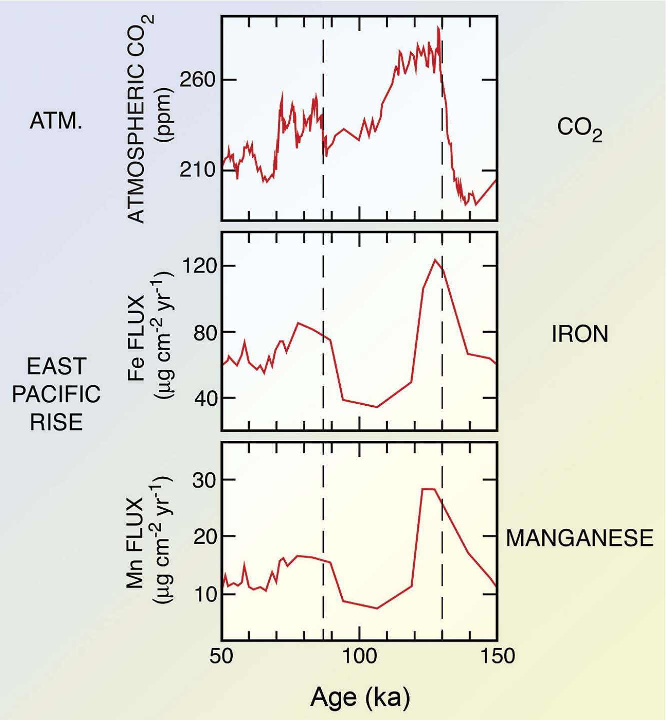


Figure 6.12 During the time of the peak interglacial which took place between 135-120 ka, the concentration of iron and manganese emanating from the East Pacific Rise jumped up by a factor of about three (Lund *et al.*, 2016). Then at the time of the 103 ka sea level maximum, it had dropped to its base level. This was followed by a smaller increase centred at about 80 ka. Not shown here is that a similar increase occurred during the time period 18 and 7 ka. Although there is no direct evidence that CO_2 accompanies Fe and Mn, were that to be the case, it would suggest that CO_2 release planet-wide was higher during times of deglaciation.

The records of temperature, sea level and dust make it clear that the planet's orbital cycles pace climate cycles. The reason is that each of these records has a clear 20 kyr component. Further, the termination of each 100 kyr sawtooth occurs at the time of a pronounced increase in Northern Hemisphere summer insolation (see Fig. 6.3). However these records have a common feature not shown by insolation, namely a 90 kyr duration downward ramp. This ramp is also seen in the atmospheric CO_2 content record. Of interest therefore is the record of monsoon rainfall (see Fig. 6.13) which lacks this ramp. For cold region records where temperature dominates, there is a pronounced ramp. In the tropics where rainfall dominates there is no ramp.

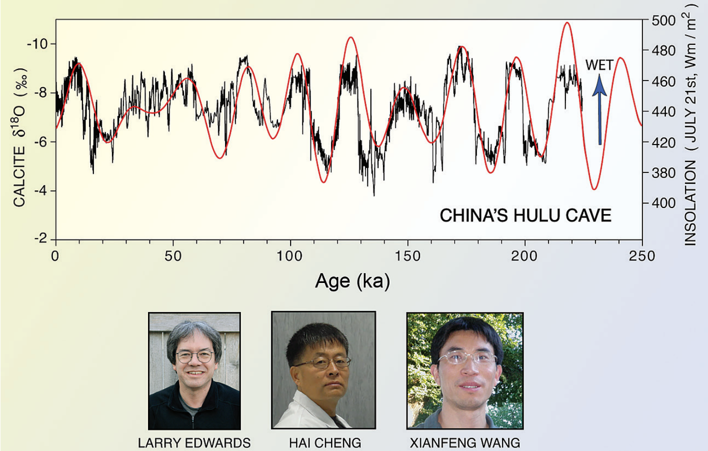


Figure 6.13 The ^{18}O record for Hulu cave stalagmites is thought to record the strength of monsoon rainfall in China. As can be seen, it follows summer insolation, deficient ^{18}O-strong monsoons. The use of ^{18}O to ^{16}O ratios in stalagmites was pioneered by Larry Edwards who demonstrated that using ^{230}Th they could be dated with very high precision. His work on Chinese caves was done in cooperation with Hai Cheng and Xianfeng Wang. Important here is that this record lacks a ramp. Rather, it has a close resemblance to Northern Hemisphere summer insolation (Wang *et al.*, 2001).

