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PROFESSOR: I talked about some general overview kinds of things. And then we talked specifically about organic matter for a while. And in today's, we'll talk about the two, by mass, most important biogenic components of marine sediments, those being biogenic opal and calcium carbonate.

And just by way of introduction, before we get into the details, say that, if you remember from before and we'll go over this again a little bit later, most of the biogenic opal that falls to the sea floor actually dissolves. But nonetheless, there has been in the past and there continues to be interest in biogenic opal and, in fact, in the silicon to-- well, the opal to organic carbon ratio in sediments as paleo productivity indicators. So there's lots of study of biogenic opal in sediments going on because of interest in it as a paleo proxy for productivity.

AUDIENCE: I just want to let you know I'm here now. I'm sorry I'm late. It's Kristen. Hi.

PROFESSOR: OK. And the second one we'll talk about is calcium carbonate. And the reason why calcium carbonate is important is because it's an important part of the marine carbon cycle. And we'll talk about that a little bit more as we get into calcium carbonate.

So we're going to do them in turn. First, we'll talk about biogenic silica, or biogenic opal. And then we'll talk about calcium carbonate.

And I have to warn you that last Thursday's lecture was pretty long. And today's is pretty long, too. You have to appreciate my position, where I spend my life studying sediment diagenesis, and the whole thing gets crammed into two lectures. And so I tend to stick much more stuff in there than really belongs, which can have two things. It can confuse you. And second, it can confuse me. So if I get confused, you make sure to stop me and tell me that I'm being confusing. OK. OK.

So to start with biogenic opal, and first you might ask what it is. It's mineral phase. And it's amorphous silica. So it's SiO_2 with water included in the mineral matrix. It's precipitated in the surface ocean by phytoplankton, diatoms, and silicoflagellates, and also by protozoans. And the main ones are radiolaria.

A fraction of opal dissolves throughout the water column. A fraction of the opal that is formed in the surface ocean falls to the sea floor. And once it reaches the sea floor, it's efficiently recycled. And overall, about 3% of the opal that's formed in the surface ocean is ultimately preserved in sediments.

In studying the early diagenesis of opal, the first thing you want to know is what's the solubility of this mineral phase. And I-- OK. Now-- OK.

So the solubility of biogenic opal in seawater was studied a long time ago by David Heard. And the experiments he carried out were first he collected sediment cores from the equatorial Pacific. He separated the biogenic opal from those cores, cleaned up the opal so they'd have a clean surface to come into equilibrium with seawater. He placed his cleaned biogenic opal in seawater and controlled the temperature and pH.

He let the opal sit in the seawater for several days. And at the end of his several day incubations of the opal in seawater, he measured the silicic acid concentration in seawater. And he presumed that the opal had come into equilibrium in seawater, so that the silicic acid concentration he was measuring in his experimental solutions was the equilibrium solubility of the opal.

And what he's found is shown in this plot over here, which is a plot of on the y-axis is silicic acid concentration in his beakers with opal and seawater in them in micromoles per liter. And he also measured solubility as a function of pH. The pH range is about 6 to 9 here.

Two things stand out. The first is that there is a strong temperature dependence of opal solubility. Opal is considerably-- is about 50% more soluble at 23 degrees than it is at deep ocean temperatures of about 3 degrees. And the second thing, and here's the number that you'll need to remember as we go along, is that the solubility of biogenic opal in seawater at 3 degrees is about 900 micromoles per liter.

Now, the second piece of this puzzle is the silicic acid concentration in seawater. And what I've shown here is a bunch of contour plots of silicic acid concentrations in seawater that I lifted from Broecker and Peng. In the upper left is in the Western Atlantic. And following clockwise, it goes to the Indian Ocean. And then down below, it's in the North Pacific.

You can see that in the Atlantic, concentrations increase. In the deep Atlantic, concentrations of silicic acid increase going from north to south. And the whole range in deep water is about 20 to a maximum of about 120 micromoles per liter. The concentrations in the deep Indian Ocean are a little bit higher, but not a whole lot. They go up to a maximum of about 140 micromoles per liter.

And then the highest concentrations in the deep ocean are reached in the North Pacific. And those are only about 200 micromoles per liter. So throughout the deep oceans, the seawater is greatly undersaturated with respect to biogenic opal. And so we've just said that some opal is preserved in the sediments. You might reasonably ask yourself why any opal is preserved since seawater is so undersaturated with respect to biogenic opal.

So opal is a mineral phase. And bottom water is undersaturated with respect to opal. So the question is, what would you expect to observe in pore waters? And how would you expect the silicic acid concentration in pore waters to vary with depth below the sediment water interface as a result of the presence of this mineral that's set under saturation in the water?

And the answer is you would get profiles that look something like this, where on the top is concentration, going from low concentration in bottom water. And I've run it up to what's a hypothetical saturation concentration with respect to the mineral phase that's dissolving. And on the x-axis is depth below the sediment water interface starting at 0. And I haven't specified a scale, but this might go down to about 20 centimeters depth in the sediments.

And what occurs when a mineral that's undersaturated is included in sediments is immediately the mineral starts to dissolve. And what's produced-- in this case, silicic acid, which is produced by the dissolution of opal-- tends to diffuse out of the sediments into bottom water. So at any depth in the sediments, the concentration that's reached is a balance between this diffusion out, which takes away silicic acid, and the addition of silicic acid to the pore waters by dissolution of opal. And as you go deeper in the sediments, the concentration of silicic acid in the pore waters will increase and asymptotically approach the saturation concentration.

So you might think that the silicic acid concentration in pore waters would look very similar throughout the oceans, where opal falls to the sea floor. It dissolves. And the silicic acid level in the pore waters asymptotically approaches saturation, which is 900 micromoles per liter. So the question is, what do you observe in actual pore waters?

And here's a sampling of what you observe, where I've lifted pore water silicic acid profiles from the North Atlantic up here, the central equatorial Pacific, the Peru margin in the Southern Ocean. And I hope these are easy to read, where if you look at the North Atlantic ones, the concentration starts at 0. That's the sediment water interface at about a little more than 20 micromoles per liter and increases. It reaches an asymptotic value, as you would expect from that simple picture I showed you. But the catch is that this asymptotic value is only about 100 to 120 micromoles per liter. This is in the North Atlantic at an oligotrophic site.

If we go to the equatorial Pacific upwelling region, again, you see the simple increasing profile where the silicic acid concentration starts at bottom water value and approaches an asymptotic value. But here, it's about 600 micromoles per liter. If we follow around and go look at the Peru margin sites. So that's a site where there are terrigenous sediments in a highly productive region. And here, again, you have the simple increasing profiles. But the asymptotic values range from about 500 to 800 micromoles per liter.

