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SCOTT DONEY: So what we've been talking about is looking at the formation of, in the upper ocean, of particulate organic matter that would then gravitationally sink, and some fraction of it would be respired at depth. And then we talked some on Tuesday also about dissolved organic matter that would be advected, and some of it would end up in the deep ocean where it would be respired.

We're going to finish up this section of the class by looking at-- rather than looking at the particulate organic matter and the dissolved organic matter itself, we're going to look at the geochemical signatures of the respiration and remineralization of this organic matter on carbon nutrients, and a little bit at the end on calcium-- the effect of remineralization of calcium carbonate and opal.

And in fact, a lot of the early information on respiration and remineralization pathways were not actually discovered based on putting out sediment traps and measuring particulate organic matter or looking at dissolved organic matter, they were based on looking at the oxygen gradients, the nutrient gradients, and more recently, the DIC and alkalinity distributions in the deep ocean.

And in particular, what we'll be looking at today is the geochemical signatures, and then also estimates of the respiration and remineralization rates.

So simply looking at the geochemical signatures gives you a sense of where things might be occurring, but it doesn't tell you how fast it's occurring. And so we need to combine information on the special distributions of oxygen nutrients, DIC, and alkalinity with, for example, transient tracers to actually get at the rates that you could then compare with, say, your estimates of the divergence of sinking particulate organic matter and see if everything held together, see if attacking the problem from two different directions gave you a consistent story.

So, just as a reminder, we'll be talking-- to convert back and forth again between the different elemental currencies. We'll be using the Redfield elemental stoichiometries, and we'll talk a little bit about how those were actually determined, and in part, that was based on these geochemical signatures.

There's lots of different variants on this, and we've talked about that, but most of the ones that I was able to find from a survey of the literature-- I should say an unscientific, informal survey, if you looked at the ratio of carbon organic to nitrogen to phosphorus to the oxygen demand for the respiration of this organic matter, the ratio was something like--

117 plus or minus 14, 16 plus or minus 1, 1 because everything's been ratioed to phosphorus, so that's invariant, and then minus 170, probably close to plus or minus 30. There are some wide-ranging values of oxygen in the literature. And there's still some open debate.

In part, there's such variation because the elemental stoichiometries are not constant in nature. And so this is an approximation or a fiction that we use for convenience, but there's good reason to think that they're not constant, both because of changes in production-- so the actual organic matter that's being produced will differ.

So for example, late in a bloom, when you have nutrient limitation, you'll tend to get high carbon-to-nitrogen ratios. Basically, the organisms are under nutrient stress and there's not a lot of available nitrogen, so they'll still attempt to grow and conserve as much of the nitrogen they have, and what results is a high carbon and nitrogen in the biomass.

Similarly, when we start to talk about nitrogen-fixing organisms-- and Karen will be coming back-- [? Karen ?] [? Calciadi ?] will be coming back and giving a fairly detailed set of lectures later-- or a fairly detailed lecture on the nitrogen cycle, but when you have nitrogen-fixing organisms, they tend to be phosphorus-limited, and so they can generate some very high N-to-P ratios and carbon-to-phosphorus ratios.

Also, there can be differentiable remineralization. There can be differentiable remineralization. And this hasn't been completely resolved in a general case, but typically we think of-- if you were to look at the length scale of sinking organic matter--

So here's the base of the euphotic zone, say, and you had some flux as a function of depth, the length scale would be-- flux would-- you could approximate flux is equal to some flux near the surface e to the minus z over. z remin where z remin would be some length scale. So you could approximate the loss of organic matter as an exponential, at least in the upper water column.

And the z remin tends to be shallowest for phosphorus. So organic compounds that are rich in phosphorus tend to get remineralized early, earlier than those with nitrogen and earlier than those with carbon.

Now it's a rule of thumb, but different systems will respond somewhat differently, but there is the idea that the Redfield ratio assumes that all the organic matter is the same, it's one bulk pool, but in reality, some of this organic matter is either tastier to the bacteria or is more labile or is in a particulate form that is more likely to be remineralized with depth, and that will lead to separation.

So you would see, as you move down the water column, the remineralization signal would change because you're actually remineralizing different material. Now-- sure.

STUDENT: So is this exponential graph the amount of organic matter or the degree of remineralization?