One other difference between high latitude and low latitude records must be mentioned. Although cold region temperature changes are synchronous in the two hemispheres, tropical precipitation changes are anti-phased. This suggests that CO_2 is most important in setting Earth temperature and that summer insolation is most important in setting precipitation. This being the case, as our interest lies in CO_2, the question is, how do orbital cycles pace its atmospheric content?

It is my guess that a re-organisation of the ocean's thermohaline circulation kicked off each 100 kyr glacial cycle. The likely driver is seasonality changes caused by orbital cycles. It cooled the Earth initiating the expansion of its ice sheets. The weight of this ice shut down volcanoes reducing the release of planetary CO_2. This caused a ramp-like decrease in atmospheric CO_2 content and its consequent cooling. Northern Hemisphere's summer insolation modulated this decline. Abrupt increases and decreases in northern Atlantic sea ice extent changed the pole to equator temperature gradient and hence iron delivery to the ocean.

Of course there are a number of alternate scenarios which could explain these records. The point is not that the one presented here is the best one but that the situation is complex. Not only CO_2 but also summer insolation, ocean circulation, atmospheric dustiness, and the redistribution of mass on the planet's surface were involved.

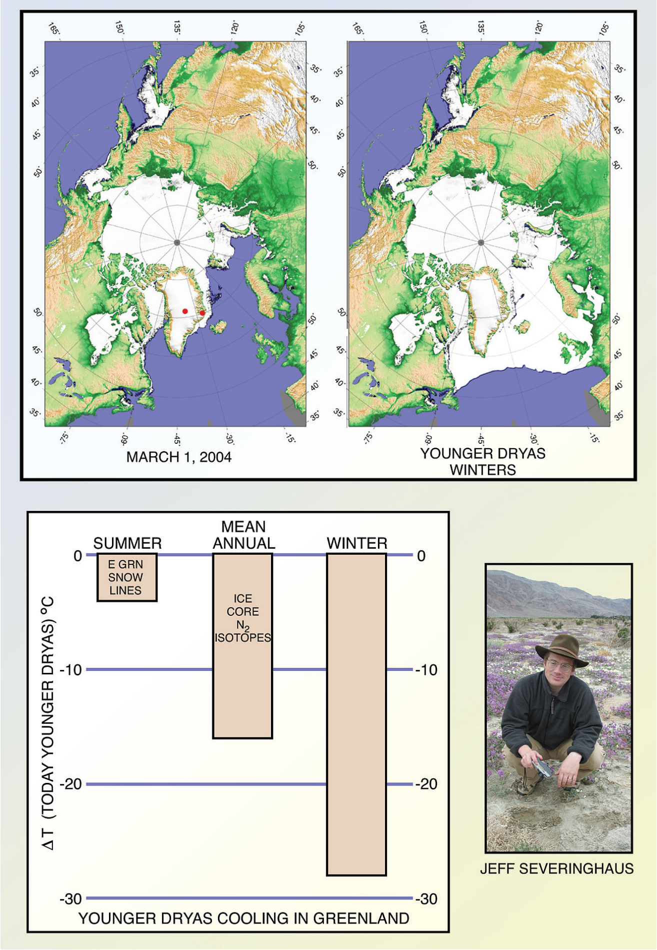


Figure 6.14 Cut off from heat from below during times when conveyor circulation was greatly weakened, the northern Atlantic developed a fresh water lid. This allowed winter sea ice to extend from the Arctic well into the northern Atlantic. As a result, winters in Norway became like those in Siberia. By contrast, summer melting brought back the warmth. Key to this is Jeff Severinghaus' use of nitrogen isotopes in ice bubbles to estimate the mean annual cooling of the Greenland ice cap during the Younger Dryas.

