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SCOTT DONEY: So what I was planning on doing was starting off by having a discussion about the Sigman and Boyle paper, and then we can go into more general questions and review. And I brought my notebook with me. I didn't bring all of, for example, Meg's lectures, but, if there are other questions that I can't immediately answer off the top of my head, I can send some emails out later this afternoon.

So let's just start off by having-- I mean, so what did you guys think of the Sigman and Boyle paper. I mean, I tried to choose a paper that was challenging, but hopefully, you've learned enough in the semester that you could at least understand what the arguments were. If not, there are parts where it's like, OK, well, I don't know the particular data sets they're talking about and some of the arguments, but what did you guys think of it?

STUDENT: I thought it was a good paper for tying things together and just thinking through a lot of the concepts that we've been having that are conceptually not the simplest.

SCOTT DONEY: What about you guys up at MIT? This has got to be-- you guys are part of the--

STUDENT: Actually--

SCOTT DONEY: Well, why don't we start then from the folks up at MIT? Because we can hear you guys quite well. I mean, did you guys understand the main themes?

Was there part of the paper that didn't make sense? Should we walk through the arguments just in a review? What would help you guys? This is really to help you guys pull things together in your mind for the final.

STUDENT: I mean, you guys-- a question-- the text.

STUDENT: I had a question about why the carbon-13 to carbon-12 system of the-- it says that the land plants have a lower carbon-13 carbon-12 ratio, and it was using that as an explanation on why you could've gotten-- if there was less carbon stored in land, you would get a decrease in carbon-13/carbon-12 ratio of the ocean atmosphere system. I didn't understand--

SCOTT DONEY: OK, good question. So we'll go over the C13-- pen is dying on me. The semester must be over-- my pen is dying. So the C13 to C12 ratio, and it's usually defined in a del notation.

And remember the del notation is simply the fact that we typically don't measure the absolute ratio of isotopes. We measure things, mass-for-mass spectrometers, almost always against some reference standard. And so you're going to be actually measuring the C13/C12 of your sample relative to some C13/C12 of a reference.

And then you're going to take this. This is going to vary about 1. If the sample and the reference had the same value, this ratio would be 1.

And you're going to look at deviations from 1. And since the deviations are pretty small, you're going to multiply by 1,000. And it's often reported as per mille or the cute little percent sign with an extra extra zero.

Now, there's a couple of things that can fractionate C13 from C12. And we went through a couple of-- there's equilibrium fractionation. And that's just that in a chemical system, let's say if you have a phase transition, if you have a phase transition, you'll often find that one phase will have a slightly different isotopic composition than the other phase.

Another is kinetic fractionation. And so for example, in the case of C13 and C12, when you form organic matter inside a cell. So you have this little-- my nice little cell, you have to diffuse in CO2. And the C12 CO2 diffuses in faster than the C13 CO2 because the C12 CO2 is lighter.

And so what you see in both land plants and in marine plants is you see that you have the del C13 is less than 0. And the reference for C13 where the reference is a Peedee Belemnite calcium carbonate. Essentially, it's a fossil.

So the reference is a calcium carbonate. It looks a lot like what you might expect the inorganic, dissolved inorganic carbon to look like. The organic matter is usually less than that. And the range is, for marine organic matter, it's something like minus 20 per mille somewhere around in there.

And for terrestrial-- and we won't go into the details-- it depends upon on the carbon fixation pathway, so some ecosystems have very different-- have different C13 signature than others. You guys remember C3 and C4 plants from biochemistry? Anyway, detail that you don't really need to know here. Somewhere between-- what?

STUDENT: Question at MIT.

SCOTT DONEY: Sure.

STUDENT: Is the diffusion rate as important as the enzymatic kinetic fractionation there?

SCOTT DONEY: For RuBisCO, basically, RuBisCO uses everything that gets to it in photosynthesis. And so it really is-- it's not a enzymatic fractionation. It's a diffusional fractionation.

There are systems that are enzymatic fractionation. And you would have to, if you wanted to go into this in detail, you would look at both of those components. But in this case, it's a-- excuse me, particularly on land plants, you have to diffuse through quite a barrier of dead air space in the leaf. And so basically, it's diffusion limited rather than enzymatic limited.

Land plants are somewhere between, say minus 10 and minus 30 per mille. And people do use the differences in the C13 of the organic matter to say something about marine and terrestrial. In the context of the Sigman and Boyle paper, what it's comparing to is the DIC of seawater, which is more like approximately 0. Yeah, more like about 0.

And so organic matter of either form is isotopically depleted in C13 relative to the inorganic pool in seawater. So if you took a large slug of organic matter from land, so you took a bunch of trees, and you chop them down, and you stuck that carbon into the ocean as CO2-- now, presumably, these got ground up as the glacier was coming. Or reverse when the glacier retreated, you started to grow trees, and you suck CO2 out of the atmosphere, but eventually that CO2 came out of the ocean to replenish the atmosphere.

If you added a bunch of terrestrial carbon to the ocean, you would change the del C13 of the ocean, and you would make it lighter because you're adding light organic carbon, and that would push down the C13 of the inorganic carbon in the ocean. So this would be in the DIC system. And the records we have for the C13 in the ocean come from calcium carbonate shells, and so it's recording that inorganic carbon concentration of seawater.

So that was the argument that they were making. Does that make sense?

STUDENT: It's not important that they were land plants. It's just important that plants are--

SCOTT DONEY: Right.

STUDENT: Biomass is being put into the ocean.

SCOTT DONEY: Yeah, it's more important-- and the reason why they focus on-- it is it's the organic matter going into the ocean. And the reason they focus on terrestrial organic matter versus ocean organic matter is, other than the dissolved organic pool, which we know so little about and have no-- this is the classic searching under the-- the drunks looking for their keys. Where do they look? They look under the lamppost, even if they drop their keys a couple hundred yards away. Well, you look because that's where you can see things.