SCOTT DONEY: This is just flux for some component.

STUDENT: Flux of organic matter into the water--

SCOTT DONEY: Yeah. And the derivative of that would be the remineralization. So of course, the derivative of an exponential is an exponential, so if I were to plot the remineralization, it would look the same. It would scale the same. Of course, it would have different units. Questions on that?

OK. Usually the way-- I'm going to switch pages. One of the ways that the Redfield ratios were originally defined was to follow-- so here's our ocean surface.

If you were to plot an isopycnal surface-- so a density surface, one of the early ideas in chemical oceanography-- one of the early ideas in chemical oceanography was that if you knew where a water mass formed with some set of properties-- so this would be the surface properties of any particular chemical species-- so you could, say, define that as this would be x0.

That if you were to trace along the flow path and look at x, it would be defined by some initial state x0 plus the biogeochemical sources and sinks.

So in this case, this would be-- for example, if it was carbon, the remineralization of organic matter would add carbon with time, and so you would expect, if you were to plot, say, distance from the outcrop, you would expect x0 to increase with distance from the outcrop because of remineralization of organic matter, respiration of organic matter.

One of the ways we will discuss that is to use what's called preformed nutrients or preformed carbon. And preformed is just a term that's propped up in the literature, and it basically just means the initial conditions at the surface. So in this case, x0 would be your are preformed nutrients or carbon.

And so what you might see, for example, is you might see a derivation where someone says, OK, I have an observed DIC concentration and I'm going to partition that and say, well, some of that was due to my preformed DIC at the surface, and then there's been an addition due to organic matter, respiration, and then an addition due to calcium carbonate remineralization.

And I could do the same thing for nutrients. I could write out the observed nitrate would be equal to the preformed nitrate plus the organic matter nitrate similarly for alkalinity, but in that case, it would just be due to the calcium carbonate, and of course, it would be twice the calcium carbonate remineralization because alkalinity, the carbonate comes in and adds two.

For oxygen, typically what is done is a little different. You don't always hear about preformed oxygen. Instead-- hey. For oxygen, often we use what's called an apparent oxygen utilization rate-- utilization. Utilization. And so AOU is just defined as what you would expect for equilibrium saturation at your potential temperature and salinity minus your observed value.

And AOU is basically a measure of the delta oxygen due to organic matter respiration because that's what you-- as an expectation you would expect the preform oxygen that leaves the surface would be saturated, and then minus some organic matter respiration term because of-- the negative sign is because you're using up oxygen.

We just typically switch it around so that we actually are talking about positive values in the case of AOU. So AOU is-- almost everywhere AOU will be positive, but that means that there's been oxygen loss just because of the sign convention of the definition. Does that make sense to everybody? This is one of those things you have to just-- you have to memorize because you're going to see it all the time, is people will talk about AOU.

This assumes equilibrium of surface waters. The surface waters that are getting advected down this isopycnal. So let's look at a couple of figures. And I'm just going to show you some of the color plates out of Sarmiento and Gruber. And they're nice because they've kind of lumped together a whole bunch of sections. And Nicky has this odd convention where he plots-- he starts in the North Atlantic and ends in the North Pacific, and he puts it on one section where it goes through the Southern Ocean.

So it basically goes-- it'll be a section that goes down the North Atlantic, through the Southern Ocean, and then up the North Pacific. So it's along the pathway of the global conveyor belt, so you would expect-- so this would be the global thermohaline circulation where you have inputs of new deep water in the North Atlantic and the Southern Ocean, and then you have generalized upwelling in the North Pacific. Of course, as we talked about early in the semester, it's much more complicated than that in any detail.

So if you want, I'll just show you a few of these, and then you can always go back and stare at these ad nauseam if you either-- while these are on reserve. So let's-- so some of this should be very familiar because we've talked about the nutrient distributions, but--

So for example, this is nitrate where you see low values entering in the northern North Atlantic and low values of nitrate coming in in the North Atlantic deep water, nitrate continuing to build up as you move into the North Pacific, and then higher values at mid-depth because that's where most of the remineralization is occurring.

Now, one of the tricks of this preformed nutrients-- oops. The original model we showed up here had only a single spot where deep water-- or water was forming, and then it was advecting down in isopycnal. The reality is, in large parts of the ocean, you'll have sources that come from multiple places.