7. FOSSIL FUEL CO_2

Many questions regarding the role of CO_2 in past climate changes are being answered. The reason is that we are now documenting the consequences of burning coal, petroleum and natural gas. The late Roger Revelle called it *"man's greatest geophysical experiment*." And that it is, for our ability to predict the outcome accurately remains marginal. We know that mountain glaciers are retreating, that Arctic sea ice is thinning, and that Greenland's outlet glaciers are retreating, but the uncertainties in the predictions of how rapidly sea level will rise remain extremely large. We know that coral reefs are being bleached. We also know that most of them recover. However, as the ocean warms, the spacing between bleaching events is likely to become shorter than the recovery time. Then what? High northern latitudes are warming several times faster than high southern latitudes. As a consequence, the Earth's rain belts are being pushed to the north. We suspect that this will dry out the already semi-arid western U.S. but we don't have the ability to say by how much. And the list goes on. By how much will extreme climate events intensify? Can we save species threatened by extinction? Can we cope with climate-induced migration of every living thing (including us)?

Although our ability to predict the rate at which sea level will rise remains inadequate, we do have indications that if we don't remove this excess CO_2 from the atmosphere, on the time scale of a century or two, a several metre rise could occur. One is that during the last interglacial, when temperatures were somewhat warmer, sea level appears to have stood 5 to 8 metres higher than today. Another, based on the presence of cosmogenic isotopes in the granite beneath the Greenland ice sheet, is that at least once in the last 400,000 years Greenland was ice free. Still another is that part of the West Antarctic ice sheet which is afloat is vulnerable to collapse. The big problem in applying these observations to our situation is the time scale. Our understanding of how large ice sheets respond to warming is not good enough to say something useful about how long it will take. It could be many hundreds of years. However, as a several metre increase in sea level would imperil much of the world's infrastructure, it behooves us to take it seriously.

One would hope that Revelle's experiment would better constrain the relationship between CO_2 content of the atmosphere and Earth temperature. We know that since 1950 the Earth has warmed by about 1 °C. During the past 70 year period, atmospheric CO_2 has risen by 100 ppm (*i.e.* from 310 to 410 ppm). Unfortunately, this doesn't allow us to predict reliably the temperature change to be brought about as CO_2 continues its rise and eventually levels off. This is because the ocean is sucking up heat from the atmosphere holding back its warming. As the ocean is mixed on the time scale of hundreds of years, this transfer of heat from the atmosphere to the ocean will continue for a long time. We know this because only 57 percent of the CO_2 we have produced by fossil fuel burning is present in the atmosphere (see Fig. 7.1). Although uncertain, of the 43 percent that has gone elsewhere, about 25 percent is in the ocean (as the HCO_3^- ion). As the main barrier for both CO_2 and heat uptake by the ocean is the rate of vertical mixing, one might guess that about one third of the extra heat has been taken up by the ocean. Hence, if it were not for the ocean, the atmosphere would have warmed by about 1.5 °C instead of 1.0 °C.

