SCOTT DONEY: So where we were on Tuesday is we were talking about the sinking of organic matter and the remineralization in the water column. So if you remember, if we plotted versus depth and plotted flux of organic matter, it tended to drop off fairly steeply in the thermocline and then was rather flat through the deep water.

And we talked about putting out sediment traps in the water column, these would be little sediment traps, to collect material. And we were talking about a couple of different hypotheses that people had for what controlled some of the processes involved in this decrease in flux as you went down the water column.

And so in order to support a change in flux with depth, you have to have either transformation of large particles, large sinking particles, into small particles that would then get respired. Or you needed some process that would just respire those particles directly.

Now, we talked a little bit about what those particles are. And I don't know if I ever listed them down specifically. But for example, this flux of particles, because of Stokes law and the viscosity of water, the flux of particles, the particles themselves that are sinking, have to be relatively large.

Remember, when we talked about Stokes law, we were talking about things that were greater than 100 microns or somewhere in that range. And so it could be large, dead cells. It could be aggregates of cells, "aggregates." And in fact, it's not uncommon for diatom blooms.

At the end of the bloom, at the termination of the bloom, often there'll be a aggregation of the dead and sometimes living cells, and then they will sink out as an algal mat. And this can be observed in the deep sea by collecting, basically, the organic mush on the bottom of the sediment layer.

And it will have a high chlorophyll content, suggesting that it's very fresh, recent material that has recently rained down onto the surface. It can also be zooplankton carcasses-- I'm not going to get "carcass" right, but carcass. I'll end up spelling Caracas or something-- or zooplankton fecal pellets.

And these are things like, for the zooplankton that form fecal pellets, things like copepods and then salps, which are gelatinous filter feeders that tend to filter out a lot of the small particles and mid-sized particles out of the water column. And then they end up producing these very tightly compacted fecal pellets that tend to sink very rapidly.

The last large component of the sinking flux is what's often called marine snow. And these are just organic aggregates that come from a variety of different sources. One of them could be, some organisms give off mucus.

There are a variety of organisms that have organic feeding structures, for example, the appendicularians, which are another form of filter feeder. And they have this organic web that they use for filtering, and they shed that on a periodic basis. And then that can go into these marine snow or marine aggregates.

And then there's also the possibility for a spontaneous formation, where you have either particle-particle interactions or DOM-particle interactions that could lead to the formation of an organic aggregate. As these aggregates grow, so let's say you've got some marine aggregate here.

As they grow, remember increased size leads to increased sinking speed. And one of the things these aggregates can do is actually collect smaller particles by essentially just, as the aggregate's sinking, it catches up with suspended material or smaller material that isn't sinking as fast. And these can be organic or inorganic, for example, coccoliths or dust, et cetera.

And so these marine aggregates, they may start off from a particular source, for example, a feeding web from an appendicularian, but then it will accumulate other material as it sinks down the water column because it basically just sweeps out in front of it, many of the smaller particles that it falls through.

Now, in addition to sediment traps, sediment traps give you flux. And that's usually organic carbon, maybe inorganic carbon, silica or opal, and a terrigenous component. And it gives you some sense of the composition.

So you can look in the sediment traps and look at the material, and you can pick out individual carcasses, you can pick out individual fecal pellets and sometimes dead cells, forams, things that are large enough. But often there's a lot of just organic mush. And the thought is that a lot of that is this marine snow.

People have gone out and actually gone into the water column doing scuba diving in the upper water column, anc then also submarine work, to try to look at these aggregates as they're actually sinking. Because once they get into the sediment traps, they just become this organic mush at the bottom. And it's very hard to actually figure out what their original size was or anything characteristic about them, other than their bulk composition.

But one of the problems with sediment traps is all the sediment trap tells you is net d flux dz, at best, the net change in flux with depth. But there could be a lot of interactions along the way where you could have, say, large particles going to small particles, going back to small particles being mediated by either some of these zooplankton.

And so we need some other way of looking at the dynamics in the subsurface of these particles. And we're going to turn back to radionuclides for two reasons-- one is they're quite useful and, two, it's chemistry class.

So this will look very similar at the outset to what we were discussing with thorium-234 for the upper water column, except we're going to choose different isotopes of thorium that have timescales that are more relevant to the thermocline in deep ocean. So in particular, if you remember, when we were doing thorium-234, we had uranium-238 decayed to thorium-234.

But that thorium-234 will decay to uranium-234, which then decays to thorium-230. So we were using this in the upper water column because thorium-234's half-life is short. It's approximately-- Do you guys remember?

AUDIENCE: [INAUDIBLE].