And if you go to the Southern Ocean, you, see exactly the same pattern of silicic acid concentration, increasing with depth below the sediment water interface. And here, the asymptotic silicic acid concentration varies from about 500 to 750 micromoles per liter.

So if you summarize these results, here are the different sites that I showed you on the x-axis. On the y-axis is the asymptotic silicic acid concentration reached in pore waters. And you see that in some locations, it's very, very far below equilibrium with opal. In other cases, such as the Southern Ocean-- in fact, if I included more sites from the Southern Ocean, there would be some that even reach apparent equilibrium with opal.

But in all these cases, there is a distinct asymptotic value. But it's not at equilibrium with respect to opal. So the question you might ask is, why is that? And what actually is determining the behavior of opal in sediments?

So Van Cappellen, Philippe Van Cappellen, did a series of studies using sediments from the Southern Ocean. And what they did, they collected sediment cores from a range of latitudes starting south of the Antarctic convergence, at this site that I'm showing with my arrow right here, and moving north to sites that are north of the Antarctic convergence in the Indian sector of the Southern Ocean.

And the first thing they did was measure sediment composition. And what they found was, of course, what they expected to find was that the southernmost sites-- and here, I've followed it along with this arrow to a sediment composition plot below-- the southernmost sites are pretty close to being pure opal. So it's a very high opal concentration in the sediments.

But as you move to the more northerly sites, there's a steady increase in this dark-shaded bars, which are the detrital component of the sediments. And there's a steady decrease in the unfilled bars, which are the opal concentration of the sediments. So they go from the southernmost stations, which are nearly pure opal, to the northernmost stations, which have a small opal concentration and a large detrital concentration.

So they didn't stop at just measuring sediment composition. They also measured pore waters, pore water concentrations of some components in these same sediments. And in the top up here are silicic acid concentration profiles from those sediments. And you have the expected shape.

But the southernmost sites, which have very high opal contents in the sediments, have asymptotic concentrations of silicic acid, which are very near opal solubility. But as they go further north and the detrital component in the sediments gets larger and larger, this asymptotic silicic acid concentration gets lower and lower. And that's summarized in the plot over here, which shows asymptotic silicic acid concentration versus weight percent detrital divided by weight percent opal. So increasing detrital concentration in the sediments is associated with a lower asymptotic silicic acid concentration.

Of course, that detrital material-- whereas opal is essentially SiO2. It's silica. Detrital minerals are aluminosilicates, so in addition to SiO2 they also contain aluminum oxides, aluminum. And so it's reasonable to expect that as detrital component of the sediments increases, you'd expect a difference in the aluminum concentrations that are found in the pore waters of those sediments.

So what's shown in the lower half of this picture? Here on the left are plots of the aluminum to silicon ratio in pore waters. And at those two southernmost stations, you can see there's essentially no structure to the profiles. And the values are very low.

If you look at the northernmost stations with a large detrital component in the sediments, you get a very different picture, where this poor water aluminum silicon ratio has a distinct maximum near the sediment water interface. And the value the highest values are something like 10 times the aluminum to silicon ratio in the nearly pure opal sediments. Now, those findings are summarized on the right-hand side, which is a plot of the maximum aluminum concentration in the pore waters in nanomolar versus weight percent detrital. The higher the detrital content of the sediments, the higher the maximum aluminum concentration in the sediment pore waters.

So they used these results, plus a whole series of laboratory experiments, to show a couple of things. And I don't have time to show the lab experiments. But I'll just describe the general findings.

First, they found-- they and others have found as well, that as the aluminum concentration in biogenic silica increases, its solubility decreases. The second thing they found from their experiments was that if dissolved aluminum and silicic acid are present, along with solids mixed in, what happens is that they react together to form authigenic aluminosilicate minerals.

And so they summarized their field observations and experimental findings in a picture of opal diagenesis in sediments that look something like this, both biogenic silica and detrital minerals fall to the sea floor. Two things happen. The biogenic silica dissolves because the pore waters are undersaturated with respect to biogenic silica. And the detrital minerals also dissolve to some extent.

The result of those is-- those two processes are that silicic acid is released into the pore waters, and aluminum 3 is released into the pore waters. This aluminum can be included in biogenic silica. It can be added to the biogenic silica matrix, making it less soluble. But that change in solubility by itself isn't enough to explain this huge change in the asymptotic silicic acid concentrations that they observe.

So something else is going on. And their experiments showed that the dissolved aluminum can react with the dissolved silicic acid to form authigenic aluminosilicate minerals. And so they concluded with a hypothesis about what could cause this variation in the asymptotic silicic acid concentration that are observed in sediments throughout the oceans.

And their hypothesis is that it's not an equilibrium value, but rather it's a kinetically balanced value, where in a sediment that's pure opal, there's very little aluminosilicate-- authigenic aluminosilicate mineral formation. And so the asymptotic silicic acid concentration is very close to opal solubility. As the detrital content of the sediments increases, there's more and more rapid formation of this alumino-- authigenic aluminosilicate. And so the asymptotic silicic acid concentration is a balance between the rate of dissolution of opal in the sediments and the rate of formation of authigenic mineral, the authigenic aluminosilicate. So the more rapid the authigenic aluminosilicate formation is, the lower this asymptotic silicic acid concentration is. OK.

AUDIENCE: Can you explain what authigenic means?

PROFESSOR: Authigenic means formed in place. Is that the-- I mean, that's how I think of it. I don't know what is "authi" mean. I don't know.

AUDIENCE: So it seems almost counterintuitive then, because as your solubility decreases, you're actually still ending up with less opal, right? It's just getting incorporated in different ways?

PROFESSOR: That's right. Well, you have two different mineral phases. Of course, the solution can't be in equilibrium with two phases. One is a very insoluble aluminosilicate phase. And the other is a much more soluble opal phase.

And what's observed is an apparent equilibrium that's somewhere in between those. The more rapid the formation of the authigenic aluminosilicate is, the lower this asymptotic-- the closer the solution comes to equilibrium with respect to that phase. Does that make sense to you?

AUDIENCE: Yeah. So then-- right. So then you're actually getting less-- and in those cases-- or rather, is there a relationship between opal preservation and the clays? Is the more clays, the less opal you end up with? Or is it not so simple?

PROFESSOR: I don't think anyone has answered that question. I'm going to show you some studies of opal, some mass balance studies of opal preservation. But I don't know that anyone has answered that specific question. Well, I can point you to somewhere to look, which I'll do in just a second. OK.

We'll end up here with a little summary of some studies of the preservation rate of opal in deep sea sediments. In order to carry out these studies, what the investigators have measured is first the rain rate of opal to the sea floor. And they've done that using time series sediment traps.