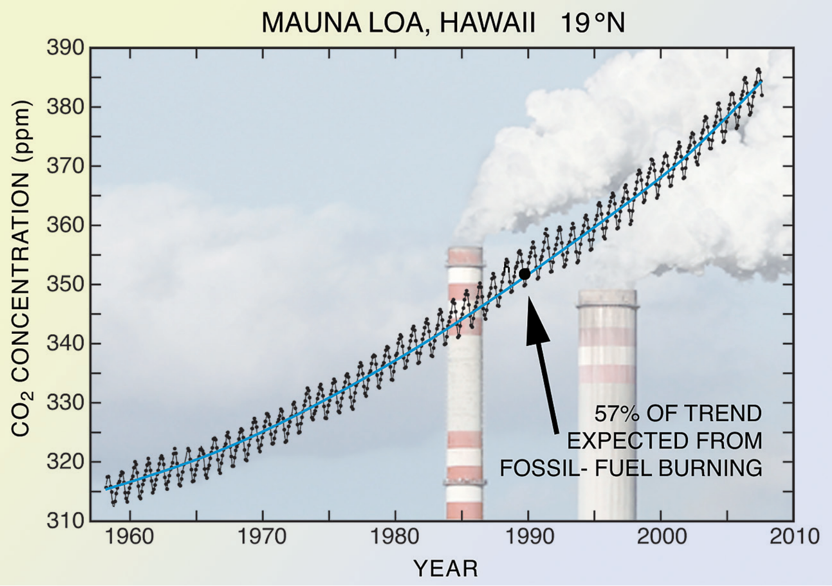
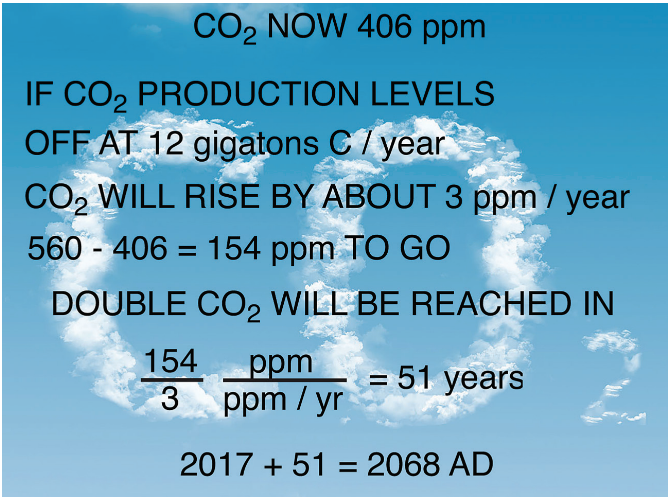


Figure 7.1 The longest direct record of atmospheric CO_2 content is that launched in 1958 by Charles David Keeling at a meteorological station high on Hawaii's extinct volcano, Mauna Loa. When compared with the record of fossil fuel use, it makes clear that only 57 percent of the CO_2 generated has remained airborne. The rest has been absorbed by the ocean or has 'greened' the continents. The record also depicts the seasonal breathing of the terrestrial biosphere (modified from Keeling *et al.*, 2005).

Between 15 and 20 percent of the fossil fuel CO_2 is being taken up by the terrestrial biosphere. We know this is happening because the O_2 content of the atmosphere is not going down as fast as it is being consumed by fossil fuel burning. The rate of 'greening' exceeds the rate of deforestation by roughly a factor of three. While greening must be driven in part by extra CO_2 and in part by NO_3^- fertilisation, we lack the ability to predict how either of these drivers will evolve. This raises a question regarding long term storage of carbon in the terrestrial biosphere. We have no way to say whether it will continue to increase or will turn around and decrease.

Revelle's experiment is far from over. As of 2018, the CO_2 content of the atmosphere is still going up a bit faster each year (see Fig. 7.2). True, the developed nations are making cuts in their fossil fuel consumption but increasing usage in developing countries is more than compensating.



CO_2 NOW 406 ppm

IF CO_2 PRODUCTION LEVELS
OFF AT 12 gigatons C / year
CO_2 WILL RISE BY ABOUT 3 ppm / year
560 - 406 = 154 ppm TO GO

DOUBLE CO_2 WILL BE REACHED IN

$$\frac{154}{3} \; \frac{\text{ppm}}{\text{ppm / yr}} = 51 \text{ years}$$

2017 + 51 = 2068 AD

Figure 7.2 If we continue our dependence on fossil fuel energy, the CO_2 content of the atmosphere is likely to reach double its preindustrial content in about 50 years.

There is a big difference between this CO_2 episode and the others we have discussed. Namely, 'intelligent life' can intervene and alter its course. Unfortunately, despite our intelligence, very little is being done.

Atop the list of things we could do is to 'retire' fossil fuels and substitute a mix of solar, wind and nuclear. We are moving in this direction but at a snail's pace. Last year less than one percent of the fossil fuel energy was replaced by renewables. Experts agree that only when a sizable tax is placed on fossil fuel use will the situation change. But, since a sizable fraction of the voting population are climate change deniers in the U.S.A., imposition of such a tax would constitute political suicide.