SCOTT DONEY: About 24 days? The half-life of thorium-230 is more like 75,000 years. And where what we saw before was that below the euphotic zone, thorium-234 was in secular equilibrium with uranium-238, we're now going to look at deviations.

And in the surface waters, thorium-234 had a deficit with respect to uranium-238. We're going to do the same thing where we're now going to look at the deficit of thorium-230 with respect to uranium-234. We talked about this for the upper water column. Uranium has a fairly long residence time in the ocean because there aren't a lot of large sources and sinks.

So we can approximate the uranium concentration as a function of salinity. And we did that for uranium-238. The activity of 234-uranium is slightly higher than the activity of 238-uranium. And Meg mentioned this when she was doing her lectures on weathering. Does anybody remember the cause of that?

AUDIENCE: [INAUDIBLE].

SCOTT DONEY: Yeah. In this process of the decay of uranium-238, it's releasing alpha particles and it's actually breaking up and damaging the mineral lattice, the crystal lattice that the uranium was originally in. And so you get a little bit more leaching out of the uranium-234 because of that damage. And so there's, in seawater, a slight elevation of uranium-234.

So some of the original work on thorium-230, or one of the seminal papers, is a paper by Bacon and Anderson, 1982. And we'll see if we can track the reference down for you. So what you have is something very similar to what we saw before, which is, you have uranium-234, that's going to decay into thorium-230, into a dissolved phase.

That dissolved phase has two paths. It can either decay itself through radioactive decay, or it can get absorbed onto a particulate phase that would then sink out of the system, being carried with the particles themselves. So the first variant of this we're going to look at is an irreversible scavenging model.

So in irreversible scavenging, there's one kinetic constant. And that's the forward scavenging of dissolved thorium under particulate thorium. And once it gets on there, it never comes back off. So the equations you would write out would be an equation for dissolved thorium, so the rate of change of dissolved thorium with time.

And we're going to be interested in the steady-state solutions of that. And so that's going to equal the activity of U-234. So that's the production term. And then we would have these two loss terms, one due to decay and one due to scavenging. And they would be multiplied by the dissolved thorium concentration.

Similarly, you would have an equation for the particulate thorium and its steady state. The source term would be coming from the scavenging of the dissolved phase. There would be decay of the particulate thorium.

And then there'd be a loss term, where the loss term is going to be the vertical gradient, the vertical gradient of the particulate thorium and the sinking velocity. So this would be something that would look like this. Let's say you had a layer, a layer bounded by say two surfaces.

So inside the layer, you have formation of particulate thorium. And you would have two fluxes of particulate thorium, one at the top of the interface, one at the bottom of the interface. Flux is going to equal w, the sinking velocity, times the thorium concentration.

And so you would have a flux in and a flux out. And so if you have net formation of particulate thorium in that box, the flux out has to exceed the flux in. So if the formation is greater than zero, then flux out has to be greater than flux in.

And the way of looking at that, the way of thinking about that is by looking at the gradient, you're actually taking this depth range, delta z, and looking at the rate of change of that flux, assuming that w is constant over that small interval.

And so this term basically gives you the divergence of the flux in and flux out term. And at steady state, if there was just production, those two would have to equal each other. Does that make sense to you guys? Does that make sense? Yeah, question?

AUDIENCE: If flux out is greater than flux in, I would think that the particulate thorium concentration would be going down. And you have formation greater than 0, I'm not sure what that means.

SCOTT DONEY: OK, so let's look back at this equation. Let's ignore for the moment the decay of the particulate thorium. This would say that the formation term, K1, thorium dissolved. So that would be formation of the particulate thorium. That's the adsorption of the dissolved thorium onto the particles.

It has to equal the gradient times the sinking velocity. And so let's say we start off with a flux at some point and then you're producing more particulate thorium, the next point should have a larger flux. And then again, the next point should have a larger flux, the next point should have a larger flux.

If I looked at the gradient of flux, which would just be d dz of W thorium P, and then we're going to approximate that by saying W is constant, you get that term. And so this is actually positive because it's increasing as you increase z. And that's just balancing the formation. So if you're forming it in the water column, it has to go someplace.

The decay term isn't going to be big enough because it's not going to hang around for very long because it's going to be scavenged onto particles that sink out. And if it's scavenging onto sinking particles, then the sinking flux of thorium has to actually increase with depth to basically balance the formation in the water column.

Does that answer that? Does that answer your question?

AUDIENCE: Scott, you're forming particulate thorium at the same rate throughout the water column, correct?

SCOTT DONEY: Yes, the assumption--

AUDIENCE: It falls out. So as you go down deeper, there's more and more falling out because there's more and more above you.

