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WILLIAM MARTIN: Today is the last chapter in the major ion in seawater discussion, and the first chapter in the carbon in seawater discussion. And what I'm going to do is talk about the chemistry of inorganic carbon in the oceans, and specifically dissolved in the ocean.

I'm going to start with a little introduction to set the stage. And I'm going to spend a good chunk of the lecture talking about inorganic carbon equilibria in the oceans, and the measurements we make and how we use those measurements. Then I'm going to finish up by talking about how we use those measurements to teach us something about biogeochemical processes in the ocean.

So without further ado, why study carbonate in the ocean? Well, the first-- whoops.

AUDIENCE: It's obvious.

WILLIAM MARTIN: It was so obvious. [? It ?] [? was ?] [? kind ?] [? of ?] [? sudden. ?] The first and most obvious thing is that we're carbon-based life forms. And every life form on Earth is carbon-based. So we need to know something about carbon cycle on Earth and in the ocean.

Second thing is that the pH, the hydrogen ion content, of the ocean, is a major master variable for many chemical and biological processes in the oceans. And inorganic carbonate equilibria play an important role in determining oceanic pH. So it's important to understand equilibrium chemistry of the inorganic carbon system in seawater.

Third, and related to the pH factor, is that bicarbonate is third most concentrated anion in the ocean. So it's one of the major ions in seawater. And finally, the marine carbon cycle is a key factor in determining the fate of anthropogenic CO2 and the sorts of societal relevance these days as well.

And finally, a little note on the bottom, which I won't say out loud. Sorry. For those of you who aren't [? pleased ?] by any of this.

So first, I'm going to give, without any numbers, a really basic and simple overview of carbon cycling in the ocean. The oceans are connected to three boundaries, at least three that I can think of at the moment-- land, atmosphere, and the sea floor. And there are exchanges of carbon across all of those boundaries.

Weathering processes on land deliver both bicarbonate, and what I forgot to write down, your organic carbon to rivers, which then carry those materials into the oceans. The oceans and the atmospherics change CO2. Once the CO2 is into the ocean, it's distributed between the various components of the carbonic acid system, I guess you'd call it-- carbonic acid and CO2.

And then carbonic acid dissociates to form bicarbonate, which in turn dissociates to form carbonate. So we often talk about total CO2 in the oceans. And what we mean is the sum of the carbonate ion plus bicarbonate ion plus carbonic acid H2CO3 plus CO2.

Another thing you'll often see. In this lecture, I'll use CO2 and carbonic acid interchangeably. When we talk about the thermodynamics of the system in the ocean, what we generally do is add together CO2 plus H2CO3, and we call it H2CO2 star. So just remember, that's the sum of carbon dioxide plus H2CO3. And just so in case anybody asks, it's mostly CO2.

There's intense inorganic carbon cycle-- organic and inorganic carbon cycle-- in the ocean. In the surface ocean, CO2 is taken up during photosynthesis to form organic matter. And to a lesser extent, but still an important extent, carbonate ion is taken up by organisms which make calcium carbonate shells. So organic carbon and calcium carbonate are both formed in the surface ocean.

Those degrade to some extent in the surface ocean, but they fall out-- some of it falls out as particles from the surface ocean into the deep ocean. Once there, respiration causes the decomposition of organic matter, again, releasing CO2 into the water. And chemical processes lead to the dissolution of calcium carbonate, which releases carbonate ion into the water.

Almost all the organic matter is decomposed before particles reach the sea floor, and something like half of the calcium carbonate is decomposed. But those processes continue in the sea floor, where, again, respiration releases CO2 from organic matter, and carbonate dissolution releases carbonate ion from the dissolution of calcium carbonate. And a tiny fraction of the original organic matter is left buried in the sediments, and a more significant, but still reasonably small fraction of the calcium carbonate is also buried in sediments.

There's a very quick nonquantitative overview of the carbon cycling in the oceans. And we're going to have one more carbon cycle overhead. And I've chosen one done by Eric Sundquist almost 15 years ago. So the numbers in the atmosphere and the surface ocean are you're a bit out of date. But I like this picture because it has a time scale on the left-hand side, which is very useful in thinking about the different reservoirs.

First thing to note is one you know about already is that CO2 in the atmosphere is increasing and continues to increase at a rapid rate. A small amount of that CO2 is taken up in the surface ocean, which is shown by this little downward arrow with a 2 and 3 next to it here.

The surface ocean reservoir is approximately the same size as the atmosphere. [INAUDIBLE] Oh, didn't I write units? In my original slide, the units were on there. But it's--

AUDIENCE: [INAUDIBLE].

WILLIAM MARTIN: Yeah, petagrams of carbon and petagrams of carbon per year are the units. And a petagram is 10 to the 15th grams.

So the surface ocean reservoir is about the same size as the atmospheric reservoir. And if you move over to the left to the time scale, the interactions between oceanic surface and the atmosphere have a time scale of years. If you look below the surface ocean into the deep ocean, that is the largest of the reservoirs that are cycled on this annual to 10,000-year timescale. So the deep ocean is a very large reservoir of carbon. So it's the largest reservoir among these, and it's cycling time is on the order of hundreds to 1,000 years.

The next important reservoir is what is called reactive marine sediments. How big this reservoir is-- actually, it's a little arbitrary, and it depends how you define it. But however you define it, it's a large reservoir, and it's cycled on a timescale of thousands of years.

Below this, by far the largest reservoir on the Earth's surface is the Earth's crust, which is an enormous reservoir, but its cycling time is measured in hundreds of thousands of years. So it's important for a very long time-scale processes.

Where am I going back [INAUDIBLE]? From this carbon cycle picture, we said already that once CO2 is dissolved in the ocean, it becomes distributed between the different inorganic carbon species, which are CO2 plus carbonic acid, H2CO3, which we lump together as H2CO3 star.

Carbonic acid dissociates to some extent to form bicarbonate, which in turn dissociates to some extent to form carbonate. So we talk about total CO2 as the sum of all those species in seawater. We know very well the equilibrium constants for the dissociation of carbonic acid to bicarbonate and for the dissociation of bicarbonate to carbonate.