We have no information about what the dissolved organic carbon pool might've been in the glacial/interglacial. And so the assumption is, well, it was probably constant. It's got a fairly long residence time. And most of these analyzes ignore that.

The particulate organic pool in the ocean is so small, only a few petagrams, that it wouldn't have a big impact. And so if you're looking for something to change a large organic carbon source that's mobile, usually you would look on land, and there's good reason to think there was less organic carbon on land. Good question. Other questions? Yeah, Caitlin.

STUDENT: I have a question about something on in the last paragraph on page 860. They talked about the organic matter reservoir. The terrestrial organic matter reservoir is decreasing during ice ages. And they say that they talked about a 500, a potential 500 teragram carbon--

SCOTT DONEY: Petagram.

STUDENT: --addition, I guess, due to either-- this is my question, how are they adding that carbon back into-- or taking it out of the terrestrial reservoir? Is it decaying on land into CO2? Or is it being transported as organic matter into the ocean and then being remineralized in the deep ocean? Or is there some partitioning between those two things?

SCOTT DONEY: For their arguments, because they're looking at-- the main focus of this particular article, of course, are these large amplitude, the large amplitude CO2 changes. And so they're trying to understand the difference between these interglacial periods with about 280 PPM and the glacial maximum that had 180 to 200. So they're looking at timescales. Remember, this is 100,000 years.

STUDENT: So it doesn't matter?

SCOTT DONEY: For their argument, it doesn't matter. One of the things we always-- one of the anthropomorphic distortions is we always think about going from a interglacial back to a glacial, but we forget that time actually-- really, the time ran the other way. So the best way to think about it, the really sharp change is you were at a glacial period, and that's actually the norm for the last 500,000 years was being in glacial period, not in the nice tropical weather we have now.

And so the way I usually think about it is, as the ice sheets retreat, you expose all of this barren land. Trees start to grow-- well, first off, mosses and lichens and all that. But eventually, you get and you build forests, and then you build peatlands because that's where a lot of the carbon is stored, is either in wood or in peat and high-latitude peat.

And you didn't have any of the boreal forests or any of the peatlands during the glacial period because that has all been scraped clean. And so that carbon had to come from the atmosphere. But the atmosphere on timescales of a few decades, you can't really draw down the atmosphere without the ocean starting to pump CO_2 back into it.

And so the way I usually think about it is the glaciers retreated, land plants started to grow, and that carbon had to be pulled out of the ocean via a gas phase. Now, what happens in the reverse when the glaciers advance, and you knock down all these forests, and you destroy the peat? And how that carbon gets released is a little bit more complicated.

And I don't think anybody's-- it's not exactly clear. Is some of the carbon buried underneath the glacier? And what happens to that? But eventually, the argument is eventually it gets to the ocean. Whether it goes through a gas phase because of decay or whether it goes as a solid or dissolved phase via rivers I don't think is completely resolved.

STUDENT: Do you think, as a follow up to that, we could think through what the difference would be if we were just releasing a ton of CO_2 to the atmosphere directly from land versus dumping a whole bunch of organic matter into the ocean?

SCOTT DONEY: OK.

STUDENT: Actually, was that what you mean in terms of time scales, I guess?

SCOTT DONEY: OK, so let's look at shorter term-- Caitlin's question is basically, let's look at shorter-term perturbations to the ocean inorganic carbon-- or the global carbon system. And there's a couple of important-- and I'm going to have to go back again. So there's a couple of important timescales. And these are important things that you guys should probably-- irrespective of the exam, it would be useful for you to have these floating around in your brain.

And they talk about this a little bit in the paper, which is they divide the ocean up into a warm thermocline box, a deep box, that vents to the poles. So you have warm thermocline, and this is basically all that thermocline circulation and wind-driven circulation. And this has timescales of, well, we'll worry about timescales in a minute.

And then you have then you have land. That was not my best tree. And then you have atmospheric CO_2.

The timescales of this are-- so we would want to know the gas exchange timescales. So if there's a perturbation in the surface air or the surface ocean on some timescale, gas exchange is going to try to drive the ocean and atmosphere back to equilibrium.

And so we talked about that. If you remember, for oxygen gas exchange timescales were typically like a month and where we got the timescale by saying that the flux of gas was equal to some transfer velocity times a delta concentration. That was the core of the gas exchange argument.

And so that if you looked at, say, that delta C at any particular time after you had a perturbation, it would be your delta C initial and then e to the minus-- let's see, it would be k over h t, where k is your transfer velocity and h is your mixed layer depth. So h is the mixed layer depth.

So that would be k has units of, say, length per time. h is in length. So this would be 1 over time multiplied by time, and so it becomes unitless which is what you need for the exponential.

For oxygen, it was about an order a month. It might be two weeks, it might be a month and a half. But that's a good approximation.

For CO2, because of the fact that you have this large additional DIC reservoir-- remember, you had the large DIC reservoir so that any change in CO2, you also had to fill up that DIC reservoir and alter that DIC reservoir. Was more like, the gas exchange timescale was more like a year. And then for 14 CO2, it was more like something like 10 years, where the difference between C14 and CO2 was, in the case of the CO2, the DIC reservoir-- you still have to fill up the DIC reservoir, but you also can shift-- you have shift in pH and between H2CO3 star carbonate and bicarbonate-- or excuse me, bicarbonate and carbonate.

So this actually went faster because, along the way, you altered-- you added a little bit of CO2 and that made the system a little bit more acidic. And so you actually got more bang for your buck in terms of the change in H2CO3 star than what you would expect if the pH had stayed constant. If the CO2 system didn't buffer-- was not the primary controlling buffer on ocean pH, then it would look more like C14. But because it does change the-- it does control the pH, it has that nonlinear feedback in it.

STUDENT: So the reason that C14 doesn't affect the pH is just because you're not adding that substantial component.