Second, they measure benthic remineralization rates, so the rate of dissolution of the opal in the pore waters. And they do that in two ways. One is to directly measure the flux of silicate across the sediment water interface using flux chambers. And the second is to calculate fluxes across the sediment water interface using pore water profiles of silicic acid. And the third component of these studies is the burial rate of opal in the sediments. And they've done that using solid phase measurements of opal concentrations and sediment accumulation rates. OK.

Here's a set of results of a bunch of these studies. And each set of three bars here represents a study at one location. And at each location, what was measured was the rain rate of opal to the seafloor, the opal dissolution rate through the flux of dissolved silicate across the sediment water interface, and the opal burial rate.

For internal consistency, in the study, you want to be able to add the burial rate and the dissolution rate and have it equal the rain rate. And that actually was very close to true in all of these studies. So they're internally consistent. And using these results, you can measure the preservation efficiency for opal by dividing the measured burial rate by the measured rain rate to the sea floor.

I suppose I should tell you where all these are from before I show the final result. The left-hand most two are from the North Atlantic Ocean, Portuguese abyssal plain and the Bermuda site. The third one there is from the Indian Ocean. The fourth one is from the equatorial Pacific. And the remaining, 1, 2, 3, 4, are all from the Southern Ocean.

And here are the burial efficiency results, summarized on the right-hand side. And you can see that all the results fall between about 5% and 15% preservation of opal, which is very near the mean that's found in essentially all the studies of opal preservation in sediments, somewhere between 5% and 15%. And as I said at the beginning, despite these low preservation efficiencies, there continues to be considerable interest in measuring opal and the opal-to-organic carbon ratio as indicators of diatom productivity changes in the past.

And I'm not going to try to make the case for this. But if you read the Nelson paper, if you're interested and you read this Nelson paper, he makes the case using measurements from the Southern Ocean. And unfortunately, I don't have it referred to directly. But there's another Ragueneau paper that's a very, very long review paper covering essentially everything that was known as of about three or four years ago on opal in sediments. And it will answer your question if anybody has answered it. And it tries very hard to make the case for using opal as a paleo productivity indicator.

One last thing before we leave the subject is a map from Sarmiento and Gruber-- not Gruber and Sarmiento-- of opal-- hmm?

AUDIENCE: Here's what the publisher wrote down in the book--

PROFESSOR: Oh, OK. Yeah. OK. A map of opal concentrations in sediments. And for those of you who have *Tracers in the Sea,* the old Broecker and Peng book, throw away the opal concentration map in that book and use this one because what they don't tell you is they measure carbonate free opal concentrations. And the result is very high values in the equatorial Pacific. Throw away that map and look at this one.

And the features of this map are, first, the highest opal concentrations in sediments are reached in the Southern Ocean, where you get sediments-- because of the high diatom productivity in the region, you get sediments that are almost pure opal. Second obvious feature in this map is that there's a belt of high opal concentrations in sediments around the equator. And it's especially prominent in the equatorial Pacific. The third feature is in the Northwest Pacific. There's also a region of fairly high opal concentrations in the sediments. But you can see it's a major phase in sediments where in the equatorial Pacific it's up to about 30% opal. And the Southern Ocean, it can be the predominant component of sediments.

Now moving on to calcium carbonate-- so calcium carbonate is the predominant biogenic component of sediments over much of the sea floor. And in fact, in big areas of the sea floor, it's the predominant component of sediments, as we'll see in a little while. Why study calcium carbonate in sediments?

It's important, and I hope that you'll talk about it later, talking about carbon cycle in the oceans, that changes in the marine alkalinity budget have been hypothesized as drivers of changes in atmospheric PCO2. And you'll go through those mechanisms, I hope. Yeah. And in addition to driving changes in atmospheric PCO2, those changes can involve changes in the accumulation rate of calcium carbonate in sediments. And the combination of those two things means that you may be able to use variations in the accumulation rate of calcium carbonate in sediments in the past to study how changes in the carbon cycle in the oceans have driven changes in atmospheric PCO2 over time. So it's important to climate studies.

The second thing is sediments represent-- surface sediments represent a pretty large, significant-- pretty large reservoir of calcium carbonate. It's the amount of carbon in surface sediments in the oceans is roughly the same as the amount of carbon in terrestrial reservoirs. And it's larger than the amount of carbon in the surface ocean by a good bit. And larger than the amount in the atmosphere by a good bit. But it's a smaller reservoir than the deep ocean.

But anyway, it's a significant reservoir of calcium carbonate. And so for that reason, it may play a long-term role in buffering the oceans as acid is added to the oceans in the form of CO2. But long term is emphasized here, where the time scale for reaction of acids added to the ocean with calcium carbonate in marine sediments is thousands of years.

So calcium carbonate is a mineral. And what happens in sediments is that calcium carbonate will dissolve in pore waters that are undersaturated with respect to the mineral. And unlike opal, there's not just one mineral to worry about. But there are-- the calcium carbonate minerals that are important in the oceans are essentially aragonite and calcite.

Aragonite is formed by pteropods, gastropods, and corals. And calcite is formed by foraminifera and coccoliths. Aragonite is about 50% more soluble than calcite. But there's another complicating factor that since seawater contains a lot of magnesium, when calcite is precipitated in the oceans, it contains varying amounts of magnesium. And calcites that contain magnesium are somewhat to a lot more soluble than pure calcite.

So in the order of solubility, aragonite is the most soluble of these calcium carbonate minerals. High magnesium calcites are intermediate in solubility between aragonite and calcite. And calcite is the least soluble of the minerals. Because of this solubility trend, calcite is the predominant mineral in deep sea sediments.

So how do we quantify its solubility? Solubility has been determined in laboratory experiments as the conditional solubility product. If you remember when we were talking about conditional equilibrium constants, these are measured in a solution that has the major ion composition of seawater. So the solubility product for calcite or aragonite in the oceans is determined in seawater. And it applies to seawater-- to solutions with seawater major ion composition.

The second thing to point out is that this conditional solubility product is the product of the concentrations of calcium ion and carbonate ion. One thing, you may, if you have a really good memory, remember about the carbonate ion in seawater. There's actually very little free carbonate ion. It's mostly complex, forming ion pairs with cations in solution. And so this carbonate ion concentration that appears in the calcite solubility product is the total carbonate ion concentration. So it's free carbonate plus ion pairs involving carbonate.

Unless somebody has done some very recent work, the two determinations of the calcite solubility product in seawater that I know of were done a long time ago by Engel and Mucci The Engel constant is approximately 10% higher than the Mucci constant. So you can say that if you take these at-- if you give them equal weight, you can say there's an uncertainty in the calcite solubility of about plus or minus 5%.