And so what we have here is a system of five unknowns. So the unknowns are total CO2, the carbonate system components, and H+. We know the two dissociation constants. And if we measure two things-- if, for example, total CO2 and pH-- we can calculate the speciation of the inorganic carbon system in seawater.

What I'm going to show next is a plot where I've assumed a value for the total CO2, a reasonable value for the oceans. And then I've calculated the speciation-- so the distribution of inorganic carbon between carbonic acid, bicarbonate, and carbonate ion in the oceans as a function of pH. And that's shown here with concentration on the vertical axis and pH, which, of course, is the negative log of the hydrogen ion activity on the horizontal axis.

And the only point I want to make about this particular plot is that at seawater pH, which is about pH 8, by far the dominant component of the inorganic carbon system in seawater is bicarbonate, which makes up about 90% of the inorganic carbon at seawater pH.

The next most abundant is carbonate ion, which is about 10% of the total. And CO2 or H2CO3 is another almost factor of 10 less than that. But normally, when you see a plot like this, you won't see it plotted the way I have here, with pH on the horizontal axis and concentration on the vertical axis.

Instead, you'll see it plotted like this, where pH, again, is on the horizontal axis, but the vertical axis is a log scale. So it's the log of the concentration. And that has-- plots like this are called [INAUDIBLE] an acid which dissociates to a conjugate base. The distribution of acid and basic species on a log-log plot as a function pH is called the Bjerrum plot.

And it has one feature which I think is really handy and which will come up later in the lecture, so I want to point, it out here. If you write the expression for the first dissociation constant of carbonic acid-- so for dissociation of H2CO3 to HCO3 minus, which I've shown on the bottom-- and I've lost my arrow here, so I can't point at it, but it's shown on the bottom at the end of that blue arrow.

You can take the log of both sides of that equation and get the log of the dissociation constant equals the log of H+, plus the log of the ratio of bicarbonate to carbonate to H2CO3 concentrations. At the point where those two concentrations are equal, that is my [? big ?] [INAUDIBLE], which is that point right there, then it's the log of 1, which is zero.

So at the pH where the acid and basic forms are equal, then the pH is equal to the negative log of the dissociation constant of the acid. So the pH equals the pKa at the point where the concentrations intersect on this Bjerrum plot. That's an important thing to remember, which will come up later. So remember that.

[? Good. ?] You hold that. So we're going to do one more thing before we get into the nitty-gritty here. We might ask the question if [INAUDIBLE] CO2 and pH are the ideal things to measure in seawater in order to determine the carbonate speciation between its inorganic forms.

And the way we'll look at that here is to do a hypothetical experiment in which we mix one water mass, which has this distinct pH and total CO2, with another water mass, which also has a known pH and total CO2. We make a 50/50 mixture of those.

Then the total CO2 of the mixture will be the weighted average of the total CO2s of the individual water masses of pH. PH does not mix conservatively. So if we want to know the pH of the mixture, we're going to need to know something else about those water masses.

So the question is, what other thing might we want to know? And something that I'm sure you talked about and you know already is that salinity mixes conservatively. So what if the other thing we want to know is actually related to the major ion composition of the oceans? That will mean that it will mix conservatively too.

So if we look at a quantity that's related to the major ion composition of seawater. And what I've shown here is a table from the Zeebe book that I put in the reading list that I recommend for everybody because it's very clearly written. And it's a great book, and for the chemistry students, it's something you might consider getting. It's not overwhelmingly expensive, and it's a very valuable book. I wouldn't understand this stuff as well if I didn't read that book [INAUDIBLE] selection.

So let's look at the charge balance in seawater. And what this table shows is on the left-hand side, the major cations in seawater, the concentration, and the total charge, which is the charge on the ion times its concentration. So the total charge attributed to sodium ions is equal to the total concentration. Since it's ionic charge is 1 for magnesium, the total charge is twice its concentration, and so on. So if we add all those up, we get the total positive-- the sum of positive charges attributable to the major ions in seawater.

On the left-hand side are shown at cations, and the same calculation for them. And for this group of anions. We add up the total charge, and we get an amount that's about 2.2 millimoles per kilogram less than the total charge of cations in seawater.

So is seawater positively charged? No. So obviously, I've left something out, or he has left something out of this table. Could you tell me what's left out of the table? Bicarbonate, he's left out of the table. That's the major one. There are a couple other things that are left out as well. What else is left out?

OK, I'll tell you. Carbonate ion is left out as well. And borate-- the borate ion is also left out. What do these things have in common? Those missing anions-- bicarbonate, carbonate and borate-- are all the conjugate bases of weak acids.

So bicarbonate and carbonate ion are conjugate bases of H2CO3 and HCO3-. And the borate ion is the conjugate base of the weak acid, boric acid. And why do these get special treatment? Well, they get special treatment because they serve to buffer the pH of seawater.

So if you add, say, hydrogen ion to seawater, then part of it will be used to convert carbonate and bicarbonate to carbonic acid, and to convert borate to boric acid. So the pH change in seawater resulting from your addition of hydrogen ion will be less than it would have been if these conjugate bases of weak acids were present in seawater. So this group of anions in seawater gets special treatment because they're very important to determining the pH of the [INAUDIBLE].

This collection of [INAUDIBLE], and a few others, which we'll talk about later, but these are the main ones, contribute to what we call the alkalinity of seawater. And the alkalinity is defined in terms of the acid-neutralizing capacity of seawater. And to read the definition, it's alkalinity and moles per kilogram is equal to the amount of strong acid that must be added to 1 kilogram of seawater to make its pH equal to that of the second equivalence point of the CO2 system. And that pH is about 4.3.

So we're going to talk about just what the heck that means and why this is the definition now. But we're going to start first by talking a little bit more about the components that make up the alkalinity of seawater at pH 8.

And if you look in the Zeebe book, it's a term that-- I think is unique to him. But it's a useful thing to remember even if you don't remember what he calls it. He calls it the practical alkalinity. And that's the alkalinity that you can use for most calculations in the oceans, again, equal to the concentration of bicarbonate plus twice carbonate ion plus borate plus hydroxide minus H+.