SCOTT DONEY: Yeah, you're adding a trace amount of CO2, and you're looking at it in terms of the change of isotopic equilibrium. So that's the first timescale. If you perturb, if either you have a perturbation in the ocean or a perturbation in the atmosphere on the timescale of about a year, the surface mixed layer will try to approach that-- or try to reequilibrate.

Now, that doesn't mean that the surface water PCO2 scope will be at atmospheric equilibrium because there's all sorts of other factors. In addition to gas exchange, you have biology and circulation. So the biology, the important factors are the net community production.

Remember, that's the conversion of CO2 plus water into C organic plus O2. And when you have a net, either a net autotrophic system, which would drive it this way, or a net heterotrophic system, which would drive the system back the other way, you actually have a net removal of carbon. One of the things people sometimes confuse, and it gets confused in the literature a lot, is they-- and this is a really important thing to keep in mind-- is they confuse net community production, which is the net reaction of the conversion of inorganic carbon to organic carbon, they confuse that with primary production, which is primary production is just the uptake by CO2 by the autotrophs.

So there can be a huge loop where you have a big-- so this would be, say, primary production. You can have a lot of primary production going on. But as long as all that organic carbon is remineralized or respired back and there's no build up or export of organic matter, then there's no net community production. And it's only when you have net community production that you can drive DOC and particulate export.

So this is probably one of the big differences between looking at the world as a biologist versus looking at the world as a geochemist. At some fundamental level, geochemists are really interested in net community production because it's that net transfer of organic matter that then does all the things in the deep ocean. It changes the DIC distributions, oxygen distributions, nutrients, anything you're interested like that, where they might not be as interested in the exact cycling of the rates of primary production.

So where I was going with this is-- going back to Caitlin's question, going off it, but a little bit of a tangent, but this is kind of a good review-- the things that alter-- you've got gas exchange that's trying to reset surface water PCO2s back towards atmospheric equilibrium. You have biology, which, for the most part, is trying to draw down PCO2. It's trying to take up CO2 and form it into organic matter and export it. And then you have upwelling and mixing, which bring up high DIC and high-nutrient waters.

And so the PCO2 at any spot is going to depend upon, excuse me, the balance between the circulation effects, which are working on these biologically driven gradients, and the local biological effect, biology. The timescales for this are comparable to gas exchange. And so that's why you see, for example, on a seasonal cycle, you see large changes in CO2 and DIC because the circulation, the biology, and the gas exchange are all kind of working on comparable timescales.

If you remember the homework assignment where we looked at the Brooks et al. analysis for the Hawaii Ocean Time-series, where we were looking at the thermal effects on PCO2 and the biological effects on DIC, that's that seasonal cycle. That's why you get a nice seasonal cycle because they're all kind of interacting on that timescale.

On longer timescales, the warm thermocline really depends upon-- you've got a mix layer, which I can't really draw because I didn't do a big enough scale, so that would be your mixed layer. Then you have that warm thermocline. Remember, this is down to about, say, 1000 meters in the tropics and subtropics.

And we looked at, for example, tritium and Freons and helium, and the time scales for ventilation for this box, the warm thermocline, are on, say, 10 to 50 years, a few-decades time. And so if you had a perturbation in the ocean or a perturbation in the atmosphere, you would start to see the response-- let's say you increased atmospheric CO2. The warm thermocline would start to fill up with CO2 on the order of a few decades.

And that's what we see now with the anthropogenic CO_2 is most of the anthropogenic CO_2 is caught in the upper half-- most of it's in the upper half kilometer or so. And that's because the gas exchange rate is no longer limiting. The gas exchange rate is able to adjust fairly quickly on the order of a year, couple of years.

And then the rate-limiting step is circulation of that water into the interior. And so in the warm thermocline, it's order of 10 to 50 years. In the deep box, excuse me, the deep box, remember, is ventilated by sinking in the polls, so sinking in the Southern Ocean of Antarctic bottom water and sinking of North Atlantic deep water. And the timescales are hundreds to thousands of years.

Now, there are a couple of longer timescales, and I'm surprised no one has asked the really fun question in the Sigman and Boyle problem, which is, let's go through the whole calcium carbonate cycle in detail.

STUDENT: Someone asked that yesterday, so feel free.

[LAUGHING]

SCOTT DONEY: So the basic argument-- OK, so the ocean circulation gives you timescales of the deep ocean is hundreds to thousands of years. You have an additional timescale, which is the calcium carbonate timescale, which is more like order of 5,000 years, something like that. It's 2,000 to 5,000, depends upon who does the calculations or the exact usage.

And then, of course, longer time frame-- if you remember back to Deedee's lecture, what are the longer timescales for the carbon system? What controls the longer the longer timescales, order of a million years?

STUDENT: Silicate weathering.

SCOTT DONEY: Yeah, so you'd have silicate-CO_2 interactions, weathering, volcanism on the order 10 to the 6 years. And so what they've done-- and this is classic-- is they've said, OK, we are interested in the timescales of something like-- they're interested on timescales of 5,000 to say 100,000 years. So they're going to ignore mixing within the ocean, so they're basically saying, well, the ocean is just well, mixed.

We don't need to really worry about-- we may need to worry about redistribution of properties, but we don't need to worry about the kinetics of how long it takes for the ocean to mix or the thermocline to ventilate or the mix layer to come to equilibrium. So they're going to ignore all the short-term processes because they're going to say, well, those are all in quasi steady state. And they'll adjust to whatever new base state we have.

And then they're going to ignore the really long time scale-- the real long time scale processes like silicate and CO_2 weathering. They'll say, well, over the timescale that we're interested, we're going to assume that those are constant and can't really affect our system. These are the same sort of arguments we made, if you remember, very back at the beginning of the semester when we were talking about, why is the sodium concentration in the ocean proportional to salinity? Well, it's because the timescales for sodium are so long that they're much longer than the ocean turnover time. So it all does kind of fit together eventually.