These days, the Engel constant has fallen out of favor for reasons that have never been clear to me. And the Mucci constant is the one that's essentially the accepted value. Being a cynic, I'd have to say that Mucci has stayed in the business, and Engel, as far as I know, is not in the business anymore. So he can promote himself, and she can't. So his constant rules. Anyway.

AUDIENCE: [INAUDIBLE]

PROFESSOR: [LAUGHS] But anyway, there's about a 5% plus or minus 5% uncertainty in the calcite equilibrium constant in seawater. And aragonite is about 50% more soluble than calcite in the oceans.

The second important determinations was when these guys measured the solubility of calcite in seawater, they also measured its temperature dependence. And they found that as temperature decreases, calcite solubility increases. Engel did experimental determinations of calcite solubility. And Millero has done thermodynamic calculations of calcite solubility as a function of pressure. The two studies are in pretty good agreement.

And what was found that as pressure increases, calcite solubility increases in seawater. The result of both of these-- remember, that as you go from the surface ocean to the deep ocean, two things change. Temperature decreases and pressure increases. So that as you go from the surface ocean deeper into the ocean, the solubility of calcite increases. Calcite is more soluble with increasing depth in the ocean.

The solubility that I've shown you up to here were determined in the laboratory. And it's always important, because conditions in sediments are different from conditions in the laboratory, to try to verify those constants using measurements in sediments. The reasons, of course, are, first, that the minerals that you clean up and use in the lab may not be exactly the same as what's present in sediments.

And the second difference of importance is time. Whereas laboratory experiments are necessarily pretty short, limited to a few months at the most, whereas calcite sits in the sediments for hundreds or thousands of years before it-- well, has hundreds or thousands of years to come into equilibrium with the pore waters.

So there have been studies-- well, a couple of studies done of poor water-based estimates of calcite solubility. And what these-- this is one, an old one by Sayles, and it may still be the only one. What's done is you measure alkalinity, total CO_2, and calcium in sedimentary pore waters. Once you have those pore water data, from the alkalinity and total CO_2 data, you can calculate the carbonate ion concentration in the pore waters. Then you can calculate the product of the measured carbonate ion and calcium ion concentrations. And that gives if-- the pore waters are in equilibrium with respect to calcite, that gives you an estimate of the solubility product of calcite in actual sediments.

Before we look at the results, just look at what the data, what data of this sort looked like. And it's worth showing because these are actually very difficult data to obtain. If you picture yourself collecting a sediment core, what happens when you say you collect a sediment core at 3,000 meters depth and bring it up to the ship in order to extract the pore waters? What do you think is going to happen inside that core?

AUDIENCE: Changes in pressure and expansion--

PROFESSOR: Yeah, the pressure decreases. Well, expansion isn't the important thing. What's important is calcite solubility decreases because the pressure has decreased a lot. And so what that means is that calcite precipitates out of these sediment cores so you can no longer measure concentrations of carbonate system components in the pore waters.

And so what you need in order to make these measurements is a machine that actually separates the pore waters from the sediments while it's sitting on the sea floor. It is a difficult thing to do. And the illustrious Fred Sayles, our emeritus scientist, is really the only one who's had a machine that's done it very successfully. And he's the one that collected these data.

So they're very difficult to collect, and there aren't a whole lot of them. But this is what alkalinity, total CO2, and calcium profiles look like. At least this was a site in the western equatorial Atlantic.

What you find is that you use alkalinity and total CO2 to calculate the carbonate ion concentration. You'll find that below a depth of a couple centimeters, it's constant. And you'll see that these calcium concentrations don't vary very much. They don't change very much, so that the product of calcium times carbonate ion is constant below a couple centimeters, below the sediment water interface.

So a set of data like this gives you one estimate of calcite solubility at one depth. That is one temperature, pressure, and salinity in the oceans. And you can do this at a whole bunch of different locations, at different water depths, and derive a picture like this, where what's plotted on the vertical axis is the water depth, so the depth of the sediments in which pore water profiles were determined. And what's plotted on the bottom is the ion concentration product, the product of calcium and carbonate ion concentrations found in the pore waters.

And the two curves that are through these-- well, I should say first, if you extrapolate these back to a depth of 0, they're in pretty good equilibrium, within the not insignificant error of Engel's equilibrium constant and also of Mucci's constant. You can't tell the difference in a study like this. And the dashed line is the theoretical pressure change in calcite solubility determined by Millero. And the solid line is the fit to the pore water data.

And you can see that within the uncertainty in the data, the in situ determined solubility of calcite are the same as the laboratory determined and the laboratory determined values and the theoretical pressure change in its solubility. So laboratory and field measurements are in good agreement.

So what's all this stuff good for? Before we get to that, I'll just mention the two ways of describing the saturation state of pore water and seawater with respect to calcite. It could also be with respect to aragonite. But we're thinking about calcite here.

First is the degree of saturation, which is denoted by the symbol omega. And it's equal to the product of calcium and carbonate ion measured in the solution divided by the equilibrium constant for calcite, the solubility product. And it's often simplified as the ratio of the carbonate ion concentration calculated from measurements in seawater divided by the carbonate ion concentration that would be at equilibrium with at that temperature and pressure.

And the reason for this simplification is that calcium is conserved in seawater and its concentration doesn't vary very much. So in supersaturated saturated seawater, omega is greater than 1. In undersaturated seawater, it's less than 1.

The second way in which saturation state of seawater with respect to calcite is described is what's called delta carbonate. And this is just the carbonate ion concentration in water, in seawater calculated from measured quantities minus the equilibrium carbonate ion concentration, the concentration that would be there if the solution were in equilibrium with calcite. So if delta carbonate is greater than 0, the solution is supersaturated with respect to calcite. If it's less than 0, it's undersaturated.

So how does calcite saturation-- well, one more thing, how the carbonate ion concentration varies with depth in the oceans. And this is another one of those plots that I pull out of my ancient files that people like Scott look at and gag. But these are very old data from the GEOSECS expedition, which took place 30 years ago? 30 years ago.

AUDIENCE: More than 30.

PROFESSOR: More than 30 years ago. But the picture you get is still the same. They measured alkalinity and total CO2 and calculated carbonate ion concentration. On the top, are all their data from the North Atlantic. On the bottom in the dots are all their data from the North Pacific. And these are carbonate ion concentrations.

You can see that carbonate ion concentration decreases from the surface ocean, going down into the water column. It has a minimum coincident with the oxygen minimum, and then increases slightly to the value in bottom water, which is still very low compared to the value in surface seawater.