One question you might ask is, why is it carbonate ion multiplied times 2?

AUDIENCE: [INAUDIBLE].

WILLIAM MARTIN: It's not that the charge is 2. We'll talk about that a little bit later. I'll show that explicitly. But it's because--

AUDIENCE: There are two.

WILLIAM MARTIN: Because it takes you have to add two protons to it to convert it to H2CO3. And you can see from this what should have been obvious from those Bjerrum plots that I showed before, and that I'm going to keep showing until you're sick of looking at them, is that bicarbonate is the predominant component of alkalinity at pH 8 in seawater. And the next is carbonate. And following that is borate. And then the water alkalinity contributes a very small amount.

But we'll go back to just what the definition of alkalinity means. Remember, it's defined in terms of the amount of acid that you have to add to reduce the pH of a seawater sample from its in situ pH to 4.3. So why those numbers?

AUDIENCE: [INAUDIBLE].

WILLIAM MARTIN: All right. I'm not actually sure why I stuck this in here, but it's the same Bjerrum plot I showed you before with the exception that I've added borate to it to, and I've shown pH 8, which is where your seawater sample starts before you start adding acid to it.

And you can see from looking at this plot qualitatively what's going to happen as you add acid. You move to the left on this diagram. And so carbonate and bicarbonate are converted to H2CO3, and borate is converted to boric acid. We'll look in a little more detail now.

This is what we call a titration curve for seawater. What that means is it's a plot of-- well, when you do a titration, you'd have a beaker of water with a pH electrode to an acid base titration with a pH electrode stuck in it. You add acid, and you measure pH. Then you add more acid, and you measure pH again.

And as you do that from its starting point until the pH gets very low, you get a titration curve, which is just a plot of pH as a function of the amount of acid you've added. And Scott may have noticed that this plot is a little strange. And it's a little strange because when I made it, I wanted to be confident that I was doing it right.

So I did it under conditions that I normally use to titrate. I work in sediment-poor waters. So we have tiny samples. So this is actually the titration of a 1 and 1/2 mL sample of seawater with 1 millimolar HCl.

If you talk to a real ocean chemist, they don't use 1 and 1/2 mLs of seawater [? to do ?] this. They use more like 250 mLs. So the numbers would look different, but the curve would look the same.

So what we want to talk about is the shape of this curve. And you can see that when you start at pH 8, there's a steep part of the curve where the pH decreases pretty fast as you add acid. Then there's a pretty long, quite flat part of the curve where the pH decreases only slowly as you add the acid. And then right around pH 4 and 1/2 or so, there's another steep part of the curve where the pH changes rapidly as you add more acid.

Now remember, I said the definition of alkalinity has you titrating seawater from its starting point down to a pH of 4.3. What's special about this pH of 4.3? So to look at that, here in blue it's the same titration curve I've shown you already. And in red, I plotted the slope of the titration curve.

And I should tell you, I left out-- it plotted against an invisible axis, so I didn't want the plot to be too cluttered. So that's not important. But just remember, it's not plotted against this pH axis here.

The important thing is that now, if you look at this steep part of the curve between pH 5 and pH 4, you see there's a very sharp-- the slope of the curve of pH versus acid added gets steeper and steeper until it reaches a point where the slope of the curve is at a minimum, and then it starts to increase. That point is called an inflection point. And it's readily determined in a titration.

So this is a point that you can determine readily and reproducibly in a titration. It's the point in the titration curve where there's an inflection point, which is where the slope goes from decreasing to increasing.

So now we've shown that it's a readily identifiable spot in the titration curve. So that makes it useful. And we've equated it to alkalinity. But really, we should say why that point in the titration curve is equal to the alkalinity as we've defined it in seawater. And so we'll do one more thing.

Again, here's that same brand Bjerrum pot again, which shows the speciation of inorganic carbon and borate and boric acid systems as a function of pH. And to its left, I've defined the alkalinity in the seawater sample, which is equal to-- I'm going to say it, at the risk of boring you just to make the point clear. It's equal to the sum of carbonate plus twice bicarbonate plus borate plus hydroxide minus H+.

Now, on the bottom plot, what I've done is I've added up bicarbonate plus twice carbonate plus borate plus hydroxide as a function of pH just from this speciation curve. And that would be the sum of those components as you add acid to your sample and the pH decreases.

And I've also plotted the hydrogen ion concentration, again as a function of pH. So you start at pH 8. The hydrogen concentration is 10 to the minus 8. And as you add acid, obviously the H+ decreases. And well, on a log-log plot, H+ versus pH is just a-- has a slope of minus 1.

But the important point here is that eventually, as you titrate your seawater sample, you get to one spot where the sum of twice carbonate plus bicarbonate plus borate plus OH- equals the concentration of hydrogen ion. And it turns out that point is exactly at the inflection point in the titration curve. And so what is that?

If you look again at the expression for total alkalinity, when the sum of these things equals the hydrogen-ion concentration, then the alkalinity is zero. So at that point in your titration, you've added enough acid to make the alkalinity zero. So the amount of acid you've added is just equal to the alkalinity of your water sample. So that shows you why this particular point in the titration curve is chosen to define the alkalinity.

And it also shows that the quantity that you determine this way is equal to that net sum of conjugate bases of weak acids, which contribute to buffering seawater. So that's what the alkalinity is and why it's useful to us.

But never to leave a simple thing simple enough to understand-- and there's actually a reason for doing this. I regret this choice of words. It's not a more precise definition than the one I've just shown you. It's a different way of saying the same thing.

And the reason for doing it this way is that seawater, of course, isn't composed-- the only weak acids in seawater are carbonic acid and boric acid. There are a number of minor components, which also contribute to the alkalinity. And although for most calculations, you don't have to worry about it too much, there are some circumstances in which you need to.

And examples of these are phosphoric acid. You know that phosphate is present in seawater. Ammonia is present in seawater. Silicic acid is present in seawater. And under some circumstances, these could contribute in a significant way to the alkalinity.