STUDENT: Can I ask you a question on that, though? I mean--

SCOTT DONEY: Sure.

STUDENT: How does moving glaciers and grinding up rock and really exposing maximum surface area of rock affecting the timescale of silicate weathering, for example? I mean, I would imagine that it can move it from 100,000 years to, maybe, you're noticing something on 10,000 years, which is really relevant.

SCOTT DONEY: There's a very interesting hypothesis of why-- what I didn't show here, if we go back to this, whoops, this is the last 450,000 years. We now have ice cores going back to about 800,000 years. Beyond that, we have the paleo record and paleo reconstructions of atmospheric CO2.

If you go back about four million years ago, the paleo record, which is based on things like C13 isotopic signatures, suggests that, in Earth's history, where we think, the planet was quite warm, there was a lot of CO2 in the air, you think giant big swamps and dinosaurs and all sorts of stuff, crocodiles living in Antarctica, one of the hypotheses for why CO2 is as low now as it is is that, when the Indian subcontinent slammed into Asia, it started to uplift the Himalayas.

And when you uplift land, you actually dramatically increase weathering rates because, essentially, you have-- well, steep slopes erode much faster than shallow slopes. So you keep having uplift, and you're exposing more and more rock. And so one of the arguments is that the uplift of the Tibetan plateau has actually led to a long-term drawdown in atmospheric CO2 because you've enhanced the weathering rate. You've exposed more fresh rock because the CO2 is taken up in the chemical weathering reaction.

For the glacial-interglacial cycles part of it-- one of the reasons why people don't look at that as much is that a lot of the glacier weathering is physical, not chemical. So it basically grinds stuff up, but it dumps it into the ocean, as in-- it's still in fairly large particles. And it's not clear that the chemical weathering rate has gone up dramatically. The other argument is that even if you-- let's say you had a million-year time scale, even if you doubled the rate of weathering over, say, a 30,000-year period, it still would be a fairly small perturbation because you'd be going from a million-year time scale to a 500,000-year timescale, but your cycles are going on faster than that. That's a good question.

STUDENT: So is the timescale for physical weathering longer than chemical weathering? Or is that separable?

SCOTT DONEY: Well, if it's physical weathering, if you just grind it up, you don't use up any CO2, it's only the chemical weathering process that's actually using CO2. It's, do I pour-- I can take a piece of chalk, and I can take it and put it into a mortar and pestle, and I can grind it up into a fine dust, and then I can throw it into the stream, and it can back to the ocean. That's physical weathering. I just grind up the rock.

Or I can pour acid on it. I could pour carbonic acid on it and let it dissolve and eat away. The physical weathering doesn't affect the chemistry where the--

STUDENT: But just in terms of the rock removal rate, is there a difference?

SCOTT DONEY: Well, I'm not sure I would pose it as a difference in time scale. There are different environments that have chemical-- weathering occurs more-- chemical weathering is really enhanced by high temp-- by temperature and humidity versus physical weathering is more common in colder environments. Think ice getting into cracks and splitting rocks open and things like that. Yeah, but I guess I hadn't thought about it in that way. Yeah, I'd have to ponder that a little bit.

STUDENT: I think they could be equal, or one could be faster than the other or vice versa, just depending on where you are and what the conditions are.

SCOTT DONEY: Yeah, and they do interact. I mean, physical weathering creates more surface area, which enhances chemical weathering. Chemical weathering can weaken rocks and enhance physical weathering. So do you guys want to do the calcium carbonate cycle? Yeah, cool.

STUDENT: One other thing that I got a question on yesterday and wasn't happy with my answer was--

SCOTT DONEY: You weren't happy with the questions.

STUDENT: I wasn't happy with the question because I couldn't answer it very well. Just the critical depth and the difference between that and the compensation depth, just to go back to the--

SCOTT DONEY: OK, so let's go back you have calcium carbonate solid. Oops. So with calcium carbonate solid, that goes into calcium 2 plus plus carbonate 2 minus. And you have some solubility product for that reaction. And we'll call it an effective solubility product and not worry about activities.

And the reason why there's no calcium carbonate solid is the activity of a solid is 1. And so the things you need to know about the calcium carbonate system, we're going to assume, for most intents and purposes, that calcium is approximately constant. It does deviate slightly in the upper ocean when you have a lot of calcium carbonate formation. And it changes with salinity, obviously, because it's one of the major salts. But we're going to primarily focus in terms of looking at the solubility of calcium carbonate on the carbonate ion concentration.

Now, there's a couple things we want to look at. One is Ksp is a function of temperature and pressure. Does anybody remember which way-- does calcium carbonate become more soluble or less soluble as you go down the water column?

STUDENT: More soluble.

SCOTT DONEY: OK, becomes more soluble. Increasing pressure and decreasing temperature. They work in concert, so as you move down the water column, it gets colder, you get more pressure, calcium carbonate wants to dissolve.

We need to know that there's different Ksp's for calcite and aragonite. And so calcite-- or aragonite is more soluble, is the more soluble form. And then there's all sorts of-- Bill went into there's high magnesium, calcium carbonate. We won't go to that level of detail.

So by the time you get down to the deep ocean, where the calcium carbonate sediments are, it's almost all calcite. Aragonite is only getting deposited-- so this is the deep sea, the deep sea sets. Aragonite is only getting deposited on shelves. So for example, coral reefs are aragonitic.

What about the distribution of carbonate ion? What do we know about carbonate ion and how it might vary in the ocean? Anybody at MIT want to take a crack at that one?

STUDENT: This was another question for my citation.

SCOTT DONEY: Oh, good. So, yeah, come on, somebody just take a guess. How is carbonate ion going to vary in the ocean? Or what drives carbonate ion to vary?

STUDENT: pH.