The second thing that you'll notice, in the bottom plot, the scatter plot is carbonate ion concentrations calculated for North Pacific data. And I've also drawn on that the envelope of points from the North Atlantic. And the point of that is to show that carbonate ion concentration in the deep Pacific is lower than the carbonate ion concentration in the deep Atlantic. And I know that you can all tell me why that is, or at least one of you can tell me why that is, or not. I know somebody--

AUDIENCE: --cancel class on Thursday.

[LAUGHTER]

PROFESSOR: I know somebody knows. You just don't want to tell me. OK, which seawater has been away from the surface longer, seawater in the deep Atlantic or in the deep Pacific?

AUDIENCE: [INAUDIBLE]

PROFESSOR: OK. And as--

AUDIENCE: [INAUDIBLE]

PROFESSOR: That's true. That's basically saying the same thing as I've showed you here. But why is it lower? So as the water ages on its trip from the North Atlantic to the North Pacific, what happens in the water?

AUDIENCE: It's continually dissolving calcium carbonate [INAUDIBLE]

PROFESSOR: OK, I'll ask you-- I'll give you credit for answering. But I'll ask you a question. If you dissolve calcium carbonate-- if all that you do is dissolve calcium carbonate in the water, will the carbonate ion concentration in that water go up or go down.

AUDIENCE: [INAUDIBLE] I'll have to draw it all out to Figure it out.

PROFESSOR: OK, it'll go up. But what do you do in a water body to make the carbonate ion concentration go down?

AUDIENCE: You oxidize organic matter.

PROFESSOR: You oxidize organic matter, which releases acid into the water. And that causes the carbonate ion concentration to decrease. So going from the North Atlantic to the North Pacific, both carbonate dissolution and organic matter oxidation occur, but more organic matter oxidation. So the carbonate ion concentration is lower than the North Pacific than it is in the North Atlantic. OK. OK.

Now, I'll put together the things I've talked about in the last couple of slides. And what's plotted here is another thing from Sarmiento and Gruber. There's two plots of carbonate ion concentration calculated from carbonate system measurements. And those are shown by the dots. The one on the left is in the South Atlantic. The one on the right is in the North Pacific.

What's also plotted, here are the dashed line, that's the carbonate ion concentration that would be in equilibrium with aragonite at these depths in the water column. And the solid line is the carbonate ion concentration that would be in equilibrium with calcite. So if you look at the North Atlantic one, you can see that these dots are at higher carbonate ion concentrations than the calcite curve. The calcite equilibrium curve down to a depth of about 4200 meters.

So the water column is super saturated with respect to calcite below about 4,200 meters and is undersaturated with respect to calcite below 4,200 meters. So I'll ask you to answer one question. If I were to plot omega versus depth, so the degree of supersaturation with respect to calcite, roughly speaking, where would the values be greater than 1? And where would they be less than 1 in this Atlantic plot?

AUDIENCE: [INAUDIBLE]

PROFESSOR: Yeah. So they'd be greater than 1 above 4,200 meters and less than 1 below that. If I were to plot delta carbonate? Remember, delta carbonate can be positive or negative.

AUDIENCE: Greater than 0 above.

PROFESSOR: Yeah. And less than 0 below that. OK. So now going from the South Atlantic to the North Pacific, the picture is in some ways the same, but in some ways quite different. The carbonate ion concentration in these dots shows a pretty similarly shaped profile.

But now, when you compare it to the carbonate ion concentration that would be in equilibrium with respect to calcite, you see that in the North Pacific, the water is only supersaturated with respect to calcite above about 600 meters. And then it's below saturation, but close to saturation for long depth interval down to about 4,000 meters. And then it becomes more distinctly undersaturated. But the important difference is that the South Atlantic water column, down to a depth of 4,200 meters or so, is supersaturated with respect to calcite. But the North Pacific water column is only supersaturated with respect to calcite, down to a depth of about 600 meters.

I have one more of these plots to show you. And that's because the North Pacific is the extreme end member with the shallowest calcite saturation horizon. This depth in the water column, I forgot to tell you that, the depth in the water column, where there's this crossover between the equilibrium curve and the carbonate ion concentration curve, is called the calcite saturation horizon. That's where the water column is just at equilibrium with respect to calcite.

OK, these are data-- these are WOCE data. So they're much more recent from-- they're WOCE and GEOSECS data, excuse me, from the western equatorial Pacific. And they show a curve that's actually typical of much of the Pacific Ocean, south of the equator anyway, where delta carbonate now shows you that the water column is super saturated with respect to calcite, down to a depth of about 2,000 to 2,500 meters and undersaturated below that.

Now I'm going to show you one more thing on saturation state of the water column before we leave the subject. And these are data from the northwest Atlantic Ocean. On the left are the water column profile from a depth of 2,000 meters to about 5,500 meters for dissolved inorganic carbon, total CO2 and alkalinity. And on the right, using those data to calculate carbonate ion concentration and presenting it in terms of omega, so degree of saturation of the water with respect to calcite.

So a value of 1 is just at equilibrium with respect to calcite. Greater than 1 is supersaturated. Less than 1 is undersaturated.

As for the plot I showed you for the South Atlantic, the North Atlantic water column is super saturated with respect to calcite, down to a depth here of something like 4,500 meters. But the important thing that I'd like to show you is there are two solid curves here. Those are both omega calcite-- well, they're both the saturation level for equilibrium of seawater with respect to calcite. One is calculated for the Mucci solubility and one for the Engel solubility.

So these are the two different determinations of calcite solubility in seawater. The one that intersects one at the shallower level is the Engel curve. The one that intersects deeper is the Mucci curve. And you can see that this plus or minus 5% uncertainty in the solubility product for calcite translates into an uncertainty of about 1,000 meters of the depth at which the water goes from being supersaturated to undersaturated. So even this small change leads to significant uncertainties.

Calcite is a mineral that dissolves in undersaturated water. And it doesn't dissolve when the water is supersaturated. And that gives us a really quite simple overall picture of the calcium carbonate concentration in seawater. And it's pretty easy to understand the basics.

This is another Sarmiento and Gruber plot, where the dark regions are regions with high calcium carbonate content in the sediments. And the black regions are spots with more than 80%-- the sediments are more than 80% calcium carbonate. The dark gray are more than 50% calcium carbonate.

And it's pretty easy to see that the high values for calcite concentration in the sediments follow the mid-ocean ridge system. So those are at relatively shallow water depths. So since calcite solubility increases with depth in the ocean, it's present in shallow-- it's at high concentrations in relatively shallow sediments and at lower concentrations in deep sediments.