Remember, when you do your titration, you're titrating all the conjugate bases. And so if you want to interpret it accurately, you should take into account these minor components as well as the major ones I've discussed already. And what this definition does is give you a really simple way of figuring out which components of your water sample you should include in the alkalinity definition.

It's dangerous to read this, [? because it's ?] confusing. But I'll read it anyway, and then I'll say how to use it, which is simple. So total alkalinity of a natural water is thus-- and I guess Dixon alone knows what this "thus" means-- is defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors-- and here's the important part-- bases formed from weak acids with the dissociation constant less than 10 to the minus 4.5. So a pKa larger than 4.5 over proton [? donors, ?] acids with K greater than 10 to the minus 4.5, or a pKa less than 4.5 [INAUDIBLE] in 1 kilogram of sample.

Remember that I pointed out that on these Bjerrum plots, which are log of concentration versus log versus pH, that the point-- look at CO2 and bicarbonate here. Remember I pointed out before, that at the point where these two intersect, the pH is equal to the PK.

So given this definition up here, and a Bjerrum plot, you can say for sure that bicarbonate contributes to the alkalinity of the seawater because its PK is clearly greater than 4.5, which is that dotted line there. And you can say the same thing for borate and boric acid. The PK is whatever it is-- 9.5.

Let's see. Those are the major components. Well, sulfate is also a major component. But since its intersection is off the plot here, we won't talk about that, but we'll talk about a similar thing. If you look at the minor components in the part of the plot that's below, look at the top one-- fluoride and HF.

Hydrofluoric acid is a strong acid. Its pKa is what? 2.5, which is greater than 4.5. So that means that in this definition, HF is a proton donor, which means that it appears as a negative term, just like H+ in the alkalinity definition, if you want to include HF and fluoride. [INAUDIBLE] Phosphoric acid is a triprotic acid. So it's H3PO4, which dissociates to H2PO4 to H2PO4- to HPO42- to PO43-.

If you look at phosphate in this plot, and you see that up there?

AUDIENCE: [INAUDIBLE].

WILLIAM MARTIN: So here's phosphate and the phosphate HPO4 pair. The PK is whatever it is. [INAUDIBLE] It's about 9. And so phosphate does contribute to alkalinity. And it takes 2 protons to get to 4.5. So it contributes 2 units to alkalinity.

HPO42-, again, you can see with its acid base pair, that pKa is about 6. So HPO42- also contributes to alkalinity. But you see the dominant component of phosphoric acid system is HPO4-. So that's the dominant component at pH 4.5. So it does not contribute to the alkalinity.

And here, this is an example of why I said carbonate doesn't contribute 2 units because it has a charge of minus 2 HPO4- has a charge minus 1, but it does not contribute to alkalinity because when you take a seawater sample and add acid to it, you don't convert H2PO4- to anything. That's the end point of the titration.

And in fact, if you follow phosphoric acid one more to H3PO4, you can see that its PK is less than 2. So it's a strong acid, and it contributes a negative. H3PO4 appears as minus H3PO4 in the alkalinity equation.

I'm sure that's all very clear. But after I've made it complicated, I'll do one more thing to make it simple again. There are several different terms that are used in the alkalinity regimes. One is carbonate alkalinity-- bicarbonate plus twice concentration of carbonate ion. Water alkalinity is OH minus H. And I should say that sometimes those two are lumped together, and the sum of them is called carbonate alkalinity just to be confusing. I don't know what [INAUDIBLE].

Borate alkalinity is equal to the concentration of borate ion. And again, we get back to this practical alkalinity equation, which is the alkalinity that's due to the carbonate water and borate systems. And that's what you can use for most of your calculations in seawater.

But in some applications, such as the things that I work on, [INAUDIBLE] sediment-poor waters where things are a little bit different, you need to think about the contributions of ammonia, the phosphoric acid system, sulfide, and silicic acid to alkalinity. In that case, you have to go back to the more complicated plot I showed before and figure out what you have to include.

So we've talked about three quantities that you can measure in a seawater sample-- the total CO2, alkalinity, and pH. I'm not going to go into any detail about measurements. I've tried that before, and it was only confusing. So we're not going to do that.

But I'll just note that you can measure total CO2-- well, there's a few ways. One, you can do a titration and get a titration curve like the one I've shown. And you can do some curve fitting to calculate the total CO2. The second and most common way is to acidify a sample, strip the CO2 out, and then quantify the amount of CO2 that you've generated by stripping it all out of the seawater.

Those of you who go to Tuesday chemistry talks, you might have seen one a couple weeks ago where another method was shown in which you strip the CO2 out of seawater by equilibrating it with a sodium-- [INAUDIBLE] gradient with a sodium hydroxide solution. Then you measure the effect of the CO2 in decreasing the conductivity of the sodium hydroxide solution.

But the bottom line is that all of these-- that a good routine measurement of total CO2 gives you a precision of about 2 micromoles per kilogram, which is about a tenth of a percent. And the people who are really proud of their seawater work get to even better than that.

But not just precision is important, but accuracy is important, too. And in order to make sure that everyone's measurements can be looked at on the same scale, so there's no inter-laboratory differences, Andrew Dixon has made available large quantities of reference seawater that's very well-characterized. And so to calibrate your total CO2 measurements, you calibrate against reference seawater.

The second thing we've talked about is alkalinity. And as I've shown, it's measured by titration. You can measure it by generating a titration curve, and then doing curve-fitting to calculate the alkalinity. Or you can do what's called a gram titration, which if you ever need to do it, you'll learn about, but I'm not going to talk about it.

And again, the precision is on the order of 2 micromoles per kilogram. So again, about a tenth of a percent. And the calibration is the same referenced seawater that's used for total CO2 calibrations.

And finally, you could measure the pH. And that's done either with an electrochemical measurement-- so that's pH-sensitive glass electrode, or with pH-sensitive dyes. And the important-- again, very good pH measurements have precision of about 0.002 pH units.

But the important thing here is that the calibration has to be against buffers that are made for use in seawater. So there are buffers that are made up in an artificial seawater medium. And again, it's Dixon who makes these buffers. [? Just ?] a CO2 system dictator, I guess. But that's an important point.