AUDIENCE: Yeah.

SCOTT DONEY: The assumption, if we went all the way back up here, was that you have a fairly uniform source due to uranium-234 decay. So you're forming thorium-230 throughout the water column at a fairly uniform rate, barring small deviations in salinity. But we'll ignore that.

AUDIENCE: [INAUDIBLE].

SCOTT DONEY: And the thorium is getting scavenged fairly quickly--

AUDIENCE: Yeah.

SCOTT DONEY: --onto the sinking particles. And so essentially, the depth is integrating all of the thorium-- the flux at any particular depth is integrating all of the production that has occurred above that depth. Let's see. I'm trying to see, I have another way that I explained it in the notes. Let me go back, and we'll try that and see if that helps.

AUDIENCE: A quick clarification.

SCOTT DONEY: Yeah?

AUDIENCE: Let's say we have a formation form greater than 0. You're talking about formation of dissolved thorium?

SCOTT DONEY: Well, here I was talking about the formation of-- There's two formations, right? There's the production of dissolved thorium from uranium decay. And that can go two pathways. It can either decay itself or it can get scavenged onto thorium. When it gets scavenged onto thorium, you can think of it as the formation of particulate.

It gets scavenged onto particles, you can think of that as the formation of particulate thorium. And so once it gets scavenged onto there, you have this net flow of thorium onto the particles. So you have a net production term. At steady state, something has to balance that. And the sinking-out flux is balancing that.

Maybe let me try showing this in equations and see if that makes sense. So if I take this equation up here and assume steady state, which I did, and then rearrange it, I would get that the activity of uranium-234 would equal K1 thorium dissolved. So this is the scavenging term plus the decay term.

We're going to make the assumption that for thorium-230, that K1 is much greater than lambda. Basically, the scavenging is going to dominate over decay in the water column. And this would then allow us to approximate. This can be written as thorium dissolved equals the activity of uranium-234 over K1 plus lambda.

With this approximation, that collapses down. And we get that the thorium dissolved concentration is approximately equal to the activity of uranium-234 over the scavenging coefficient.

AUDIENCE: Question about that.

SCOTT DONEY: Sure.

AUDIENCE: So generally, we used to always pick things where the scavenging rate was on the order of your timescale of the life or whatever. Because otherwise, you're using a meter stick to measure the distance to the moon or something. You know what I mean. It's not an appropriate measurement.

SCOTT DONEY: This isn't perhaps ideal. Because what you'll see is that the amount of thorium that's left in the water column is very small relative to the uranium activity. We'll show that in a minute. The problem is that there's not another set of isotope systematics that is better and easily measured. So you take what you got. And in this case, the radionuclides just don't line up as well with the processes.

AUDIENCE: [INAUDIBLE].

SCOTT DONEY: That said, as long as you can make precise measurements of thorium, you can use this. But what you'll find is that thorium concentrations are orders of magnitude lower than the original parent. So it's quite a ways out of secular equilibrium. I don't know if I have a plot of that. Well, you'll see that in the homework, the homework that goes online tonight.

So what does that say? If thorium dissolved is approximately equal to the uranium activity over K1, if we were to plot that with depth, we know that uranium is basically a conserved species in seawater. It's only going to vary with salinity.

So the thorium dissolved concentration is going to be approximately a constant with depth, assuming that K1 is constant. And we'll say we're dealing with a homogeneous water column for the moment. Now, if we go back to the original equation for particulate thorium, we can write out similarly and solve this equation.

Now, we now know what thorium dissolved is, right? We have an approximation for that. So I'm going to plug that in. And so from the d thorium particulate dt equation, we're going to get that the activity of U-234 is going to equal lambda thorium particle. So this is now the formation of dissolved thorium from uranium-234.

And remember, we approximated thorium dissolve times K1 is equal to the uranium activity. So we're going to plug that in there. We have gamma, we have the loss rate of particulate thorium by radioactive decay. And then we have wd thorium p dz.

We're going to make the assumption now that the activity of uranium-234 is much greater than the activity of thorium on particles. Remember, gamma times thorium, the decay constant times the number of atoms just gives you the activity.

And then that will allow us to solve for-- U-234 is approximately equal to-- this is an assumption-- solve for the vertical gradient of the particulate thorium. So the vertical gradient of the particulate thorium is equal to a constant times W.

If we assume W is constant, that says that the thorium particulate concentration is just going to be equal to A U-234 over W times depth. So if we go back to our diagram up here, this would be the dissolve curve, this would be the particulate curve.