The other thing that really stands out here is the North Pacific, which is extremely low in calcium carbonate. And as we've seen, there are two reasons for that. First is that the water column becomes undersaturated with respect to calcite at a very shallow depth in the North Pacific. The second is that the North Pacific is very deep. And the combination of those two things means that the North Pacific is essentially devoid of calcite. So those are the main features of the calcium carbonate distribution in marine sediments. And they're pretty easy to explain.

AUDIENCE: [INAUDIBLE]

PROFESSOR: OK.

AUDIENCE: I'm not sure what Scott said. We couldn't hear him.

PROFESSOR: Did you hear that?

AUDIENCE: Yeah, she couldn't hear me. Ironically, I hear her saying--

PROFESSOR: That she couldn't. So what Scott was saying that you will get to explain that distribution in your homework. Lucky you.

So I've said that changes in the marine carbon cycle can lead to changes in the calcium carbonate concentration in sediments. And so it's of interest to know how you might determine changes in calcium carbonate accumulation rate in sediments over time. And of course, the obvious way to do it is to measure percent calcium carbonate in the sediments. It's an easy thing to measure, and it does indeed vary at a given place over time.

So you might ask-- well, first, there are two definitions that are important in studying percent calcium carbonate in sediments. And they're shown in-- these pictures here, what these pictures are of, and these are examples from the North Atlantic Ocean, are measurements of core top percent calcium carbonate in sediments taken from a range of water depths in the ocean. So each one of these dots represents a sample taken from a core that was taken at the water depth that's shown on the y-axis.

And what you see is the details of these curves vary in different places in the ocean. But the general shape is the same. Where there's-- from shallow going to deep, there's a region where the concentration is either pretty constant or scattered with a slight decreasing trend as you go deeper in the water column. Then there's a kink in the curve. And from that kink, the calcium carbonate concentration drops off pretty rapidly to a water depth, where core top calcium carbonate concentration is 0.

So there's two definitions that arise from this curve shape. The one is the location of this kink. And that's called the sedimentary lysocline. And that's the depth at which there's sedimentary evidence of dissolution of calcium carbonate. And in this picture that sedimentary evidence comes in the form of a decrease in the calcium carbonate concentration in core top sediments. So the lysocline is where the depth at which there's evidence of dissolution.

AUDIENCE: Sorry, the lysocline is the--

PROFESSOR: It's basically the kink, the depth of the kink in that curve, where you can see they've simplified lines through the data. And the two lines look like this, where there is a very decreasing-- a very slowly decreasing part and a much more rapidly decreasing part below that where those two lines meet. The depth is the lysocline.

The other definition, which is a much simpler one, is called the calcite compensation depth. This is the depth at which core top calcium carbonate concentration drops to 0. And it's called the compensation depth, because just by mass balance arguments, that's the depth at which the rate of dissolution of calcium carbonate in these sediments is exactly equal to the rain rate. And the result is a calcium carbonate concentration that's 0.

So the question you might ask yourself here, if you're going to use these definitions and say you're going to use measurements of percent calcium carbonate over time in sediments as an indicator of the accumulation rate of calcium carbonate in the sediments, how does that relate to the rain rate of calcium carbonate to the sea floor? Or worded in another way, is percent calcium carbonate in the sediments a sensitive indicator of the rate of dissolution of calcium carbonate in those sediments?

And the important point to consider here is what I showed you in the distribution of calcium carbonate sediments in the ocean. And what that showed you is that at these shallow water depths, well above the calcite saturation horizon, the sediments are 80% to 90% calcium carbonate. And that's because in these pelagic environments, away from the continents, the material to the sea floor is in many places in the ocean made up mostly of calcium carbonate. So that gives rise to this example here, where this curved line here represents the sea floor. So this would be a rise in the ocean, where at the top of the rise, the sea floor is well above the calcite lysocline, which is shown by the dashed line. And at the deeper depths on the rise, the sediment water interface is below the lysocline.

So suppose this is one of those regions in the ocean where the rain rate, the material to the sea floor is about 90% calcium carbonate, which is not an unusual occurrence. So above the lysocline, where no calcium carbonate is dissolving, the inputs are reflected in sediment composition. So if the rain rate-- the material rain to the sea floor is 9%-- is 9 parts calcite to one part other stuff, other non-reactive stuff, then the sediments that are accumulating when there's no dissolution of the calcite are about 90% calcite.

Now say we go below the saturation horizon, a little bit further down this rise, the rain rate of material to the sea floor is still 9 parts calcium carbonate and 1%-- 1 part other non-reactive stuff. But now we're below the calcite lysocline. And suppose, for the sake of argument here, that 5 units of this calcium carbonate rain to the sea floor are dissolving. So now what's accumulating is 4 parts calcium carbonate and 1 part other non-reactive stuff.

So that means in this location the sediments are 80% calcite. So more than half of the carbonate calcite rained to the sea floor is dissolving. But the sediments are still 80% calcite. And the upshot is that because calcium carbonate is such a large component of the rain to the sea floor, percent calcium carbonate in sediments is a very insensitive indicator of the dissolution of calcium carbonate.

So why go through that argument? Well, it's because-- just because bottom waters that are lying above the sediment water interface are supersaturated with respect to calcite doesn't necessarily mean that the pore waters in the sediments just below the sediment water interface are also supersaturated with respect to calcite. And to see why that is look at here at what happens when organic matter is oxidized using oxygen as an electron acceptor.

When that happens, the organic carbon is released to the pore waters as CO2, which is an acid. And in addition, when the organic nitrogen is oxidized to nitrate, that releases acid into the solution. So oxic decomposition of organic matter releases acids into sediment pore waters.

So the question is, what happens to those acids? Well, they're going to be neutralized because it's a buffered solution. And they can be neutralized in a couple of ways.

First, they can react with carbonate ion to form bicarbonate. Second, they can react with borate ion to produce bicarbonate. Or third, they can react with solid calcium carbonate to produce bicarbonate.

So if you picture what happens as, for instance, CO2 is added to the pore waters, the CO2 concentration will increase in the pore waters and the carbonate ion concentration will decrease in the pore waters. What that means is carbonate ions can diffuse into the pore waters from bottom water. CO2 can diffuse out of the pore waters into bottom water. And when both of those things occur, they tend to cause neutralization of this acid that's added to the pore waters by carbonate ion that's in the water to produce bicarbonate.

On the other hand, the competing reaction is the reaction of these acids with solid phase calcium carbonate. And to the extent that the CO2 that's released into the pore water reacts with calcium carbonate, that obviously causes dissolution of calcium carbonate in the sediments. So in many places in the ocean, pore waters can have enough acid added to them by oxic decomposition of organic matter to become undersaturated with respect to calcite. And then these metabolically produced acids will cause dissolution of calcium carbonate in the pore waters.