The equal-- well, especially if you're doing electrochemical measurements, you cannot calibrate versus buffers that don't have an ionic strength equal to that of seawater. Just remember that. It's very important.

AUDIENCE: [INAUDIBLE].

WILLIAM MARTIN: All right. Where can we [? find ?] [? it? ?] It's like being a lawyer. You should never proceed to a slide when you're not sure what it is.

We have what I call the "more than I ever wanted to know" section. And in a way, it's-- well, it's a detail, but its actually an important detail if you want to use all the measurements correctly. And the first part of this section is about pH scales.

We talked about this already. For laboratory chemistry and for work that you might have done as an undergraduate, you undoubtedly, whether you knew it or not, calibrated your pH measurements against low ionic strength buffers that were calibrated. Is it still called the NBS pH scale? Or is it called--

AUDIENCE: NIST.

WILLIAM MARTIN: NIST pH scale. And the important thing about these is they're buffers that are made up in low ionic strength solutions. Seawater has a high ionic strength. And you cannot use these low ionic strength buffers to calibrate measurements that are made in seawater. [INAUDIBLE].

So the NBS, or NIST, pH scale has been abandoned for measurements in seawater. And if you ever see anybody calibrating their pH electrode, then this buffers. When they want to make measurements in seawater, you can hit them over the head. Say, no, you can't do that. And I'll show you the consequence of that on the next slide here.

Analyzing hydrogen ion concentration in seawater actually yields a measurement which gives you the sum of the free hydrogen ion plus bisulfate plus HF. And so if you want to actually know, for your purposes, the free hydrogen ion concentration, you have to know the contributions of bisulfate and HF.

Of course, we know the total sulfate concentration because it's conservative, and it's a major ion. In the same way, we know the total fluoride concentration. But if we want to calculate a species, we need to know the dissociation constants for HSO4, or the acidity constant for sulfuric acid and for hydrofluoric acid very well.

They, who shall remain undefined, have decided it's better to-- but we can send you the picture-- to define a new pH scale. And in fact, I got tired of this argument, so I haven't kept up. And I don't know which of these two options they've settled on, if either one.

The important thing is just to make sure that you understand if you do work in [INAUDIBLE], that there are different pH scales. And that you need to know which one you're using, and that if you're using H+ measurements on one of these scales, you need to use equilibrium constants on the same scale. That's the important thing.

So the two scales-- one is called the total pH scale. It includes free hydrogen ion plus bisulfate and neglects the contribution of HF. Or the seawater pH scale, which includes free H+ plus bisulfate plus HF. There are two different pH scales.

And I've said here that the pH measurements are reported on the total hydrogen ion scale, which was certainly true at the time I made this slide. I'm not so sure anymore. But there are also equilibrium constants that are reported on the total hydrogen ion scale. And the same is true for the seawater scale. There are pH, seawater scale measurements, and equilibrium constants that are on the seawater scale, hydrogen ion scale.

You can convert between the scales if you know the HSO4 complexation constant and the HF complexation constant. And here's the difference between the pH scales between the seawater scale and the total hydrogen 9 scale at pH 8 is about 0.01 pH units, or about 2%. The difference between the NBS, or NIST, scale, and the total hydrogen ion scale is about 0.1 pH unit, or 20% That's why you should never, ever calibrate your electrode for use in seawater on the NIST buffer with NIST buffers, because there's a large error.

And a good pH measurement has a precision of 0.002 pH units. So these scales are important if you want to interpret the measurements accurately.

There's a second important piece of this "more than you ever wanted to know" section, and it's about equilibrium constants for calculations in seawater. And just as an example, I've taken the dissociation of bicarbonate into H+ plus CO32 minus and written the equilibrium constant, which is the product of H+ and CO32- divided by HCO3-. You all know that.

In an ideal solution, again, this equilibrium constant is just the product of the concentrations in that solution. To clarify what that means, in an ideal solution, the concentrations of all the solutes approach zero. What that means is that there are no interactions between the ions that are in the solution and the water molecules that they're dissolved in, and there are no interactions between the different ions in solution. So that's a hypothetical ideal solution.

But in a real solution, these ion solvent and ion-ion interactions are important. And so in a real solution, you would write the [INAUDIBLE] of every one of these concentration terms would be multiplied by a corresponding activity coefficient. This activity coefficient are generally less than 1 for ions in solution, and they account for electrostatic interactions between the ions and between the ions and the solvent. Have we talked about this at all?

AUDIENCE: No.

WILLIAM MARTIN: OK. Well, just explain-- OK, well, just explain-- I think it's pretty easy to explain why [? this ?] happens. You know that the water molecules, H2O, and the hydrogen and the organization of the atoms in the molecule is such that there's a small positive charge on one side of the water molecule and a small negative charge on the other side.

AUDIENCE: We did do h-bond dipole.

WILLIAM MARTIN: OK. So you know that. So if you put an ion in solution it, of course, is the center charge. And so what happens is the water molecules, since they're polar, they're dipoles, they are rearranged around the iodine solution. So those are ion-solvent interactions. And they're important in determining the activity, the chemical potential of the ions in the solution.

And that obviously if you have two ions in solution, then they feel each other's electric fields. They affect each other's behaviors as well. And so these activity coefficients are necessary to account for these ion solvent and ion-ion interactions. And so the equilibrium constant is a product of the activities of the ion in solution rather than their concentrations. And the activity of an [? iodine ?] solution is its activity coefficient multiplied by its concentration.

Now, there's--

AUDIENCE: [INAUDIBLE] determine those activities. Are they calculated?

WILLIAM MARTIN: They're calculated. They're calculated on-- Scott and [? Meg ?] are explaining [INAUDIBLE]. And Meg is our activity [? trawl ?] fishing expert. But they're calculated. And in fact, a single ion activity coefficient is a theoretical construct.

AUDIENCE: You can learn how to do it, too.

WILLIAM MARTIN: Yeah. So in seawater, it has an ionic strength of about 0.7, which is a high ionic strength. I'll have you take that as [INAUDIBLE]. And because it's a high ionic strength, it's very difficult to calculate activity coefficients that are applicable to seawater.