So you might have-- along the same isopycnal, you'll have a northern source and a southern source. Source. And those might have different preformed nutrient concentrations. And so what's often done is people will use salinity to correct for source water.

And it's pretty straightforward in the case of a single-- if you have either a single endmember or two endmembers. It looks, in some ways, like what we were looking at for rivers.

So let's say we have a two-endmember case. So you have one surface water, you have another surface water, and you have water that is a mixture of these two endmembers. I have to switch pages. You guys, everybody ready? So again, the two-endmember case where you've got water, that's a mixture of two endmembers.

Well, if I were to plot against a conservative tracer-- in this case, we'll use salinity, so we're going to treat salinity as a conservative tracer. Along the isopycnal surface, which is a pretty good assumption as you're far enough away from the surface and there's not a lot of diapycnal mixing and you're not in a region of salt fingering.

If I plotted whatever tracer I wanted, say C0-- or C, in this case, I'd have these two endmembers. So these are my surface endmembers. And so what's going to happen-- let's say there's no biogeochemistry, there's just mixing, what's that plot going to look like?

STUDENT: A straight line?

SCOTT DONEY: It'll be a straight line right. So this would be no biogeochemistry. It would just be conservative, you'd have conservative mixing. So what you would-- just like in the river in the estuarine case, what you'd be looking for are deviations from linearity from a salinity curve. So it's very analogous to what's done in estuaries.

And this-- at any particular point, this would be the delta C net, would be-- the net contribution of biogeochemistry would be the deviation from that straight line.

STUDENT: What is the y-axis in here?

SCOTT DONEY: It would be any tracer, just C. Any arbitrary tracer. It could be oxygen, it could be nitrate, silicate. And so, in fact, one of the ways that the people go out and make Redfield ratio measurements, or estimates, is they go out and they map tracer distributions along isopycnal surfaces and then correct for the mixing from the different endmembers, these different pre-formed endmembers, and then compare-- so they would compare the delta phosphorus net to delta nitrogen net to delta carbon net along a series of isopycnals.

And you have to find a place where the biogeochemical signal is large relative to all the advection and mixing signals because if there's not a large contribution of organic matter or you're not looking at a big enough distance, what you get is most of these things end up being linear, and it's just the advection and the mixing between two different endmembers rather than the biogeochemistry.

So you can't just look at-- you can't just plot-- don't simply plot, say, phosphate concentration over DIC and expect to get a Redfield ratio because a lot of what's there actually has to do with equilibrium, the preformed equilibrium-- or the equilibrium concentrations of the preformed surface concentrations that the water gets advected into the interior with.

There's one complication, which is the fact that a lot of times, you don't have just a simple two-endmember case. You might have three or more endmembers.

And it gets rather messy, and you don't always have a good-- you don't always have a good set of conservative tracers because once you get away from-- remember, along an isopycnal, temperature and salinity are correlated, so you can only use one or the other, you can't use both, because as you change salinity along an isopycnal, you have to have a corresponding change in temperature for you to stay along the isopycnal.

So there are a variety of techniques that people have tried to use for these multiple endmember cases, and there's basically a series of mixing models where people try to set up mathematical techniques where they can pull out and resolve from the data the surface endmembers that go into the mixing model.

The problem is, sometimes it's difficult. We don't always know the surface endmembers. And it's sometimes difficult to figure out the fractions of the different sources. And so it is a complication, and you should be aware of that a lot of this work depends upon how well you can do this separation. Fraction of sources or mixing ratios.

I do just want to say one thing about this surface endmembers. Part of the reason why we don't know this is the surface endmembers should really be the winter water-- waters. The water at the out-- so what you want is the water that forms at the actual outcrop of an isopycnal surface in winter.

And so if I were to plot my density surface, what you'll see in the thermocline is, during the summer, this isopycnal-- so this is, say, a particular isopycnal with a certain water mass. And during the winter, it might outcrop like that. And so this would be winter. But during the summer, you'll get much warmer water there. So let's say this is cold.

And so during the summer, this will outcrop much further poleward. So this would be poleward. But all of this water-- this is all in the seasonal thermocline, and that's not the water we want to look at. And so unfortunately, a lot of our geochemical surveys are done during the summer, particularly in high latitudes, because of weather constraints.