Another option is to remove CO_2 from the atmosphere and bury it. A few groups are currently carrying out research aimed at creating a removal device and a few others are researching means of storing it. We are currently adding about 35 billion tons of carbon dioxide to the atmosphere each year. Were the removal of an amount of the CO_2 equal to that produced in 2017 accomplished with modular units capable of removing one ton of CO_2 per day, then about one hundred million units would be required. Each module would have the mass and complexity of an automobile. Were they mass produced, each would likely cost something like \$25,000. Hence, one hundred million would cost about 2.5 trillion dollars.

The CO_2 removed from the atmosphere would be stored in either sandstone or in basalt (see Fig. 7.3). During the last 20 years, Norway's Stat Oil Company has been pumping the CO_2 separated from methane into a sandstone stratum beneath the North Sea. As liquid CO_2 is less dense than H_2O, it slowly diffuses up through the sandstone's water-filled pores. This rise is monitored seismically. Calculations suggest that before it reaches the shale which caps the sandstone, it will dissolve in the surrounding pore water. As CO_2 charged H_2O is more dense than H_2O, it will eventually begin to sink. However, as sandstone contains no cations, the CO_2 will remain forever as a gas.

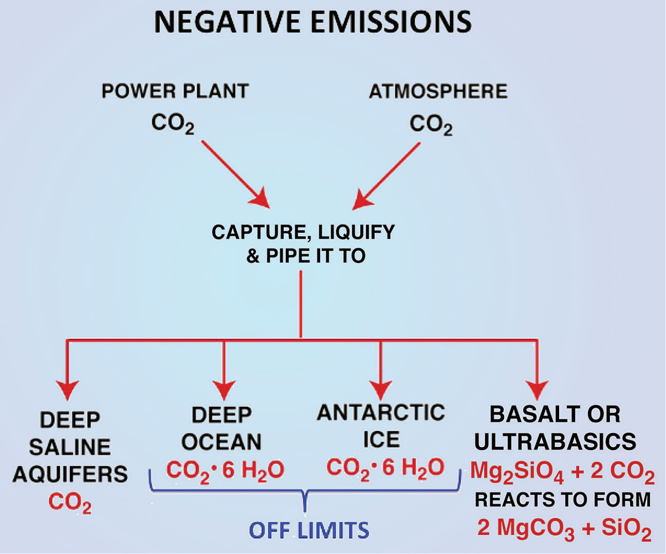


Figure 7.3 Options for storing CO_2 captured from power plant or retrieved from the atmosphere: it would be stored in either sandstone or basalt. Although it is feasible to store it in the deep sea or in lakes beneath the Antarctic ice sheet, these options are environmentally unacceptable.

Storage in basalt has the advantage that CO_2-acidified water will release Ca, Mg and Fe from the rock. These cations will combine with CO_2 to form carbonate minerals. To make this work, the CO_2 would have to be dissolved in H_2O at a pressure of ~10 or so atmospheres before injection. Such an experiment was conducted in Iceland. In order to constrain the rate at which CO_2 was mineralised, ^{14}C-tagged CO_2 and SF_6 were added as tracers. As SF_6 is an inert gas, monitoring the ratio of $^{14}CO_2$ to SF_6 allowed the extent of precipitation of carbonate minerals to be determined. It turned out that after only 100 days, this ratio had dropped by a factor of 10. Good news and bad news. Good news because the CO_2 was reacting with the basalt very rapidly and being locked away in carbonate minerals. Bad news because the carbonate minerals would tend to clog the pore space. As drilling deep wells is expensive, each one would have to accommodate a large amount of CO_2. Fracking to the rescue?

Columbia's Peter Kelemen makes a case that ultrabasic rock would be even better than basalt. His studies in Oman show that the carbonisation of these rocks causes them to expand producing a myriad of fine cracks. Further, as the pore water in ultrabasic rocks has a very high pH, they are 'hungry' for CO_2.