And for that reason, what's done is that what are called constant ionic medium equilibrium constants are used. These constants are measured in solutions with the same proportions of major ions as seawater. They're measured as a function of temperature and salinity. And the pressure dependence is generally calculated from thermodynamic data. So these are equilibrium constants, which are applicable to solutions that have the same ionic composition as seawater.

So now the dissociation constant for bicarbonate to carbonate would be written like this, where it's the total hydrogen-ion concentration multiplied by the total carbonate HCO3 minus concentration. And now again, we're back to concentrations because the activity coefficient is all subsumed into the equilibrium constant.

But what's this T? We've talked about what the T on H+ means. That means it's the hydrogen-ion concentration on the total hydrogen-ion concentration scales. The CO3 to minus T actually is an important thing because there's very little free carbonate ion in seawater. Most of it is complex to the major ions, major cations.

But in these equilibrium constants, the total-- the sum of carbonate plus MgCO3 plus CaCO3 dissolved in solution that we include. These seawater constants, and as I've written it on the total hydrogen-ion scale, are available in the literature as functions of temperature, salinity, and pressure. And those are the ones you want to use for seawater.

So now we know all about total CO2 alkalinity and pH. And we know about the equilibrium constants that are used to calculate the speciation of the inorganic carbon system in seawater. So we're ready to work with the carbonate system in seawater.

And what we have is the total CO2, which is a sum of CO2, bicarbonate, and carbonate, alkalinity-- which I've read so many times you don't want to hear it again-- plus or minus minor components that you may or may not want to include. And we have another expression here, which is a mass balance for borate.

So the total borate is equal to boric acid plus borate. And remember that total borate is conserved in seawater. It's conservative in seawater. So this value is just a constant times the salinity.

We have 1, 2, 3, 4 equilibrium constants-- two for the carbonate system, one for boric acid, and one for water. And if you add up the unknowns and the number of equations, and if you measure total CO2, alkalinity, and salinity, what you'll find is that you have seven equations and seven unknowns. And you can solve this system for the speciation of the inorganic carbon system, boric acid, and water.

And just to show this one more time. That's actually what I did to calculate this Bjerrum plot. And I'm going to use it just one more time. I think it's not going to appear again anymore-- use it just one more time to show you some useful approximations for back of the envelope calculations.

And the first one is that you see that at pH 8, total CO2 is made up of bicarbonate plus carbonate plus a small amount of CO2. So if you want to do quick, fast calculations, the way it's done is just to ignore the CO2 contribution.

For alkalinity, you can do the same thing. Twice the carbonate plus bicarbonate, and in this simple treatment it ignores borate and OH- and H+. And if you use these two approximations, then you can calculate the bicarbonate ion concentration roughly as the difference between alkalinity and total CO2.

One point to note is that, as we'll see, you may have seen already, and I'll show you if you haven't seen it already, as when seawater leaves the surface ocean, it has a certain pH. As it circulates through the deep ocean, you might say as it ages, its pH decreases. And so as seawater ages, its pH drops below pH 8. It goes in the left direction on this plot.

And the thing that's worth pointing out is that the further away from pH 8 you get, the lower the pH gets, the worse these approximations are. So that's something to keep in mind.

So now we're going to talk about some biogeochemical processes. And we'll talk about how these biogeochemical processes affect total CO2 and alkalinity. And the first two processes on this page occur in the surface ocean, and they have to do with first, the production of organic matter by photosynthesis

During this process, CO2 is taken up to form organic carbon and oxygen is released. Remember that CO2 does not contribute to the alkalinity. So if you take up CO2 into organic carbons, the changes are the total CO2 decreases by 1 mole per mole of organic matter form, and the alkalinity doesn't change.

And there is a smaller effect, which is that organic matter that's formed in the surface ocean contains not just carbon, but it contains nitrogen as well. If this nitrogen is taken up from nitrate in the water, then for every nitrate that's taken up into organic matter, there's a small increase in alkalinity.

So there's an increase of one unit in alkalinity for every nitrate that's taken up into organic matter. But since the ratio of nitrogen to carbon is 16 over 106, that's a small effect. So the formation of organic matter by photosynthesis causes a drop in total CO2 of one unit and no change in alkalinity.

Now, if we go to the precipitation of calcium carbonate, which is formed by some of the organisms in surface ocean. That reaction is calcium plus carbonate ion forms calcium carbonate. You can see that, again, total CO2 decreases by 1 moles for every mole of calcium carbonate formed. But now remember, every mole of carbonate ion contributes 2 moles to the alkalinity. So for every mole of calcium carbonate formed, there's a decrease in the alkalinity of 2 moles.

One question you might ask is how these processes affect the ability of the ocean to take up CO2 from the atmosphere. If there's a-- well, the ocean always tends to equilibrium. The surface ocean tends to equilibrium with the atmosphere, which is determined by-- and you'll talk about this later-- via Henry's law constant.

So that the CO2 content of the surface ocean in equilibrium with the atmosphere is equal to a constant times the partial pressure of CO2 in the atmosphere. And if there's a perturbation in the equilibrium, then the system will tend back towards equilibrium.

So say you have processes in the surface ocean which remove CO2 from the surface ocean. That will tend to drive surface ocean towards taking up more CO2 from the atmosphere in order to come back into equilibrium. Scott's not [? scowling. ?] [INAUDIBLE] I haven't said anything [INAUDIBLE].

So what we can do, if we want to consider the effects of these processes on the ability of the surface ocean to take up CO2, what we can do, remember that I showed that if we measure total CO2 and alkalinity and the salinity of the water sample, we could calculate the inorganic carbon speciation. That means for a given total CO2 and alkalinity, we can calculate the CO2 concentration in the water.

And so that's what I've done here. I've got alkalinity plotted on the vertical axis. Total CO2 on the horizontal axis. And what I've done is taken a whole bunch of pairs of alkalinity and total CO2s. And for each pair I've calculated the CO2 concentration at equilibrium. And I've used that set of calculations to draw contours of constant CO2 concentration.