So you'd expect to see uniform thorium concentration and increasing particle concentrations of thorium. And since flux equals W thorium P, the flux of thorium should also increase linearly with depth. Now, that's the prediction. This is the prediction for the irreversible model.

The problem is that when people went out and actually made observations by either putting out sediment traps and measuring the flux, or pumping large volumes of seawater at depth to see how much thorium was on the particles, what they observed was that thorium dissolved actually increased with depth and so did thorium particulate.

So there must be something wrong with the irreversible model because it didn't work. So Bacon and Anderson formulated a slightly more complicated model, one where they now allow reversible scavenging. So the uranium still goes to the dissolved.

But then, you can have dissolved thorium going onto the particulate phase and then thorium coming off the particulate phase going back into the dissolved pool. And then you have sinking. And you also have decay. You also have decay of this, but it's very, very small.

We can similarly then write out a set of equations, again, for thorium dissolved, assume steady state. It's going to look very similar to the last one, except for the addition of one term. So you have production by radioactive decay symbolized by the activity of U-234.

You have a loss term of scavenging a dissolved thorium onto the particles. You have radioactive decay. And then you have a source term due to the release of thorium off of the particulate phase. That's a K minus 1. Often, you'll see rates written as K1 and K minus 1.

So K1 is the forward reaction for 1, K minus 1 is the backward reaction rate for equation 1. Then we'd have the same sort of thing for the particulate phase, where you'd have K1, thorium dissolve, plus w d thorium P dz minus K minus 1 thorium P minus lambda thorium P.

And if we make the same assumptions as we made earlier, we'll say K1 and K minus 1 are much greater than lambda, then you get that thorium dissolved is approximately equal to A U-234 plus K minus 1 thorium particulate over K1.

So before, we got a term, that it was the dissolved thorium depended solely on the activity of uranium-234. Now with reversible dissociation, we find that it also depends upon the flux. So this is a production term because it's radioactive decay. This is a production term for dissolved thorium because it's a release of thorium. And so we actually need to account for both of those.

Let's see, the model for dissolved thorium is actually somewhat more complicated. But we can still approximate it. You write out a very long equation, but what you find when you actually scale things properly is that the particulate thorium still scales approximately as U-234 activity over the sinking velocity, which is what we found for the irreversible model.

And that's simply because the end reaction or the main sink of thorium production from uranium decay still is the sinking thorium flux on the particles. So it has to get there somehow. And so it eventually all does still pileup in the particles and sink out.

And the nice thing is, this now is much more consistent, this simple, reversible model is much more consistent with the observations in that you have dissolved thorium increasing linearly with depth. And that increase has to do with-- it's basically scaling because there's more particulate thorium at depth that's releasing more dissolved thorium at depth from this term.

I had mentioned earlier this assumption that the scavenging rates were much greater than lambda. The half-life was in the order, 75,000 years. The particle residence time, based on estimates of thorium in the dissolved phase and in the particulate phase, is only about 40 years.

And so very little of the thorium actually hangs around long enough to decay in the water column. Almost all of it is scavenged onto particles on some decadal timescale and then ends up sinking out to the bottom.

Now, in addition to being useful for estimating scavenging rates-- so these are scavenging rates. They tell you a lot about, particularly, this whole solution that the irreversible model didn't work. There needs to be some way for exchanging thorium on and off of particles.

Now, the next step would be, if you could actually start to differentiate between small particles and large particles, you might be able to begin to distinguish some of the models that we talked about earlier, between whether the flux of organic matter is simply sinking down and decaying, or whether that sinking flux might get turned into smaller particles and then aggregate back to larger particles, sink down, smaller particles, larger particles.

This solution where you see this increase in thorium with depth, says that it's likely that at least thorium must be coming off of the large particles that are sinking down. Because that's what's transporting additional thorium down to depth. It's likely that organic matter is also coming off and on, as well, associated with these reversible processes.

So the thorium data and some of the other radionuclides are starting to elucidate what the interactions are between the different pools of small particles and large particles. But the conclusions aren't yet robust enough to be completely convincing, in part because these measurements are fairly hard and there isn't enough data yet. Or at least, it's on the borderline of having enough data to really make a good case.

There's one other thing I wanted to say about the thorium before we move to protactinium. Oh, that's right. The other thing is you can use thorium-230 as a deep sediment trap calibration. Because if we go back up, remember, actually, you can look here, that this particulate thorium flux is increasing as we go down the water column.

And since you know the activity of uranium-234 and you know the depth over which you're integrating-- sorry, I'd forgotten that Z, I think, when I first wrote this out. This is the same as the irreversible case where it's the integrated over Z. You might not know W specifically, you might not know the thorium particulate concentration specifically, but the flux is constrained by the total amount of activity of uranium-234 and the depth.