And sometimes you have to actually try to interpolate back to what the conditions were in winter so that you know what the winter source waters are because it's actually the winter water that gets advected down for the most part onto the isopycnals, not what's happening on the summer. Does that make sense to everybody? Is that OK with you? Everybody up at MIT?

STUDENT: What's the scale on that diagram? Like latitude-wise.

SCOTT DONEY: It could be 10 or 15 degrees of latitude.

STUDENT: So you just-- like you said, survey up there? You can just go down there--

[COUGHING]

--deeper?

SCOTT DONEY: Well, one approach is to look along the isopycnals and see where you think winter water was formed the last time winter water was formed, but stuff has already-- there's been biogeochemical changes already to that water, and so people have attempted to build tools to correct back to what they think winter concentrations might be.

The best way, of course, is to figure out a way to make your measurements remotely on some autonomous platform. Throw the thing out there and let it bob around in the winter making measurements rather than being out there at sea during the winter. But just a caveat to that.

So I showed you the-- remember, this was the nitrate. So this was the nitrate distributions, North Atlantic deep water, North Pacific. If we were to look at an estimate, then, of the preformed nitrate-- this is the nitrate that's coming in, what you see is that the gradients are much smaller. There's a fairly-- there are differences between the preformed nitrogen that's being formed in the northern North Atlantic versus the Southern Ocean, but they are considerably smaller.

For phosphate, that's not true. If we look at the preformed concentration of phosphate, there's actually quite large gradients between what's formed in the Northern Hemisphere and what's formed in the Southern Hemisphere. And this difference between the preformed phosphate between the northern and the southern waters is actually used a lot to help to partition that out. There are various techniques that have been developed to try to tool.

But what you need to do is, for example, if you're interested in the remineralization, you would take, say, for nitrate, you'd take the nitrate field-- let's do it for phosphate because it's a bigger signal. You take the phosphate field, you then subtract off the preformed phosphate, and then you get the remineralization phosphate term, which is what you're actually interested in because that's the biogeochemistry.

And the other thing-- I'll either put-- these figures are probably just a couple of sections on the homework, the upcoming homework, so you guys can get spend a little more time looking at them, but we had talked about AOU. Remember, by the way the definition's set up, AOU is always positive.

So for example, the North Atlantic deep waters will have low AOUs, and as you move into the North Pacific, you get higher and higher AOUs because you're using up oxygen.

OK, so that's the large-scale distribution of nutrients. The next question is, can we get some rate estimates out of that? And there's a couple of techniques that have been developed to try to get-- oops-- to get geochemical rate estimates that you could then compare with some of the other more biological techniques or more process oriented techniques.

Remember, we talked a lot in the upper ocean how one of the advantages of geochemical techniques is that you're not actually manipulating the system, you're not doing incubations, you're not trying to grow bugs. So the geochemical techniques have that advantage, that they-- no direct manipulation of the system. They also have the advantage and disadvantage that they integrate over large time and space scales.

So if I'm going to use the geochemical gradients of nitrate through the North Atlantic-- or through the Atlantic to try to estimate remineralization or respiration, I'm inherently making a basin-wide average right, because I'm using basin-wide gradients. I can't distinguish between what's going on here and a point 100 kilometers away, but I might be able to give you some average value over the North Atlantic over the ventilation timescales of that water.

So it might be 1,000 kilometers or multi-thousand kilometers and decades. But maybe that's a better estimate than somebody going out 1 February and making one measurement at one on one particular day because that might have been-- there might have been a storm or a bloom event, or they might just have had some big piece of marine snow that got stuck in their incubation bottle and might alias their results.

This has been-- a lot of the focus has been on oxygen and AOU, in part because of the larger database and the longer historical database for oxygen and AOU. So one of the terms you'll see is the OUR, which is the Oxygen Utilization Rate, so it's now being turned into a time rate. And that's simply the rate of change of AOU with time, and that can be approximated as delta AOU over delta age where age is some age derived from some tracer.

And usually the assumption is that we start at the surface with zero AOU and then we just look at the age, though, people have done more localized estimates as well.

STUDENT: Why [? would ?] [? the ?] AOU to be zero unchanged.