And once I've done that, I've taken a starting point, which is this black dot. I'll add a total alkalinity of 2,350 micromoles per kilogram and a total CO2 of 2,250 micromoles per kilogram. And I've said, first, suppose that we form 50 micromoles per kilogram of organic matter, what's the effect on the CO2 concentration in the sea at equilibrium in the seawater that we've left behind?

So what we've said is that decreases the total CO2 by 50 micromoles per kilogram, but doesn't change the alkalinity. So that's this black arrow moving to the left of this plot. And you can see that what happens is we've gone from a CO2 concentration of about 37 or 38 down to a CO2 concentration of about 28. So we've decreased the CO2 concentration in the water sample as a result of removing organic matter.

What that means is it increases-- it enhances-- that's the right way-- the surface ocean's ability to take up CO2 from the atmosphere. What if we do the same experiment with the formation of calcium carbonate? Remember, do a question from the same starting point. We're forming 50 micromoles per kilogram of calcium carbonate. But now the total CO2 decreases by 50. The alkalinity decreases by 100.

So if we draw that vector, [INAUDIBLE], we decrease total CO2 by 50, decrease alkalinity by 100. And we find that now we've gone from a CO2 concentration of about 37 or 38 to a CO2 concentration of about 50. So removing calcium carbonate from the surface ocean actually increases its CO2 concentration, so decreases its ability to take up CO2 from the atmosphere.

So here, we have two processes which remove carbon from the surface ocean. One, the formation of organic matter enhances the surface ocean's ability to take up CO2 from the atmosphere. The other, the formation of calcium carbonate, reduces its ability to take up CO2 from the atmosphere. So there's a biogeochemical application of our [INAUDIBLE] knowledge of a inorganic carbonate equilibrium in the ocean.

Now, what if we turn it around, and instead of looking at the formation of organic matter and calcium carbonate, if we look at the destruction of organic matter in calcium carbonate. So here, first we reverse photosynthesis, and oxic metabolism is used to oxidize organic matter releasing CO2 in the water. And it's the exact reverse of photosynthesis.

Total CO2 increases by 1 mole per mole of organic matter that's oxidized by oxygen. Alkalinity doesn't change because it's CO2 that's released into the water.

Now, if we consider calcium carbonate dissolution, then again, the reverse of what we talked about before. For every mole of calcium carbonate that's dissolved, it releases 1 mole of total CO2 into the water. And since it releases it into the water as carbonate ion, it increases the alkalinity of the water by 2 moles per mole of calcium carbonate that's dissolved.

And if you're like me and you're interested in carbonate ion concentrations in seawater, you might ask how these processes affect the carbonate ion concentration with seawater as it ages during its transit through the deep ocean.

So remember, we probably haven't talked about this. Say a parcel of deep water forms in the North Atlantic. The large scale circulation takes us from the North Atlantic to the Southern Ocean, and eventually finds its way up to the Pacific Ocean. As it makes that transit, both organic matter and calcium carbonate fall into the water. Organic matter can decompose, releasing CO2. Calcium carbonate may dissolve, releasing both total CO2 and alkalinity.

So we might ask how some of those processes affects the carbonate ion concentration and also the pH of deep water as it ages in the ocean. I've done exactly the same thing as I did before. I've taken a whole bunch of pairs of alkalinity and total CO2 concentrations, and from those concentrations, I've calculated carbonate ion concentration for each pair. And I've used a set of carbonate ion values to draw contours of constant carbonate ion concentration.

And again, I've taken a starting point, which is 2,300 micromoles per kilogram with alkalinities, 2,050 micromoles per kilogram of total CO2, and I've drawn vectors which represent the oxidation of organic matter and the dissolution of calcium carbonate.

The oxidation of organic matter of 50 micromoles per kilogram of organic matter adds 50 micromoles per kilogram of total CO2 but doesn't add any alkalinity. So if we do that, we follow this vector here, we go from our starting point, which was at 180 micromoles per kilogram of carbonate ion concentration, and we end up at about 150 micromoles per kilogram of carbonate ion. So the oxidation of organic matter by oxic respiration in the ocean decreases the carbonate ion concentration for the seawater.

Second thing I've done is say suppose we're dissolving calcium carbonate in that seawater sample. Same starting point. And we're dissolving 50 micromoles per kilogram of calcium carbonate, which adds 50 micromoles per kilogram of total CO2. And now also adds 100 micromoles per kilogram of alkalinity.

So if we follow that vector from our starting point up to its ending point, we've added 50 micromoles per kilogram of total CO2, 100 of alkalinity. We find that it started at 180 micromoles per kilogram carbonate ion in the water and ended at 220. So we've added carbonate ion. We've increased the carbonate ion concentration of the seawater by dissolving calcium carbonate.

So oxidation of organic matter in a seawater sample decreases its carbonate ion concentration. Dissolution of calcium carbonate increases its bicarbonate ion concentration.

So what if we look at some observation data. We can [INAUDIBLE]. I plotted-- I've shown G06 data for the North Atlantic on the left-hand side, for the North Pacific on the right-hand side, alkalinity in the top, total CO2 in the middle, carbonate ion in the bottom. And I've mentioned already that deep water in the North Atlantic is relatively young. Deep water in the North Pacific is relatively old. So it's had a lot of organic matter, oxidation, and calcium carbonate dissolution within it during its transit from the North Atlantic to the North Pacific.

And if you have incredibly good eyes, and you look at the deep water and see that the alkalinity has increased going from the North Atlantic, deep North Atlantic to the deep North Pacific. So what does that tell you has happened? If it's a single parcel of water that's made a transit from the deep North Atlantic to the deep North Pacific, what must have happened if the alkalinity does increase?

Calcium carbonate has dissolved in the water. Go down one panel. We look at total CO2. And again, if you have much better eyes than I do, you can see that the total CO2 has increased as well. Now, total CO2 increase can be due to both organic matter oxidation and dissolution of calcium carbonate.

But there's one more thing. Remember, what happens if all the organic matter oxidation occurs in a water sample? What happens to the carbonate ion concentration?

AUDIENCE: [INAUDIBLE].