And that can happen both below the calcite saturation horizon and above it, because now the pore waters, because of this addition of acids from the oxidation of organic matter, the pore waters can be at a lower saturation state than the overlying bottom water. So calcium carbonate can dissolve in sediments even if the sediments lie above the calcite saturation horizon in the water. And you wouldn't see that in curves, in plots like I just showed you of percent calcium carbonate in core tops versus water column depth because they're so insensitive to dissolution.

So the question is, this process can certainly occur in theory, does it actually happen? And, OK, here's one effort to show that it actually does happen. You can tell that this was in the old days, back before they had lots of computer graphics, because the graphics in this paper are awful. But anyway, this is a Burke Hales paper.

AUDIENCE: [INAUDIBLE]

PROFESSOR: Pardon?

AUDIENCE: [INAUDIBLE] not talking stencils.

PROFESSOR: No.

AUDIENCE: --stencils.

PROFESSOR: This is primitive computer graphics days and also Hales who wasn't into pretty graphics. But anyway, what he did was he used a procedure called in situ microelectrode profiling. And I think I described this for oxygen profiles in sediments before, he had an instrument that landed on the sea floor and on a plate that was lowered down towards the sediment water interface. There were both oxygen electrodes and pH sensitive electrodes. And so he could measure concentrations of oxygen in the pore waters and the pH of the pore waters on a very fine depth scale, close to the sediment water interface.

And here, these are results. And they're plotted as for pH in the pore waters. They're plotted as delta pH. So that's the difference in the pH of the pore waters compared to the overlying water.

And these dots, which I point out if my arrow would reappear, these dots are the measurements of pH in the pore waters as a function of depth below the sediment water interface. And the depth is in centimeters. So that's 1 centimeter and 2 centimeters. So on the upper-- this much of the sediment column, that's a profile of the pH of the pore waters. And you can see that the pH in the pore waters is lower than the pH in overlying water. That's because of the dissolution-- because of the decomposition of organic matter in the pore waters.

What he did then was he built this model of combined oxidation of organic matter by oxygen and dissolution of calcium carbonate. And he did several different runs. And what I've outlined in red in this plot here and in this plot here are what his model predicted-- the pore water pH would be if no calcium carbonate dissolution were occurring as a result of the addition of these acids to pore waters.

And you can see that those are significantly lower than the pHs he actually measured in the pore waters. And based on his model, his conclusion was that the reason for this difference is that calcium carbonate is being dissolved. And therefore, the decrease in pH of the pore waters is less than would occur if no calcium carbonate were dissolving in the pore waters. So this was taken as evidence that as a result of oxic respiration and the acid that's released to pore waters because of it, calcium carbonate was dissolving in these sediments.

Now, the two stations where I've drawn circles around their numbers, station 5 and station 7, are at depths in the water column, which are at or above the calcite compensation depth, the calcite saturation horizon. So if there were no metabolic acids added to the pore waters by oxidative respiration, there would be no calcite dissolution in these sediments. You can see that by his calculations in these sediments, as a result of respiration, something like half of the calcium carbonate that was falling to the sea floor was dissolving. So this metabolic dissolution can be a very important process in the calcium carbonate cycle in sediments.

Just to show you one other set of data, it could be argued, and it has been argued, that they have to apply a carbonate speciation model to their pH data in order to calculate the saturation state with respect to calcite. And therefore, their conclusion that metabolic acids drive calcite dissolution depends on their speciation model for carbonate species in seawater. And if that's wrong, then their result is wrong.

Another approach determines is the measurement of alkalinity profiles in the pore waters. And here, remember that oxic decomposition of organic matter essentially doesn't change the alkalinity of the pore waters. In fact, it decreases it slightly. But calcium carbonate dissolution increases the alkalinity of the pore waters by addition of carbonate ion.

So if you measure alkalinity concentrations in pore waters and you find that the alkalinity increases, then that must be because calcium carbonate is dissolving in the sedimentary pore waters. And that's what was found here at a site on the Cape Verde plateau, which is well above the calcite saturation horizon, where delta carbonate in the bottom waters is about plus 20. So since it lies, since the site lies well above the calcite saturation horizon, then the only way for the pore waters to become undersaturated with respect to calcite, leading to calcite dissolution is formed from the addition of acids, from oxic respiration in the pore waters.

So this was more pore water-based evidence that calcium carbonate does dissolve in sediments that lie above the calcite saturation horizon because of oxic metabolism. But people measuring concentrations of pH and alkalinity in pore waters aren't the only people that have tried to determine the occurrence of metabolic dissolution of calcium carbonate in sediments lying above the saturation horizon. And what's shown here is evidence based on direct measurements of alkalinity and calcium fluxes out of the sediments.

So if calcium carbonate is dissolving in the sediments, then there must be a flux of calcium out of the sediments and a flux of alkalinity out of the sediments. So these fluxes were calculated-- were measured directly using chambers sitting on the sea floor rather than calculated from pore water data. And what's shown here is the alkalinity flux divided by 2.

So the alkalinity flux divided by 2 should be equal to the rate of dissolution of calcite. Remember that every time a calcium carbonate dissolves, it releases carbonate ion into the water. And that represents an increase of 2 units in the alkalinity.

And what's plotted here are alkalinity flux divided by 2, so that's calcite remineralization flux, determined with benthic flux chambers for, on the left-hand side of this plot, stations where the water is undersaturated with respect to calcite. So that's where the bottom where the sediments lie below the calcite saturation horizon. And not surprisingly, you see that there's a flux of alkalinity and of calcium out of the sedimentary pore waters.

What's plotted on the right-hand side here in these dark gray boxes, are sites where the same measurements were made at stations where the sediments have a low concentration of calcium carbonate in them. And their definition of low is 50% calcium carbonate. But what's plotted in the black here are sites that lie-- where the sediments lie above the calcite saturation horizon, but where the concentration of calcium carbonate in the sediments is high, above 50%. And what they saw in these cases was essentially no dissolution of calcium carbonate in the sediments.

And an important point is that I showed you pore water data from one spot that showed a clear increase in total alkalinity with depth in the pore waters. And that actually is one of these spots where they found an alkalinity flux into the sediments, instead out of the sediments. And these sites also include a couple of places where pH data led to the prediction that calcium carbonate was actually dissolving in the sediments.

So we have two different types of measurements directly contradicting each other in these high calcium carbonate sediments. These guys have made two arguments. And both of them relate to-- well, one of them relates to the potential importance of complexation reactions with the surface of calcium carbonate minerals, saying that these calcium carbonate minerals may buffer the solution. So that, for instance, the speciation model that's used-- that's applied to the pH profiles is just wrong. And because that speciation model is wrong, it leads them to an incorrect prediction that there will be dissolution of calcium carbonate in the sediments.