SCOTT DONEY: Ah. Let's go back to the definition of AOU. So this was the definition of AOU at the surface. It was the thermodynamic gas exchange-- or the gas exchange equilibrium that you'd expect at that temperature and salinity minus the observed oxygen.

So to first order, you expect surface waters to be in equilibrium with the atmosphere. That's not always true, but during the winter, that's a reasonable assumption unless you have very deep mixing. In some places, like the Labrador Sea, where you have a lot of deep convective mixing, you bring up-- you rapidly bring up deep water that has a positive AOU, the gas exchange just can't keep up, and so the convection collapses and the water sinks back down and still has an AOU signature.

But in places with relatively shallow mixing, the gas exchange will equilibrate oxygen. Remember, oxygen has a time scale of about a month-- or a few weeks to a month. And so as long as you have enough time for gas exchange to occur, this should be true.

The same is not true for DIC, and that's why you don't see people writing CO2 saturation minus-- DIC saturation minus DIC observed as frequently because the DIC doesn't have enough time. Remember, DIC has a much longer gas exchange time scale, so it doesn't have enough time to equilibrate.

We'll come back to that I guess the last two lectures. We do anthropogenic CO2, and we'll talk about some of the techniques that people use to estimate anthropogenic CO2, and we'll get into CO2 disequilibrium.

OK. So, what we were talking about was oxygen utilization rate, where it's the AOU divided by age. So where do you get the age model from? Where do you get the age estimates?

One of the first papers on this was by-- estimates by Riley in 1951. And he tried to combine geostrophic velocities with oxygen gradients to try to get it at OUR.

So essentially, if you had a-- let's say you had flow along an isopycnal, and if you knew what the velocity was, and you knew that you had an oxygen value at some point 1 and you had an oxygen value at some point 2, you could difference these to get your AOU, and then you can estimate the time scale if you know the velocity of how long it takes to get from one point to the next point.

Probably the next big paper in this realm was actually by Bill Jenkins, who's down here at WHOI. He had a whole series of papers, but it started with a paper in 1980 where he used the tritium/helium age method. And we went over this-- we went over this some when we were doing ocean physics, but I'll just review it briefly.

Remember that tritium is an isotope of water. Decays to helium-3, which is a gas. So this is part of H2O-- or actually, H3HO. And it decays with a half-life of about 12 and 1/2 years.

The assumption is that when you take a parcel of water from the ocean surface and it sinks down, the assumption is that in this surface box, there was no excess helium-3 where that would be excess above saturation. And so usually when you see-- almost always when you see helium-3 measurements, they're actually reporting the excess above thermodynamic saturation with the atmosphere.

And so if you were to write out the-- assuming no mixing of that parcel, if you were to write out the time derivative of tritium, it's going to be equal to minus lambda times tritium. Similarly for helium-3, and this is excess helium-3, it's going to be equal to plus lambda times the tritium.

And so usually the-- you can solve this since we know that any excess helium was originally-- is just dead tritium, it's tritium that decayed, we can think of the tritium concentration in the box as equaling the initial tritium when it was at the surface times some decay, exponential decay rate. And then that initial tritium can actually be set as equal to the tritium that you have at present plus all the excess helium-3, assuming that you haven't had any gas exchange.

So as long as this parcel followed a path where it was at the surface and then sank down and has been isolated from the atmosphere, this helium-3 will grow in and basically gives you a clock because you can then solve this equation. You measure you measure this, that's the same thing. You measure that, and then you lambda, so you can solve for t. And this is the H.

So if you do this-- and this was originally done off of Bermuda because it's a convenient spot in the ocean to go to because it has an island and a biostation and a ship. Bill and colleagues looked, as a function of depth, at the age. So this would be the tritium/helium-3 age. And it tended to be close to 0 at the surface and somewhere around 30 years at depth. And this was-- the depth was the thermocline, so this would be 1,000 meters.

You could then plug this-- if you had the AOU measurements-- so you have an AOU profile, they could then combine the age estimate with the AOU profile and come up with a profile of OUR. So a profile of the oxygen utilization rate.

And what they found was that at the peak, which was pretty shallow, right below the euphotic zone, in the shallow aphotic zone, AOU was 10 to 30 micromoles per kilogram per year-- or per year. And by the time you got down to the base of the thermocline, it was more like 1 to 3 micromoles per kilogram per year.