SCOTT DONEY: pH. Yay, OK. So what changes pH? We should've talked about this.

STUDENT: You're talking about the difference between surface and deep in the Atlantic and the Pacific, right? We're not talking about differences in surface concentration because we talked about both things yesterday.

SCOTT DONEY: Well, we could do both, but, yeah, surface to deep, Atlantic to Pacific. If I were to draw my box ocean, and I have 0 to 6,000, and I start in the Atlantic-- the Altanic, the Atlantic, and I go to the North Pacific, how is it going to change along that path?

STUDENT: It's going to Increase from the Atlantic to Pacific.

SCOTT DONEY: OK, so it's going to be-- pH is going to be high in the deep North Atlantic, and it's going to be low in the Pacific, North Pacific. And why?

STUDENT: Organic matter.

SCOTT DONEY: Yeah, organic matter, respiration, because of respiration. And similarly, it's going to be even higher in surface waters for the most part. So as you take surface water and you advect it down, you add organic matter, you drive the pH down. Now, what happens when you lower the pH of seawater? What happens to carbonate ion?

STUDENT: Decreases.

SCOTT DONEY: Right, so this would be the same path for carbonate ion. There are temperature overlays to all of this. So if you looked in surface waters, there are temperature overlays.

But generally, if you think about-- if you were thinking about polar surface waters, where there's no temperature change as it goes down into depth, it's the organic matter respiration, so you'd see a higher carbonate ion concentration in surface waters. And then as you went down and added more and more organic matter, you'd drive the system. Even though, along this path, you're increasing DIC, you're actually decreasing carbonate ion.

There's more carbon, but there's less of it in the carbonate ion form. Excuse me. OK--

STUDENT: I have a question.

SCOTT DONEY: Sure.

STUDENT: You have the North Atlantic surface waters being higher pH and the bottom water. So is that the water is sinking down, and is it remineralizing the whole time? And is that why there's a difference between surfaces?

SCOTT DONEY: The change of surface waters to deep waters isn't going to be huge in the North Atlantic. But there is some remineralization in the North Atlantic. And just in general, the pH of surface waters typically is higher than the pH of bottom water, of bottom waters, just that there's that contrast between surface and deep. So--

STUDENT: A temperature effect or just--

SCOTT DONEY: No, it's--

STUDENT: --mineralization is occurring at the surface.

SCOTT DONEY: Right at the location of sinking in the North Atlantic, everything's going to be fairly homogeneous. But if you were looking in the middle of the North Atlantic and the subtropical gyre and you were comparing it to the bottom water that was underlying it, you're going to have higher DIC concentrations in the bottom water than you are in the surface water because, in the surface water, you've been taking up CO2. Taking up CO2 to form organic matter, that's going to increase the pH.

So there will be a surface-to-deep concentration gradient. And if you look-- I think we showed some of these-- Bill showed some of these plots in class-- if you look at the carbonate ion concentration with depth, it tends to do something like that. So this would be carbonate ion concentration. And your, eek, your Ksp's look like that.

STUDENT: What your C-- what your carbon will be?

SCOTT DONEY: Well, yeah, I mean, yeah, this would be the-- Well, yeah, this would be CO3 2 minus equilibrium. Is actually going up because it requires-- it's more soluble. So you need a higher bottom water concentration of carbonate ion to stay in saturation. Does that make sense?

STUDENT: Another question.

SCOTT DONEY: Sure.

STUDENT: I know that temperature is important when you're talking about the solubility of CO2 aqueous in the surface water, like the drawdown from the atmosphere, but in looking at general ocean patterns of the carbonate system, is that really the only area where temperature is really a key player?

SCOTT DONEY: Well, I mean, once you get into the deep ocean, the temperature differences in the deep ocean, once you get below about 1,000 meters, you're really talking about fairly small temperature gradients. By the time you get to about 1,000 meters, your temperature's about 4 degrees Celsius, and bottom waters are between 0 and 2 degrees Celsius. So once you get below, say, about 1 kilometer, the temperature gradients are small enough that other things swamp them out. In the upper ocean, yeah, there are temperature gradients, and they are important in the details. If you were to do this for a living, you would need to look at temperature effects on speciation.

In terms of the calcium carbonate cycle, the main arguments, the biggest one is the temperature and pressure effects on carbonate equilibrium, where you do see fairly big changes in the upper kilometer, and then once you get below a kilometer, the big changes are pressure. That make-- I'm dodging the issue because, yeah, if you wanted to get into the details, all the Ks, the Ksp's, K1, all of those temperature--

STUDENT: That's why it gets kind of confusing. But when we're looking at big-picture trends, obviously, for carbonate, the Ksp's temperature is really key and also, in surface waters, looking at drawdown of CO2. And for a lot of the other things, it seems like it's safe to say that temperature isn't the primary effect.

SCOTT DONEY: For the most part, the Sigman and Boyle do go through the argument that if you dropped if you dropped the deep water temperature from, say, 4 degrees to 0 degrees, you would increase the solubility of CO2 and you would take up some CO2. So if you had such big dramatic changes, the deep ocean's is a large reservoir. If you dropped it by 4 degrees, that would be a big change, and it would affect CO2 solubility.

But if you were looking in the modern ocean and looking at the contrast between the deep North Atlantic and the deep North Pacific, the temperature change isn't nearly big enough to drive the kind of changes we see in carbonate ion. There it is the biological CO2. OK, so--

STUDENT: Another question.

SCOTT DONEY: Oh, sure.

STUDENT: Could you draw the DIC profile on there too.

SCOTT DONEY: So DIC would be low in the surface water, and it would be high at depth.

STUDENT: Why does carbonate have a minimum at about a kilometer? And then Bill Martin showed a plot that had a minimum in about a kilometer and then it popped back up again.

SCOTT DONEY: OK, I thought you meant-- I was like, did I draw a minimum? Remember where the oxygen minimum is? The oxygen minimum is about 1,000 meters.