And so if you have a sediment trap where you can measure how much thorium-230 ends up in your trap for a particular time-- that would be sinking-out flux of thorium-230-- you can compare that to what you expect based on the amount of decay of uranium-234 in the overlying water column. And if those don't match, then probably something's wrong with your sediment trap. There's been some hydrodynamic effect and you've either over collected or under collected.

Similarly, this is often and commonly used in sediment work to look at the accumulation in the surface layer of thorium-230, basically, the flux of thorium-230 that's making it into the sediments, and comparing that with the overlying activity of uranium-234 to see if there's winnowing or convergence of sediments.

If you're in a spot where there's bottom currents that are resuspending sediments and then depositing it all in one spot-- it's like in a snowstorm, when the wind blows and then all the snow piles up on the side of your garage or the side of your house, and there's no snow out on the street. Well, the same thing happens with sediments.

And this gives you an idea or a calibration point for saying whether there's been excess deposition of sediments or a deficit of sediments. You can use the thorium-230 flux estimates in the water column to get at that and calibrate your sediment data as well, so surface sediments. Thorium-230, that I want to go over, and that has to do with comparing thorium-230 with another isotope system, namely protactinium.

So thorium-230 has a half-life, we said, of about-- it's either 72 or 75, now I'm forgetting, 72,000. Protactinium-231 has a half-life of 32,000 years. So they both have fairly long, half-lives. And protactinium-231, the source of it is uranium-235. So all of what we've said about uranium being stable and conservative in seawater also holds for protactinium.

So just as how you can use your uranium estimates to come up with a source flux of thorium, you can do the same thing for protactinium. So it has a known seawater source. Now, the difference is that thorium is more particle reactive than protactinium.

And so the idea is that you know the production ratio of protactinium to thorium in the water column. The thorium is assumed to be removed locally. So all the thorium that forms in the water column sinks out right underneath where it's formed. The protactinium eventually gets scavenged, but it can move laterally before scavenging.

So protactinium, it's not scavenged as quickly, so it might advect a bit. Remember, we were saying that the scavenging timescale for thorium was about 40 years. Protactinium might be more like a couple of hundred. And so it can actually in the deep water, it can move.

And what you often see, so this is about 40 years, this scavenging time. This is more like 100 to 200 years of scavenging time. And if you were to plot, make a little schematic of your ocean, so you have thorium and protactinium being formed in the water column. Some of it's going to sink and be scavenged right there.

And some of the protactinium is actually going to advect over and get scavenged someplace else. And in particular, it's going to get scavenged in regions like the margins where you have high productivity and high organic flux. So regions such as the margins, if there's just more organic flux sinking down, you have more surface area under which to scavenge.

So this would be a region of high scavenging. And this would be low scavenging. So if you were to look in the sediments or in the sediment traps, what you'd find is that out here, you would have low protactinium-to-thorium ratios. And here you would have high protactinium-to-thorium ratios.

With the argument that all the thorium is constant because it just depends upon water depth, but that some of the protactinium that was formed out here that it should have fallen here had a long enough time that it ended up in this high-scavenging environment, and it got trapped and removed in the margins.

So there's been considerable work to understand this as a modern day proxy for scavenging. But you can also use it in a paleo sense, because these isotopes have a fairly long half-life. So you can go back through the glacial-interglacial cycles and see, did scavenging change?

After you've decay corrected them, did my accumulation of protactinium to thorium in the open ocean or protactinium to thorium in the margins change during glacial cycles? Which might tell you something about how productivity changed there relative to modern conditions.

So any questions on uranium isotopes, thorium isotopes? Because we're going to change gears a little bit. Nope? Any questions up at MIT? OK. So far we've been talking a lot about sinking particles.

We're now going to go back, remember, so this is, say, the euphotic zone. And there were two pathways we talked about for export. There was the particulate organic matter pathway. But there's also this dissolved organic matter pathway.

And so we want to go back and talk a little bit about dissolved organic matter and how that impacts export and what the fate of that dissolved organic matter is. So I'm just going to flip the page so I have a clean page.

OK, so dissolved organic matter. We've talked a lot that we don't know the chemical characterization of DOM as well as we would like. It's a very heterogeneous set of organic compounds, many of which were not what was originally produced.

The DOM has undergone chemical reactions and cross-linking. And so some fraction of it is a large geopolymer. And so it's hard to characterize, other than in some of the bulk characteristics, which we talked a little bit about and we'll talk a little bit more today.

And we talked the other day about its measurement using things like UV oxidation or high-temperature combustion, where you're basically just burning or oxidizing the dissolved organic matter, turning it into CO2 and then analyzing the CO2.