And this was actually occurring about the same time that people were putting out sediment traps, and the sediment trap data was showing that the particle flux was dropping off fairly dramatically in the upper ocean, and then not so much in the deep ocean. And so to first order, these appeared to be consistent, that most of the remineralization/respiration's occurring in the upper couple hundred meters right below the base of the euphotic zone, and then tends to drop to much lower rates in the deep water.

If you integrate that-- so if I do a vertical integral of OUR with depth, I get the water column demand. And that tends to be fairly large. They were getting values of, say, 3 to 6 moles of oxygen per meter squared per year.

Which at the time, when Bill first published, this was a strikingly large number because people thought that the product-- if you converted this to carbon units, people thought at the time, that all the primary productivity at Bermuda-- the total primary productivity, not export production, but primary productivity, was in about the same-- was about the same values.

And so there was a big ongoing controversy of a lot of the people doing incubation studies arguing that the geochemical techniques had to be wrong and the geochemists scratching their heads saying, well, we can't figure out why it's wrong. These numbers have held up over time, and estimates of the primary productivity have been reevaluated.

And it appears that, as [INAUDIBLE] cycle, you miss a lot of events. And so if you're not careful, you're totally biasing-- you totally bias your estimate, and you tend to bias it low because the events tend to be very episodic. And so the primary production might go along like this and then have some big event and another big spike. And so because it's so skewed, you tend to always-- you tend to estimate low values.

STUDENT: When did they come fix the trace metal issues with the--

SCOTT DONEY: The trace metal issues were early to mid '70s. So this was post-- a lot of the data that went into Epley and Peterson in '79 is just still horribly trace metal-contaminated. And so there was some of that in this argument, that there were trace metal issues as well, so it is a combination-- yeah, you're right, it is a combination of the trace metal effects and the primary production and some really, really pig-headed people.

There are some caveats and biases with the-- mixing can tend to screw up tracer ages. And I won't go into detail about that, but there's been a lot of work on that, of how you-- remember, the assumption was that the water left the surface and went down as a nice Lagrangian parcel, but if there's mixing, it can tend to alias the tracer ages.

And one of the ways is people have looked at is multiple tracers. So they'll look at CFCs, they'll look at radium-228, which tends to have a continental source-- continental shelf source that comes out in the surface water and then gets advected into depth. And then they'll also use the tritium/helium. And by combining tracers, you can resolve some of these mixing issues.

OK, I might actually get all caught up today. So these have-- the tritium/helium/freon approaches have been used quite a bit in the upper ocean and are now an accepted technique for backing out oxygen utilization rates. They've now been applied to dissolved inorganic carbon, alkalinity, nutrients, you name it, as a tracer. People have tried to use these age approaches to get at the production rates, the geochemical production rates in the thermocline.

In the deep water, there's just not enough tritium or CFCs to be particularly confident about your age model because the water is, for the most part, pretty old, and you have a little bit of a signal coming in from these transient tracers. And so what's typically done for the older waters is to rely on radiocarbon to get at those slow remineralization rates.

And some of this was work-- well, this has been pioneered by a number of people. Harmon Craig, Walter Monk, Wally Broecker starting in the '60s and in the '70s when they started to make the first radiocarbon measurements. And so what was done was to use radiocarbon for your age model. And you had to make corrections because of endmember mixing. So this would be age model for deepwater.

And so often, what you would see is that the radiocarbon would have different endmembers, just like we were talking about for preformed. And some of the assumptions were very crude. They didn't even use salinity.

Sometimes they used salinity, sometimes they just used latitude and treated the whole deepwater as one box because there were so few measurements. This was back before the AMS techniques, so you needed very large volume samples to measure radiocarbon, and it was rather tedious to collect.

And so what people would do would be to just fit-- look at the observations relative to a mixing curve, estimated delta for delta tracer relative to the approximation of a mixing curve. And so for example, you could plot delta oxygen or minus delta oxygen-- nope, sorry. Plus delta oxygen because I stole this from a different place. Or AOU versus delta delta 14C where the second delta is just the fact that you've corrected it for the mixing model.