And we've got to back up a minute, so I'll use some space up here. The subsurface, DIC, nutrients, oxygen are all controlled by a combination of organic matter, remineralization. And the organic matter remineralization rate. Remember, the organic matter, if we looked at the sinking particles from the sediment traps, tended to be really high at the surface and then drop off and be pretty flat in the deep water.

So it's the remineralization rate. So this is the sinking flux. The remineralization rate is the derivative of that. So you still have some remineralization rate through the thermocline, so this is 1 kilometer, but Not a huge amount of remineralization in the deep water.

In fact, there are some people who argue that, in the deep water, most of the remineralization is actually going on within the sediments or at the sediment surface. But in the shallow water column, a lot of it's going on above 1 kilometer. A lot of it's going on in the water column.

So you tend to get in some basins an oxygen minimum, which would then be a nutrient maximum at somewhere about 1,000 meters. Now, some of that is because that's a region where local ventilation is relatively slow and organic remineralization's relatively high. And some of that is an artifact of the fact that you're bringing in water masses. You have lateral advection that's bringing in water masses that have different starting properties, and so you could get a maximum like that if you just happen to be advecting in an intermediate water mass that has a different set of properties.

But it is common to see those. And if you had an oxygen minimum because of organic matter respiration, you'd expect a carbonate ion-- excuse me. You'd expect a carbonate ion minimum because if you have a lot of organic matter respiration, you're going to change the pH, and you're going to change the amount of carbonate ion.

So if I wanted to, in some places, it looks more like that. And that would give a corresponding-- like that. OK I'm going to go to the new page. The good news is I don't have to do modeling classes this afternoon. So if my voice dies at noon, I'm fine.

So just to repeat what we had up there, so this was a vertical profile of carbonate ion and the saturation carbonate ion. Now, Bill, in his lecture, defined a bunch of terms. And these are just they're arbitrary terms, but it's useful to know because that helps you understand reading the literature and communicating with other people who've learned these arcane jargon terms. So what was it called when the bicarbonate ion concentration went from being saturated in the shallow water to being under undersaturated at some depth?

STUDENT: I know that's saturation

SCOTT DONEY: Yeah, so you have a saturation horizon. What was it called when-- so saturation horizon is based solely on bottom water, chemistry, and thermodynamics. And the argument is, well, above the saturation horizon, you should-- all the calcium carbonate-- the water's supersaturated with respect to calcium carbonate, all the calcium carbonate that hits the sea floor should be buried with no degradation.

Now, there's a caveat which we'll get back to in a minute. Below that depth, you can start to have influence of remineralization because the water is undersaturated. So the next one is the lysocline. And that was just the depth where what?

STUDENT: You have sharp change in the [INAUDIBLE] floor.

SCOTT DONEY: Yeah, well, the lysocline is basically where you could start to see a decrease in the calcium carbonate percent in the sediments. Another way that people define the calcium-- or the lysocline is they actually look in the sediments to see if they-- the forams have very pretty little shapes and their little shells, and you can spend a lifetime defining species and genera by looking at-- or genus, by looking at different shell forms.

Well, if your shells start to look all corroded, then you're probably below-- that's where the lysocline is. You can actually see whether the shells show any examples of pitting or degradation. And then, finally, there was the calcium carbonate compensation depth, which is where, basically, all the calcium carbonate is gone. It's all remineralized.

So no more calcium carbonate in the sediments. And so the classic is if you go along and you look at a mid-ocean ridge is you'll get basically a snow line. Calcium carbonate sediments are white. You basically get calcium carbonate at the tops of the ridges, and then, as you go down, you get no calcium carbonate sediments.

Now, one of the key arguments that Sigman and Boyle discuss is that we have records of lysocline variations with time. So this is the CCD, is way down here. The lysocline-- lyso-- aah. Lysocline, oh, I can't spell anything tonight.

The lysocline's going to be shallower than the calcium carbonate, sedimentation-- or the CCD, that compensation depth. And so you could imagine that the lysocline might be very sensitive to bottom water. If bottom water got more acidic, you'd start to see-- if bottom water got more acidic, the lysocline might extend all the way up to the top of the ridge.

And so if you took a set of cores, If I took cores like here, here, here, here, and here, and then I looked downcore, so I would have time, and I would also have depth by making these sediment cores. I could reconstruct over time how that lysocline depth has gone up and down. And that might be a sensitive indicator for my bottom water, my bottom water calcium carbonate-- or my bottom water calcium carbonate saturation state or the bicarbonate ion concentration. Caitlin.

STUDENT: I mean, wouldn't kinetic effects also determine that to some degree? When you're looking down a sediment core, what if there were just a whole bunch of coccolithophores in that spot for some reason at one time, dumping calcium carbonate down. Would that be then remineralized in sediments? Or would it be preserved?

SCOTT DONEY: Well, if you got-- and this is where it gets very complicated, and I didn't-- this paper's now six years old. And there's been a ongoing discussion of a lot of these issues. And there are people-- there was a very nice talk this summer by Bob Anderson, who argues that maybe we're misinterpreting the lysocline data.

And it does have to do with the complications that I don't want to get into too much. But let's say you had a sediment that did have calcium carbonate. Now let's say the lysocline dropped and you deposited some calcium carbonate rain down and didn't get dissolved.

What happens later on when that sediment is sitting at the bottom and water chemistry changes? Does it all go away? And that leads into a whole series of arguments that does get into the kinetics and pore water chemistry and diffusion rates and things like that. And that, basically, complicates the clean story that Sigman and Boyle argue.

STUDENT: And I have a feeling you're going into metabolic dissolution.

SCOTT DONEY: I was going to touch on metabolic dissolution.

STUDENT: And how that affects where the saturation horizon falls with respect to the lysocline of the CCD.