Caltech's Jess Adkins is promoting a quite different approach to CO_2 storage. He would use captured CO_2 to dissolve limestone producing $Ca\ (HCO_3)_2$ which would be dumped into the ocean. Whether this approach is feasible depends on whether Adkins can find a way to efficiently recycle the catalyst, carbonic anhydrase. Without it, the reaction between CO_2-acidified seawater and limestone would be far too slow. However, as carbonic anhydrase is very expensive, unless it can be recycled many thousands of times, the scheme would not be financially competitive. It should be mentioned that two cubic kilometres of limestone per year would be required in order to match today's yearly production of fossil fuel CO_2.

As is the case for switching to renewable energy sources, progress toward capturing and burying CO_2 is proceeding at a snail's pace. Government is providing only very limited funds for research in this area. Venture capitalists view the lead time for recouping their investment as far too long. So far, most progress has been fueled by private money.

Were the cost of removing and burying the CO_2 \$100 per ton, then the annual operational cost would be about 3.5 trillion dollars. Were this cost to be shared equally by all 7 billion humans, each person would have to chip in \$700 per year. And this would only keep CO_2 from rising. If a billion such units were put into operation, the CO_2 content of the atmosphere could be brought down by about 20 ppm per year. The hardware and operation costs would be about \$7000 per year per inhabitant.

The very slow progress in retiring fossil fuels and in recapturing CO_2 has focused attention on an option which had previously been considered off limits. It involves compensating for the warming by increasing the Earth's reflectivity. As first pointed out by a Russian meteorologist, named Mikhail Budyko, this could be done by adding sulfur dioxide to the stratosphere (see Fig. 7.4). Observations regarding the fate of SO_2 added to the stratosphere by large volcanic eruptions, tell us that on the time scale of weeks stratospheric SO_2 is oxidised forming H_2SO_4 aerosols. About 10 percent of the Sun's rays intercepted by these aerosols are reflected back to space. The rest are forward scattered and reach the Earth's surface. Models suggest that doubling the CO_2 content of the atmosphere is equivalent to cranking up the Sun's energy output by about two percent. Hence to compensate for the warming generated by doubled CO_2, 20 percent of the incoming sunlight would have to encounter H_2SO_4 aerosols. This would require a standing stock of 50 million tons of these aerosols. As they would remain aloft only about one year, they would have to be replaced on this time scale. It turns out that the cost of such an action would be about 50 times less than that for either replacing fossil fuels or for capturing and burying CO_2.

ALBEDO MODIFICATION

A LA BUDYKO

SO_2 GAS $\longrightarrow$ H_2SO_4 AEROSOLS

SIZE ~ 0.3 MICRON

BACK SCATTER 10% OF SUN RAYS

IN ORDER TO COMPENSATE FOR DOUBLED
ATMOSPHERIC CO_2 CONTENT
32 MILLION TONS OF SO_2 / YEAR
WOULD BE REQUIRED

RESIDENCE TIME IN STRATOSPHERE ~ 1 YEAR

REDUCED OZONE
MORE ACID RAIN
BLEACHED SKY
REDDER SUNSETS

PINATUBO (1991 VOLCANO) PUT UP
32 MILLION TONS SO_2 INTO SRATOSPHERE

Figure 7.4 Geoengineering by adding SO_2 to the stratosphere.

One might ask how these large amounts of SO_2 could be delivered to the stratosphere. It could be done with a fleet of several hundred jumbo jets. But more likely it would be done with huge balloons. They would be launched in the tropics so that the SO_2 would follow the same path as the air upwelled into the stratosphere at low latitudes. Of course, considerable research involving atmospheric circulation models backed with tracer experiments would have to be carried out so that the SO_2 would be spread uniformly across the entire planet.