And when you do that, you get a plot that looks something like this. Waters that have high radiocarbon tend to have high oxygen. And as you get to older waters, they tend to have lower-- strike that, hang on. I'm having sign convention problems here.

So this would be delta AOU or delta minus oxygen. So where you have high delta AOU-- hang on. Did that backwards again. Where you had-- well, where you have younger waters, you don't have nearly as much change in oxygen, and where you have older waters, you have a large change in oxygen. And they got rates of approximately 1 micromole or less per kilogram per mL. That's what the slope would look like. And that gives you your OUR estimate.

And if you convert that into-- if you convert this into age for the Atlantic and Pacific, it's something like 10 to 15 micromoles per kilogram per century. Remember before, we were talking about at the base of the thermocline, it was 1 to 3 micromoles per kilogram per year. We're now talking about something that's about a factor of 10 less because it's 10 to 15 over 100 years.

And those are probably still the best estimates we have for remineralization rates in the deepwater because a lot of the biochemical assays, say, for electron transport in bacteria or for differencing sediment traps are just too imprecise to really get a long-term average value that we would trust.

STUDENT: Is that in the deep Pacific?

SCOTT DONEY: What?

STUDENT: That's in the deep Pacific, is it?

SCOTT DONEY: Those are values for both the deep Atlantic and the deep Pacific. I took a compilation-- this was a plot that was a compilation of both, where they plotted everything together and calculated one slope. OK. Bill's going to talk a lot more about calcium carbonate. I think he will.

So I was going to move out of organic matter. So this was the organic matter remineralization. I did want to talk a little bit about opal, or silica, before we conclude, and then we'll wrap up a little early today.

So opal, we talked about you form a lot of silicate-- or silica in the surface water due to diatoms. About half of that is remineralized in the euphotic zone. The other half sinks down to depth and is remineralized either in the water column or at the sea floor with some fraction of it getting buried.

The reaction we're looking at is something like this. It's a hydrated silica. So the biogenic opal is not pure. It's not pure silica, but it's actually a hydrated amorphous silica combining with water. And the n just means that there's a variable number of waters in the hydration.

To go back to silicious acid. And then that silicious acid can lose protons. That would be two protons because you add a proton there. I will give you a-- I'll give you an important secret. For reasons that escape me, in the chemical oceanography literature, people often write silicate as SiO3, which annoys some of the chemists, particularly some of the chemists at MIT, to no end.

So if you're doing general exams and you're in chemistry, save yourself some grief by writing it out as siliceous acid and taking the protons off.

STUDENT: But you will see it in all three of those different forms?

SCOTT DONEY: You'll see it written as all three of those forms, but just giving you a hint because I've seen it enough. It'll always come up, why did you-- what's the valence of silicon and siliceous acid? And they make you walk all the way through it, and it's just easier to save yourself the grief.

STUDENT: It's painful.

SCOTT DONEY: Yeah. I can't remember if you had to do that.

STUDENT: Wasn't me. I got warned, I think. Because when we were studying, we were like, wait a second. No consistency.

SCOTT DONEY: No. That's because chemical oceanographers aren't actually chemists.

STUDENT: Well, when you're looking for the Ksp's and you start freaking out, in which case.

SCOTT DONEY: And these are the k-values for these acid-base-- for the acid-base reactions. As you increase the pH of seawater, you will tend to decrease the amount of siliceous acid. And it's actually the siliceous acid that's involved in the dissolution solubility reactions with the amorphous hydrated silica.

And so as you increase the pH of the water, you actually increase the solubility. And so one of the things that affects siliceous acid dissolution is the pH, and so there's a coupling between the CO2 system and the siliceous acid system.

And there's a-- I'm trying to remember if it's in-- is it in Pilsen? There's a rather entertaining discussion of how you would-- how you go about computing the Ksp for silica where he walks you through some of the issues of what you would-- if you were a geochemist and you just went to a geological table, and what you'd get out versus what you actually get in the real ocean.

And the way this was done was people would go out into the deep ocean and-- they did this both for calcite and aragonite and for silica, is they would take, say, diatom shells or benthic forams, put them out in the water at depth for a period of time, and then see how much they'd remineralized. Or see what the-- if you put enough out, see what they would come to equilibrium with in the lab.