WILLIAM MARTIN: What happens if only calcium carbonate dissolution occured? It increases. Now if you look at the deep water again, and if you have even better eyes, the carbonate ion concentration that's calculated from alkalinity and total CO2 values in the deep North Atlantic is about 100, or a little more than 100, micromoles per kilogram. The same quantity in the deep North Pacific is about 90 micromoles per kilogram. So what two things must have been happening?

AUDIENCE: [INAUDIBLE].

WILLIAM MARTIN: We know carbonate dissolution has occurred because the alkalinity increased. And now, since we know that carbonate ion concentration has decreased, we know that in addition to that, organic matter must have been oxidized along the way.

I have one more picture. This is a picture that comes from Broecker and Peng, "Tracers in the Sea." And I'm not going to discuss it in detail, but I do recommend that you read this because it's a really good exercise in using these simple calculations. But I want to point out what's been done and just the very broad first brush conclusion from this picture.

Was plotted in alkalinity versus total CO2 space. There's a bunch of alkalinity and total CO2 concentrations in temperate surface water around the oceans-- in Antarctic surface water, which we won't think about that, North Atlantic deep water, Antarctic deep water, and what is it?

AUDIENCE: [INAUDIBLE].

WILLIAM MARTIN: North Indian and Pacific [INAUDIBLE] of water. So first, let's look going from surface water to Antarctic deep water. You can see that connecting the surface water to the deep water gives you a certain slope in alkalinity versus total CO2 space. You can use the stoichiometric relationships where organic matter adds total CO2 but not alkalinity. Carbonate dissolution adds both alkalinity and total CO2 to interpret this slope.

And if you do that, you find that the ratio of calcium carbonate dissolution to organic matter oxidation that's implied by this set of analyses is about 0.29, a little less than 0.3. So the amount of calcium carbonate dissolved is about 30% of the amount of organic carbon dioxide.

Now what if you go from the Antarctic deep water to North Pacific deep water? It has a much steeper slope. And again, which means that more alkalinity is introduced in the water per unit of total CO2 that's added to the water, which means, of course, that more calcium carbonate is dissolving. And if you interpret this slope, you see that the ratio of calcium carbonate dissolving to organic matter oxidizing is about 1.

So the processes going from temperate surface water to Antarctic deep water are dominated by organic carbonate-- organic-- pardon me-- organic carbon oxidation. But if you go from Antarctic deep water to North Pacific deep water, then there's approximately equal amounts of carbonate dissolution and organic matter oxidation. And I'm going to stop there.

So we've shown how biogeochemical processes affect total CO2 and alkalinity in the ocean. We've started to show how you can use distributions of total CO2 and alkalinity to learn about biogeochemical chemical processes. But we've not discussed the biological and chemical processes that control the formation and decomposition of organic matter, or the formation and dissolution of calcium carbonate.

And another thing, which I didn't put up here, is that we haven't discussed ocean atmosphere interactions. Those are all things that are going to be applications of what I hope I've shown in the lecture today that are going to be discussed in a lot of detail later on in [INAUDIBLE]. [INAUDIBLE] And that's that. I finished early for once in my life.

AUDIENCE: I have a question.

WILLIAM MARTIN: Yeah, OK.

AUDIENCE: On the North Atlantic alkalinity profiles, why is the alkalinity higher at the surface--

WILLIAM MARTIN: [INAUDIBLE].

AUDIENCE: The immediate surface.

WILLIAM MARTIN: OK. Why is it higher at the surface than it is deep?

AUDIENCE: [? Because ?] its alkalinity is not-- if photosynthesis hasn't contributed to alkalinity that much, what's the process that's decreasing the alkalinity at the surface?

WILLIAM MARTIN: Well, is it right to look at what's increasing the alkalinity at the surface or what's decreasing the alkalinity as it goes deeper? I would interpret it more as what happens to the alkalinity as you go deeper in the water column. As you go deeper in the water column, organic matter is oxidized. And so that would decrease the alkalinity. No, it wouldn't. Scott, help.

AUDIENCE: Sorry.

WILLIAM MARTIN: I'm thinking of carbonate ion concentration.

AUDIENCE: [INAUDIBLE]

WILLIAM MARTIN: Why the alkalinity in the North Atlantic decreases as a function of depth. Is that a water mass thing?

AUDIENCE: It's just so [INAUDIBLE].

AUDIENCE: It depends on where you did the-- depends on where the [INAUDIBLE].

WILLIAM MARTIN: Yeah. Actually, Scott's absolutely right. Depends on where you're doing it. If you look at the envelope of surface concentrations, some of them are higher than the deeper values, and some of them are not. And is that dependant on salinity?

AUDIENCE: A lot of it's salinity in the Atlantic. [INAUDIBLE] So go out in the yard.

WILLIAM MARTIN: So alkalinity in the surface ocean is conservative, [? essentially ?] [INAUDIBLE] And so the variations in surface ocean alkalinity have to do with varying mixtures of seawater and fresh water. OK. Does that answer the question?

AUDIENCE: So if you could take a few profiles from a small area, then you would say-- you would think that the alkalinity would just increase with depth? And so this plot has averaged out by the geographical areas [INAUDIBLE].

WILLIAM MARTIN: Yeah. This is actually all the alkalinity profiles that they measured during the GEOSECS expedition in the North Atlantic. That's why it's plotted as an envelope. It's actually a whole bunch of individual profiles plotted together. And the variations have a lot to do with water basins.

AUDIENCE: And the other point [INAUDIBLE] not a lot of [INAUDIBLE]. [? the ?] [? North ?] [INAUDIBLE] I wouldn't expect a huge difference between surface and deep waters because of calcium carbonate to the solution. Not a lot of calcium [? carbonate ?] dissolves [? versus ?] Pacific [INAUDIBLE].

AUDIENCE: [? Also ?] surface deep waters forming in the North Atlantic, it's more similar to surface water [? that could ?] offset [INAUDIBLE].

WILLIAM MARTIN: Have you talked about water masses [INAUDIBLE] in immediate waters?

AUDIENCE: [INAUDIBLE].