As is the case for any proposed environmental intervention, the accompanying downsides must be evaluated. For H_2SO_4 aerosol cooling, at the top of the list is the consequent reduction in ozone. Ozone is consumed when SO_2 is converted to H_2SO_4. Hence its reduction would allow more UV to reach the Earth's surface. The 1991 eruption of the Philippine volcano, Pinatubo, injected 32 million tons of SO_2 into the stratosphere. As a result, the global ozone inventory dropped by about four percent. Next on the list is that the sulphuric acid aerosols would bleach the blue skies and enhance red sunsets. Of course, when these aerosols reached the troposphere they would acidify the rain. At the dosage required to balance a doubling of atmospheric CO_2 content, this mode of H_2SO_4 acidification would rival that produced by coal burning power plants. However, there would be an important difference. As the H_2SO_4 produced in power plants is added to the troposphere, it returns to Earth within hundreds of miles of its source. Geoengineered H_2SO_4 would be spread across the planet. Finally, how would these aerosols alter stratosphere dynamics?

There are several reasons why this 'Band Aid' has not received much attention. First, were it put in place, the incentive to replace fossil fuels and to recapture CO_2 would be diminished. Second, there is the concern that this approach would not uniformly undo the temperature and rainfall anomalies created by the CO_2 warming. If so, it could create international tension. Finally, people are uneasy about allowing humans to intervene in climate. Most ecologic interventions have created as many problems as they solved. However, as doing nothing will lead to irreparable loss of ice and species, careful thought must be given to the geoengineering option.

8. END PIECE

The geologic record makes a strong case that CO_2 has been instrumental in driving past climate changes. But as made clear by the record for the last 150 kyr, it has not acted alone. Insolation cycles, ocean circulation re-organisations, latitudinal temperature gradients also contribute. On far longer time scales, tectonics, volcanism and the Sun's luminosity have as well.

Progress in sorting out the extent to which CO_2 has contributed is currently impeded by our inability to reconstruct the atmosphere's CO_2 content reliably for times greater than a million years. All of the proxies involving living organisms are flawed because in each case the results are impacted by factors other than atmospheric CO_2 content. There is, however, one proxy which may remedy this. It is the ^{13}C record kept in air trapped in soil $CaCO_3$ (see Fig. 8.1). Not only could it avoid the pitfalls of ^{13}C records in organic matter, but it has a higher upper limit than those based on photosynthetic fractionation. Further, soil $CaCO_3$ is ubiquitous in dry lands and it is applicable over the entire Phanerozoic time period. Morgan Schaller is currently hard at work evaluating the many issues surrounding its implementation.

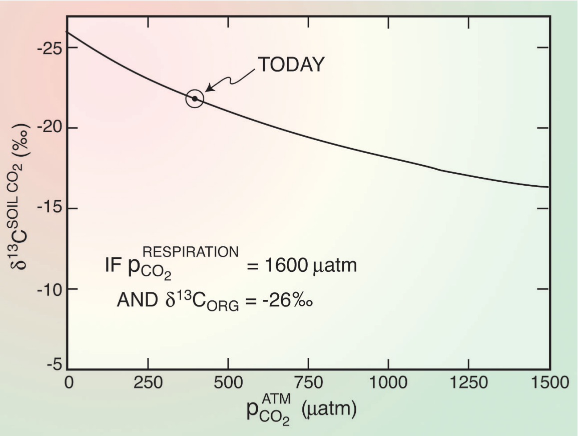


Figure 8.1 The dependence of the $\delta^{13}C$ in soil air on the atmosphere's CO_2 content for a respiration CO_2 partial pressure of 1600 μatm and $\delta^{13}C$ of -26 per mille. Morgan Schaller proposes that measurements of the CO_2 content of air trapped in soil $CaCO_3$ and of its $\delta^{13}C$ will allow him to calculate the atmosphere's past CO_2 content. Although he makes a convincing case that the air trapped in these carbonates is pristine, there are numerous issues related to his observation that the liquid water present in the soil $CaCO_3$ contains amounts of HCO_3 and CO_3 exceeding that of CO_2 (see Section 5). He will have to establish the $\delta^{13}C$ of the soil CO_2 to an accuracy of better than ±1 ‰. At 1 ‰, the uncertainty of a measurement in the 500 μatm range would be about 150 μatm. In the range of 1000 μatm, a one per mille uncertainty would correspond to 250 μatm. Achieving this accuracy, although a sizable challenge, should be doable.

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