If you go out in the water column and look in the upper thermocline, so this would be the upper 1,000 meters, and look at the dissolved organic matter as a function of depth, by the time you get down to about 1,000 meters, you're going to have a fairly uniform background concentration of about 40 micromoles per kilogram.

And as you head up to the surface, in many places, you'll actually see increases, with surface values ranging between, say, 60 and maybe 90 micromoles per kilogram. And those are micromoles of carbon. These are in places like the subtropics and convergence zones.

Subtopics are regions of convergence. Remember, the water is being upwelled in the subpolar and the equator. And so the water in the subtropics has been at the surface for a fair length of time. And if this organic matter pool is kind of building up, it would be transported into the middle of the subtropics.

And so it's had some time to build up concentrations. If you look in the polar waters, particularly in the Southern Ocean, they tend to have lower dissolved organic carbon concentrations, not that much above this deep background. So that gives you some sense of the profile with depth.

We could also look, for example, along the path of deep water formation. So if we started in the North Atlantic, Southern Ocean, North Pacific, now we expect the nutrient concentrations to do what, as you go from the deep North Atlantic? So this would be deep. To go from the deep North Atlantic to the deep North Pacific, nutrients will?

AUDIENCE: Increase.

SCOTT DONEY: Increase. Oxygen is going to?

AUDIENCE: Decrease.

SCOTT DONEY: Decrease. Some of the early data suggested that there was a slight decrease of dissolved organic matter, dissolved organic carbon, from something like maybe 48 to 34. The more recent data, it looks more like that. And so it's not completely clear that there is a gradient.

There may be, but that still needs to be worked out. And in fact, right now they're trying to collect enough dissolved organic carbon samples on some of the new global transects to be able to really clarify what the deep water concentrations of DOC are and whether we can map them out as well as we can map out nutrients and things like that.

Now, these concentrations are actually fairly high. They're not as high obviously, as dissolved inorganic carbon. Remember, dissolved inorganic carbon, DIC, was something like approximately 2,000 micromoles per kilogram.

But 40 is a lot of organic matter. And 60 to 90 is a huge amount of organic matter, particularly in the subtropics, where the amount of biomass or the amount of particulate organic matter may be one or two orders of magnitude smaller.

So there's a lot more DOC than there is POC in the ocean. And the global estimates are that there's something around 700 petagrams carbon as DOC, where there was only about, say, 3 petagrams carbon as POC.

What else do we know about the dissolved organic pool? Well, we can make measurements of DON. DON is something like 4 to 6 micromoles per kilogram, which would give us C-to-N ratio of 10 to 15. Does anybody remember what typical Redfield ratio is for carbon-to-nitrogen ratios?

AUDIENCE: [INAUDIBLE].

SCOTT DONEY: Carbon to nitrogen, not carbon to phosphorus.

AUDIENCE: 106 to 16.

SCOTT DONEY: 106 to 16, so 6.6. So by comparison, Redfield would be about 6.6. So the material is carbon-rich or nitrogen-poor. If you were to go down the list of carbohydrate, protein, DNA, lipid, you'd be looking at things like carbohydrates, just based on C-to-N ratios.

You might think that, well, maybe the source material for DOC looks more like carbohydrates than it would, say, proteins, because the C-to-N ratio of carbohydrates is fairly high, it's carbon-rich material, where amino acids have a lot of nitrogen in them.

AUDIENCE: I have a question.

SCOTT DONEY: Sure.

AUDIENCE: Backing up to the deep water graph. When you say DOC, are you meaning interchangeable with DOM?

SCOTT DONEY: Yeah, this was in carbon. If I go back up to this plot, these concentrations, actually, these were the amount of carbon in DOM. So these measurements were based on carbon measurements.

These are carbon measurements. And now I'm saying, well, what are the other components? How much nitrogen and how much phosphorus is in that organic matter? Is that OK?

AUDIENCE: Yeah, along the trajectory from North Atlantic to North Pacific?

SCOTT DONEY: Yeah.

AUDIENCE: I guess I would think that more organic matter is either sinking or being dropped and it would increase. So why is it decreasing and not increasing? And then if DOC has a long residence time, it's pretty stable. So it's not being destroyed by other processes. Why would it decrease rather than increase?

SCOTT DONEY: Well, that's a good question. If it's decreasing, that means there has to be a net loss. If it truly was decreasing-- and what it may be, from some of the data I've seen, what it might end up being once we have more data is, there was a sharp decrease in the North Atlantic.