SCOTT DONEY: OK, typically, the saturation horizon is based on bottom water concentrations. We know that the sinking particles bring with it both calcium carbonate and organic matter. And organic matter, when it decays, is an acid.

It forms carbonic acid. So if you were looking in-- let's say we had-- this is my sediments. So you have all these little organic matters decaying away.

And when I decay organic matter in the sediments, I decrease the pH of the pore waters. And this is happening both in the sediments and then also right at the sediment water interface, right in that little fuzzy filmy boundary. And there were some very nice papers-- and Bill showed some of these results where people have gone in with the microelectrodes and looked at oxygen profiles.

And from the oxygen profiles, you can actually see where the organic matter is being remineralized. And if there's enough organic matter being remineralized, it can lower the pH near enough to the surface that some of the-- even though the carbonate ion concentration in the bottom waters might be greater than the corresponding equilibrium-- so the bottom waters are saturated-- in the pore waters, in the shallow pore waters-- and it has to be shallow enough to the surface so that stuff can actually diffuse, make it back out. But in the shallow pore waters, it might be reverse.

Pore water might be less than saturation because of organic matter decay. And what that can do is, even though the bottom waters are supersaturated, you are getting dissolution. And you would have a flux. You'd have a dissolution out of DIC because you'd have this dissolution of calcium carbonate in the water. And what would happen is that will-- the saturation horizon stays the same, but the lysocline can be shifted up above the saturation horizon.

OK, I would like to-- we've only got about 15 minutes left. We've talked a lot about carbon. I realize the whole world revolves around carbon, but unfortunately, the class didn't. And so are there questions outside of-- this is a nice review for a lot of it, but it didn't touch on, for example, thorium isotopes or-- it did touch on nitrogen, the nitrogen cycle a little bit. But were other questions more broadly about the class that you have this burning desire to know?

STUDENT: We're having another review on Friday.

SCOTT DONEY: Well, that sounds fun.

STUDENT: Oh, yeah, you don't have to be there. I'm just saying, we're going to have more time. You should come. We can keep you busy.

STUDENT: So it's not clear to me when we're talking about the critical depth how the critical depth versus--

SCOTT DONEY: OK, critical, which critical depth?

STUDENT: Well, versus mixed layer depths for blooms.

SCOTT DONEY: OK, great.

STUDENT: I'm having some trouble conceptualizing why you get a bloom and why you don't.

SCOTT DONEY: OK, let's ignore depth for a minute and take out depth. Let's say you just had a beaker of phytoplankton, and you had them in your incubator and you were torturing them, and you started off by keeping them in the dark.

At some point, as you decrease the light, the photosynthesis would be less than the basal respiration rate, and these guys would crash because they can't maintain-- they can't grow enough. Their joint program stipend isn't as big as their rent, and their bank account goes to 0. As you increase-- so let's say this is light and this is p or r. So let's say r was constant.

There's a certain amount of respiration that had to go on, it was very simplistic. And it might be constant R is a function of, say, carbon biomass. So every day, they lost 10% of their body weight for respiration. If you plotted photosynthesis rate, it might look like that.

We looked at those PI curves where this was some maximum rate and this is some initial slope. This is alpha of the initial slope. All the argument is is there's some critical light level-- call it i crit, where until light reaches that point, the respiration exceeds photosynthesis.

So from this point over that way, so the growth curve would look like this. It would be-- this was 0. This was net growth.

So it's negative, and it's positive. And so as the light starts to ramp up, when it's negative, the net growth is negative. The system crashes.

The complication is that there are two things going on at the ocean surface. As you go through a seasonal cycle, light is increasing. So it's just like putting a bottle in an incubator, but you also have changes in mixed layer depth.

And the reason why that's important-- so here's your sea surface is let's say you have-- this is your winter temperature profile. You have a very deep mixed layer depth. Say you're up off of Iceland. So this would be z.

Even though the phytoplankton up at the surface are seeing relatively high light, they don't stay there very long. And so the argument is that you want to look at the mean light over the mixed layer. Or alternatively, you can just think of it as you're going to look at the integrated production or the integrated net production over the mixed layer.

And it does depend a little bit on how the phytoplankton respond. The Sverdrup hypothesis is based on an integrated production. So you're going to compare the integrated production to the integrated respiration. But you're looking at the same basic thing that if the integrated production's less than the integrated respiration, you're going to be in this negative zone. And then if the integrated production is greater than the integrated respiration then you can have a bloom.

And the reason why people think there are blooms in the North Atlantic, one of the original arguments is that there are lots of nutrients there. There's lots of iron. There's nothing else to limit them.

As the mix-- and you have deep winter mix layers. So you drive the phytoplankton to very low levels during the winter, but you drive their predators to even lower levels because their food source basically sucks during the winter. There's very low phytoplankton.

And so as the mixed layer shoals, as you start to march up and you get shallower and shallower and warmer and warmer, you have all the conditions ready for bloom. Temperatures are warmer, so growth rates are faster. You have more solar insolation because it's getting further into the spring, and the mixed layer is shallower, so the community is seeing a higher average light level than it was when mixing is deep.

And their predators aren't are poised to eat them. In some place like the North Pacific, you don't get really deep mixed layers at least in the Eastern side of the North Pacific, and you have this iron limitation. So even when the phytoplankton get enough light, they can't grow that fast. And so they can't outpace their predators, so you don't get the big spring bloom.

How about from MIT? Questions of a generic, general sense? Nope. OK.

STUDENT: I have a question.

SCOTT DONEY: Sure.

STUDENT: I don't understand how the microbial loop is actually a loop.

STUDENT: Oh, how sad.

SCOTT DONEY: Did you guys just lose power?

STUDENT: No, she was asking--

STUDENT: It's OK. Keep going.

[LAUGHING]

SCOTT DONEY: What happened?

STUDENT: A little funny, I don't know.