That, of course, doesn't answer the disagreement between their measurements and the pore water alkalinity profiles. To try to reconcile those two different measurements, what they've said is that, well, those alkalinity profiles have a pretty high resolution, but it's not high enough because it's alkalinity is diffusing up very close to the sediment water interface. And there it's precipitating as calcium carbonate. And so that there's no net dissolution.

Now, that argument was actually discounted a long, long time ago, where people said, well, if that were the case, then marine sediments would just be covered with a blanket of inorganically precipitated calcium carbonate because so many of the sediments lie above the calcite saturation horizon. These guys counter that argument by saying, well, the process is very, very slow, and it's actually recycled inorganic calcium carbonate.

So this alkalinity diffuses up. Inorganic calcium carbonate precipitates very slowly and is mixed down. And it's actually this inorganically precipitated calcium carbonate that's dissolving and causing alkalinity profiles to show an increase with depth. Then it's being mixed back to the surface. So it's dissolving-- alkalinity that appears as a result, diffuses back to the surface and just causes a cycle of precipitation of a very small amount of inorganically precipitated calcium carbonate.

So one person, me, said, well, if we can't measure this in solution, what if we try measuring it in the solid phase? And the way this approach worked was it used the fact-- have you talked about this? That the thorium-230 flux--

AUDIENCE: [INAUDIBLE]

PROFESSOR: OK. The thorium-230 flux to the sea floor is essentially constant at a given location, because thorium-230 is produced by decay of uranium-234, which is conservative in seawater. And thorium-230 is essentially all removed by scavenging and falls to the sea floor. So at a given location, there's a constant accumulation rate, a constant flux of thorium-230 to the sea floor.

What happens if there's a constant flux of thorium-230 to the sea floor, it'll have-- and the mass accumulation rate of the sediment is decreasing as you go deeper from the sediment water interface down into the sediments, because the flux of thorium-230 is constant and the mass accumulation, the total mass accumulation is decreasing, then the concentration of thorium-230 in these circumstances will increase because its concentration is the ratio of its flux to the mass accumulation rate.

So you can imagine a case where the mass accumulation rate is decreasing because calcium carbonate is dissolving. If that's happening, then what you would see is an increase in the concentration of thorium-230 in the sediments going downward from the sediment water interface. If calcium carbonate is a major component of the sediments, then its dissolution will cause a significant decrease in the total mass accumulation rate. And you'd expect to see the concentration of thorium-230 increase with depth in the sediments.

Here's a spot from the western equatorial Pacific, lying above the calcite saturation horizon, where excess thorium-230 profiles were measured. And you can see looking at the upper left, that the excess thorium-230 concentration in the sediments increases by about 25%. And you can use that, plus the calcium carbonate concentration profile with depth in the sediments, to calculate a calcium carbonate accumulation rate in these sediments. And you can see that it decreases by 25% or so, I think, 25% or 30% in the upper 1.5 centimeters of the sediment column, which is just the region where you'd expect calcium carbonate to be dissolving as a result of metabolic dissolution.

So here's solid phase evidence that calcium carbonate is dissolving in the sediment pore waters at a site that lies above the calcium carbonate saturation horizon. When I showed these data to Jahncke, the one who says that process doesn't happen, he says, well, you're just not measuring on a fine enough depth scale. And actually this thorium-230-- actually, the calcium carbonate, you're not seeing any net dissolution of calcium carbonate. It's actually just precipitating again very close to the sediment water interface.

But there's a catch there. And the catch is that this is about 30% of the calcium carbonate flux, so that the inorganically precipitated calcium carbonate, which is easily distinguishable from biogenic calcium carbonate, would be clearly visible. But it's not. And so this is a counterargument, saying that, yes, indeed, metabolic dissolution does occur, even though measurements of dissolved phases in the-- dissolved species in the sediments lead to contradictory conclusions.

And as far as I know, there has been no real resolution of this. And so there are two camps. One says metabolic dissolution certainly does occur in sediments and is an important process. And the other camp that says, no, it doesn't. And included in that second camp are a lot of paleo oceanographers who don't want it as a complicating factor in interpretation of their results.

So conclusions about calcium carbonate-- dissolution obviously is driven by undersaturation in the water. Calcite is the most important carbonate mineral in the deep sea. Calcite solubility, plus the action of biogeochemical cycles in the ocean, mean that the degree of saturation of seawater with respect to calcite decreases with increasing depth at any given spot and decreases going from the deep Atlantic to the deep Pacific. And that, of course, results in the simple distribution of calcium carbonate that I showed in that ocean-wide plot of calcium carbonate concentrations in sediments.

But oxic metabolism can drive dissolution of calcite in sediments lying above the calcite saturation horizon. This metabolic dissolution may play an important role in the marine carbonate cycle. But its occurrence is debated.

Just to bring these points home-- of the calcium carbonate that dissolves in the oceans after it's formed in the surface, about half of the dissolution occurs in the sediments. And up to about half of that dissolution occurring in the sediments may be metabolically driven. So it's an important process that one day we should figure out. OK.

AUDIENCE: Professor?

PROFESSOR: Yeah.

AUDIENCE: How [INAUDIBLE] do you think it's the percentage of carbonates to estimate water depths in sediments [INAUDIBLE]. If you look at a core of sediments and you see the amount of carbonate, how it fluctuates, could you reconstruct that-- is that saying, OK, there's less, so maybe it was deeper and it was under the [INAUDIBLE], or it was uplifted or something like that?

PROFESSOR: Now, if water-- I think the more likely cause of changes in calcium carbonate concentration is a shift in the depth of the calcite saturation horizon, rather than a change in water depth. So I think that's what you'd be measuring. Do you understand--

AUDIENCE: Yes.

PROFESSOR: Anything else? OK.

AUDIENCE: We have a question down here.

PROFESSOR: OK.

AUDIENCE: Does all of this also apply to aragonite, or is that just a lesser component of the total carbonate?

PROFESSOR: Aragonite is important in shallow sediments. And in fact, aragonite and high magnesium calcite are very important on continental margin sediments. Now, you can apply all these arguments to that, but I don't know that it's been done--

AUDIENCE: Yeah. Because aragonite is more soluble, very little of it makes it into the deep sea sediments. It just doesn't make it to the seafloor. And there's some data now that suggests when you look at alkalinity distributions in the upper ocean, in the thermocline, that you actually can see regions where alkalinity is being added that correlate quite nicely with where the aragonite saturation horizon is.

And the argument is that things that are falling that are made out of aragonite, like pteropod shells, get remineralized in the water column much shallower before they actually make it to the sediments, because they're more soluble. So that's some work that Dick Feely's been doing.