And then it might be relatively flat, and then a little bit of a decrease in the North Pacific. The original paper didn't have enough data to well describe this curve. And then there might be some scatter. So let's say there's a net loss.

So you mentioned there might be a source due to decaying organic particles. So along this trajectory, particles are sinking down. And some of that, those particles are being destroyed and forming new dissolved organic matter. What would be a sink?

AUDIENCE: Water upwelling out of the deep water?

SCOTT DONEY: Yeah. Another one would be a few 100 years to 1,000 years' lifetime, maybe some of it's being removed by respiration. So based solely on this kind of plot, you would say that, well, there might be a source, but the net sink from respiration has to be larger than that. So as the water ages, you're losing dissolved organic matter in the deep water.

That's certainly what you would think from this plot, where you've got, in some regions, more dissolved organic matter in the surface region and less at depth, that as you move down the water column, this dissolved organic matter has been respired. If this water, some of this gets mixed down or advected down, there must be some respiration going on to remove that dissolved organic matter.

But that's a good question. In fact, one of the things people are looking at right now are one fraction or subset of this dissolved organic matter is the part that's colored, that's chromophoric. So remember we talked a little bit when we were talking about optics, how the junk, the gelbstoff, in the water absorbs a lot of photons, particularly down into the blue region.

Well, you can actually measure that and look at it in the deep water. And one of the questions they still don't know in the deep water is, is respiration a bigger sink than release of, say, chromophoric dissolved organic matter from particles is a net source? And so they don't even know, if you were to take a parcel and age it, we think if you age a parcel, even in the deep water, that dissolved organic matter will go down, that there is a net sink over time.

But for the chromophoric subset or subfraction we don't even know what the sign of that is yet. There's conflicting data on that. Yeah, that was a good question. Sorry, I had looked at this plot long enough, I didn't even think to put it in the right context. So that was a good question. Does that make sense to you guys?

AUDIENCE: Another one I guess I don't understand is, you said earlier that the dissolved organic matter is resistant to being respired and has a long residence time.

SCOTT DONEY: Yeah.

AUDIENCE: You're making the case that it respires in the deep ocean. And you're simultaneously making the case that it's accumulating in the surface because of ocean circulation.

SCOTT DONEY: Right.

AUDIENCE: But they respire in both spots.

SCOTT DONEY: The question is, in the surface, it's what's the net? In the surface, you have a lot of production. And so you have production of dissolved organic matter. And so the production, let's say we go back to our subtropical gyre. So these are isopycnal surfaces.

So let's say you have upwelling of water and net convergence. And along the way you have production of DOM. You would also have some respiration. But let's say that respiration is slower than the production term. So as you moved along that axis, you might see DOM concentrations increasing as you got into the interior of the subtropical gyre.

But once some of this water gets pumped down into the deep, there's a lot less production. And in fact, there might be very little production, depending upon what's going on with the particles. Then, respiration is going to take over because you've moved away from the production zone.

And so you just have a net sink. And so the question is, what are the relevant timescales? The timescales in the deep water are hundreds to thousands of years. Up here, we're talking, 1 to maybe 10 years for surface circulation, or tens, tens of years.

And so let's say you had a slow respiration term, even if you had a slow respiration term that was working everywhere, you wouldn't see it up in the surface because it's only working over about 10 years. Where if you've got 1,000 years for that slow respiration term to work in the deep water, it could lead to a slow decline of DOC. So you just have to compare the timescales.

How much time do we have? OK, I did want to get back and cover a couple of other things today. If memory serves, next Tuesday's lecture, we should be on time for finishing this block of lectures.

And so after I'm done today, if there's still questions on dissolved organic matter, we can come back to it on Tuesday. Because I think I should have enough time to finish everything. And then next Thursday, Bill Martin will be talking about some of the sediment fluxes.

So we talked about the DON. The DOP is relatively small. So this would be dissolved organic phosphorus. It's only maybe 0.1 to 0.4 micromolar. It's not nearly as well characterized. Most groups don't measure it.

Most groups who do this measure DOC, some subset of that measure DON, and a smaller subset measure DOP. These would be on the surface. There's hardly any DOP at depth. And this gives C-to-P ratios of something like 200 to 600, which is quite a bit bigger than the canonical Redfield, which is, say, 116.

Now, I've mentioned that DOM is heterogeneous. And it's actually a spectrum. There will be a whole spectrum of characteristics. But we try to lump it into a few pools. So you'll often see DOM fairly artificially partitioned by timescale into a labile component.

And this would have timescales of, say, hours to days. And it's going to be small. It's going to be less than 5 micromoles per kilogram. And that's only going to be in the upper water column. And this is micromoles of carbon. There's a semi-labile. You can tell this is an exact term, semi-labile, of days to maybe months.