So they would do kinetic experiments where they'd put these things out and watch them dissolve with time, or they would put these in the lab in seawater and basically allow it to dissolve until it came into equilibrium with the water.

Because these are not pure mineral phases, and particularly because of this amorphous hydration, a lot of the kinetics you would estimate from pure phases and the solubility product you'd estimate from pure phases are unrealistic. They're not going to be very useful for environmental work.

The Ksp for silica, for the amorphous silica in the ocean, is something like 1,000 micromoles per kilogram at 3 degrees. It's much larger than what you would get, say, for quartz. And it's basically the-- it has a much more imperfect crystalline structure, and it's much easier for it to solubilize, and you need a higher silicate concentration to balance that. It'll come into equilibrium with a much higher silicate concentration.

Now, 1,000 is actually the highest values you see in the ocean. I think you can see the-- I don't know if you can see the color bar here. This is the silicate distribution along that section that we've been-- I've been showing you. Values are quite low in the surface ocean, less than 10, and in fact, a lot of the North Atlantic has values less than 10.

The highest values you see in the North Pacific are up somewhere around 200. So essentially, everywhere in the water column, everywhere in the water column, it's undersaturated with respect to this amorphous silica. The reason why the particles actually can make it to the sea floor and not dissolve has to do with the kinetics and the sinking velocity.

So the kinetics have to be slow enough such that we know silica reaches the bottom. In fact, there are large parts of the oceans that the sediments are made up of diatom frustules which says that the kinetics must be slow enough sinking through-- that the sinking velocity is-- can get them to the bottom before they dissolve. Or they're somehow protected by some organic coating or some other factor. Well, usually the organic-- the organic coating.

The fact that silica isn't dissolving in the water column once you get out of the surface layer, there's a fair amount of remineralization in the surface layer because you have processing by organisms. You have copepods that are eating diatoms, and that gets into-- you're processing through guts. Lots of biological processing.

Once you get below about 1,000 meters, it looks like most of the silica actually makes it down to the bottom, and then some of it dissolves there because it then it has a long time, it's sitting on the bottom exposed to deep waters, and some of that remineralizes.

And so if you make a plot with depth of H for SiO-- or, excuse me-- H2SiO4-, what you see is that you have low values at the surface-- oh, I didn't draw that very well. What I was trying to do was show you that it tends to build up deep in the water column.

So if I were to show you nitrate-- so this would be, say, nitrate versus silicate. That silicate tends to build up deeper in the water column and be more bottom-intensified than nitrate. And I can show you that in these plots.

So this is nitrate. You get a big subsurface maximum around 1,000 meters, where silicate, the maximum is either at the bottom or in the deep waters. And that's just a function of where the remineralization is occurring. Nitrate is coming mostly from-- coming all from the organic matter.

The organic matter, a lot of it's going to be mineralized in the upper 1,000 meters, where the silicate, most of it that escapes the euphotic zone is making it to the bottom and it's getting remineralized there, and so it has more of a bottom signature.

STUDENT: [INAUDIBLE]

SCOTT DONEY: Sure. Any questions on silica cycling? Sure.

STUDENT: In that mineral layer at the bottom, is silica saturated in the water?

SCOTT DONEY: No. It's still not-- it's never saturated in the water column. It does get saturated if you move down the sediment core, and Bill will talk about that some next week. Yeah?

STUDENT: For the silica plot that you should-- there's a build-up-- like, it's higher concentrations along the bottom, but then when you get to the Pacific, there's higher concentrations also in the water column.

SCOTT DONEY: Right.

STUDENT: Is that from upwelling? Or what is that?

SCOTT DONEY: The geochemical signature is going to be a combination of the remineralization rates plus the ventilation. And so in the North Pacific, the younger waters are actually coming in along the bottom. They're really cold Antarctic bottom water, and so that's penetrating right along the bottom, and then the water is above it are actually are somewhat older. And so that water has just had more time and seen more remineralization over time.

OK. There are lots of other-- we could do-- I've shown you nutrients and silicate. We could look at-- there are other biologically influenced elements. Things like barium. Even to a degree, strontium is slightly biologically influenced. Those are tangential to the main emphasis of the course. So I think what we'll do is we'll stop there. Bill will pick up and talk about sediments for two lectures.