STUDENT: We were asking a question, but you didn't hear. Oh, well, the camera changed too. So you guys always suddenly got very dark, and your desk got very orange.

SCOTT DONEY: Why don't we do your question. Then I'll do the microbial loop question. What was your question?

STUDENT: Why would the partitioning-- it says that if DIC increases when alkalinity remains constant, you get more of your DIC pool as carbonic acid and aqueous co2. I don't understand. When Kristen was talking in recitation, she was saying that the increasing DIC would just elevate all the concentrations but not change the partitioning.

STUDENT: Those two things are not-- they don't-- they're not the same because if you think about the [? Darren ?] plot, then you just go up higher. The total amount would increase, but you wouldn't be moving side to side on it.

SCOTT DONEY: If you want more time-- we're having some problems with the transmission.

STUDENT: So why would increasing DIC change your partitioning? Because that's what it's saying in the paper, but Kristen was-- we were talking about two different CO.

SCOTT DONEY: OK.

STUDENT: CO's constant--

SCOTT DONEY: Let me give you my answer because I wasn't there for Kristen's discussion. Not sure the context. When you increase DIC, OK. So when you increase DIC But alkalinity is constant, the way you do that is you're adding-- the only way to do that is to add CO2, gas, or carbonic acid. If you're increasing the DIC, but the alkalinity is constant because, remember alkalinity is defined as the sum of or the carbonate alkalinity is the sum of carbonate-- or bicarbonate ion plus 2 times carbonate ion.

OK, so the trick is-- and this is the nonlinearity of the carbonate system that drives people over the Wall. If alkalinity is constant, I have to maintain this relationship. So there's a variety of different ways of looking at it. One is that I'm actually adding an acid. And that acid, carbonic acid, is going to decrease the pH.

And so I'm going to tend to favor if I have H2CO3 star-- bicarbonate and carbonate. If I decrease the pH, I'm going to tend to push the, reaction-- a decreased pH. I'm going to tend to push the reaction in that direction.

And if you remember, there were a set of equations that control the acid base equilibrium between these different species. All of those depended upon pH, and so there's no way for these the relative fractions of these to stay the same as you change the pH. And remember, Bill drew this nice little diagram or had drawn where you have-- as a function of pH, you have bicarbonates in the middle, carbonate and H2T03 star, basically, showing that is basically showing, in graphical form, this relationship that, as you increase the-- or, excuse me, as you increase protons, decrease the pH, the speciation tends to shift.

And basically, the reason it comes down to is CO2 is the main buffer factor in seawater that's controlling the pH. If I were doing this in the laboratory, I could set up a system that had some other buffer factor controlling the pH, so imagine a situation where the pH remained constant, and as I added CO2, it would be equally split between these different fractions. But that's not the chemical setup of seawater. Is that--

STUDENT: Think of more than just that plot and raising DIC, you have to think about, how you can raise DIC and seawater without changing alkalinity.

SCOTT DONEY: Well, the obvious way of increasing DIC without changing-- I mean, there's a couple ways to increase DIC. The two obvious ways are the z obvious end members. I can increase DIC by adding CO2 gas, and that will not change alkalinity.

And in that case, like I said, pH goes down, PCO2 goes up, and carbonate ion goes down. Sometimes you'll see-- and I think it's actually a little misleading-- sometimes you'll see this written as this reaction. Sometimes you'll see this written as this reaction. And people say, oh, well, the CO2 uses up carbonate ions.

I don't like this for two reasons. One, this is not actually a chemical reaction. The chemical reaction is the acid base disequilibrium.

And two, it's not actually quantitative. If you add CO2, it doesn't all get taken up bicarbonate ion and you know that because that CO2 is actually-- that CO2 or H2CO3 star actually does increase. And so this implies that it's all used up, and it all ends up in bicarbonate, but you'll see this a lot in textbooks.

The other way to increase-- or another end member for increasing DIC is by dissolving calcium carbonate. And so there you you're really adding carbonate ion. And when that happens, alkalinity actually goes up at 2 times DIC because, for each mole of carbonate ion, you're adding 2 equivalents of alkalinity.

When you do that, then pH actually goes up, PCO2 goes down and carbonate ion goes up. And we just happen to have a nice-- the Sigman and Boyle paper has a nice plot of that where they plotted alkalinity and DIC. And then, overlaying that, they've contoured PCO2, and so you have low PCO2 up.

When you have low DIC and high alkalinity, you have low PCO2. When you have high DIC and low alkalinity, you have high PCO2. And then they've put arrows-- for example, if you they've done the reverse rather than adding organic matter, if they take out organic matter, DIC goes down. There's a small change in alkalinity because of the effect of nitrate.

There's a small alkalinity effect, but that's pretty-- that's second order. So when you take out organic matter, DIC drops, alkalinity remains approximately constant. And PCO2 goes down out.

For example, when you-- oh, here. I can redo it so I can actually draw on it. I see alkalinity. So these are constant lines of PCO2.

This is low and high PCO2. This is organic matter input. Just what we showed above, you add organic matter, PCO2 goes up, carbonic acid goes up, alkalinity stays flat.

The perversity of the CO2 system is that if you dissolve calcium carbonate or add calcium carbonate, alkalinity goes up, DIC goes up, but the slope that 2 times DIC slope is higher, is a steeper slope than the lines of PCO2 slope. And so PCO2 actually goes down even though you're adding carbon. Does that help at all? I feel like I'm starting to get to the point where I'm arguing in circles a little bit.

STUDENT: That's what happens in this system.

SCOTT DONEY: If anybody wants, I have a little Matlab code. If you run Matlab, I can give you the code and you can play with this to your heart's delight. To convince yourself that this is-- oh, I didn't see a lot of takers.

[LAUGHING]

STUDENT: It'd be hilarious.

SCOTT DONEY: It'd be hilarious, OK. It's noon. I'm going to wrap up.