And that's going to be anywhere from about 0 up to maybe 30 micromoles carbon per kilogram. And this is, if we go back to that plot on the previous page, this bulge of DOC that you saw in the subtropics, that's this semi-labile stuff. It lasts long enough to build up in the surface.

But it's not so refractory that it isn't respired before it gets into the deep water. And then there's a refractory component, which is hundreds to thousands of years. And that's this background that's about 40 micromoles per kilogram. Now, you do have a net production of DOC near the surface.

And this net production gets exported mostly into the thermocline. And that's via mixing and advection. The current understanding is that in the upper thermocline, if you were to compare the respiration of this dissolved organic carbon versus the total respiration, it's going to be less than about half of total respiration.

There were some hypotheses a decade or so ago-- oh, gosh, no longer than that-- going on two decades ago, that DOC could be the dominant source of organic matter for respiration in the upper thermocline. But a closer examination of the data and new data suggests that that's not actually true.

In addition to DOC spatial gradients, we also know something about DOC dynamics via radiocarbon measurements. So you can measure the radiocarbon content of dissolved organic matter. And a fair amount of this work has been done, one of the leaders on this is Ellen Druffel who's out at UC Irvine, and Bauer. And I can't remember Bauer's first name off the top of my head.

This is fairly new work in the last, oh, say, 10 or 15 years. But if you were to look as a function of depth-- And most of their samples have come from the North Pacific. So if you plot radiocarbon, so you have minus 1,000, which is essentially completely dead, minus 500, 0, 500. So this is delta C-14.

And Bill went over quite a bit about radiocarbon before the midterm. Does anybody remember what the pre-industrial ocean was, say, for inorganic carbon, the surface levels? Well, what was the pre-industrial atmosphere for radiocarbon? What does delta C-14 mean? Oh, come on, we got three minutes left.

AUDIENCE: You don't actually want the content. You just want 0.

SCOTT DONEY: Yeah.

AUDIENCE: OK.

SCOTT DONEY: Why 0?

AUDIENCE: Because that's the definition.

SCOTT DONEY: Yeah the pre-industrial atmosphere had a delta C-14 of approximately 0. That was the standard that's used for delta C-14 was set up such that the pre-industrial atmosphere had about 0. And that meant that freshly produced biological material in the pre-industrial period had a delta, 14C of about 0.

The surface ocean was somewhat depleted. The inorganic pool was somewhat depleted relative to the atmosphere because of reservoir effects. It just takes some time for radiocarbon-rich CO2 to mix into the ocean. And during that time, you have the chance for decay.

So if I were to look at the pre-industrial ocean, the dissolved inorganic carbon would have been slightly below 0 in the surface and then would have decreased some with depth. So this would be DIC. And it decreases with depth because deep water is older than surface water.

And so you'd expect deep DIC pools to be somewhere around minus 200 per mil. Because of the release of C-14 into the atmosphere by weapons testing, if you actually go out and look at the actual values now they're above 0. And that's because you've had an invasion of bomb C-14 into the surface water.

Currently, particulate organic matter all has a bomb spike. If you go out and look at sediment trap material or even suspended particles, they tend to be elevated above the DIC concentrations and elevated above what we think pre-industrial levels were. This is one line of evidence that the suspended particles in the deep ocean have to be communicating with the large sinking particles.

Because if you were to go out to the deep North Pacific and look at a suspended particle, if that had advected there from the North Atlantic or the Southern Ocean, it should be a couple hundred years old. It shouldn't have any bomb radiocarbon in it, but they do. And that's another line of evidence that in addition to the thorium isotopes, that there's exchange of material between the sinking particles and the suspended particles.

If we go out and look at the dissolved organic matter, there's a surface increase, but the dissolved organic matter is really old relative to both the current source of particulate organic matter and the current dissolved inorganic carbon pool. So some fraction of the DOC must be really old.

And in fact, if you just do calendar ages based on radiocarbon, you get that in the deep water DOC in the Atlantic is about 4,000 years old. And in the Pacific, it's about 6,000 years old. Now, that doesn't mean, remember, DOC is not a homogeneous organic material. It's heterogeneous.

Some of the DOC might actually be dead. It might have no radiocarbon at all. It might be really refractory. Other components might have some recent, there might be some exchange between the POC and the DOC pool. And in fact, there is evidence for that in the radiocarbon data.

But on the whole, DOC has a much lower radiocarbon. And that's one of the reasons why we talk about DOC as being quite refractory. So we'll stop there. And we'll pick it up with looking at Redfield ratios and preformed nutrients and respiration.