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**PROFESSOR:** So for the next two days, I'm going to talk about marine sediments, which is the field that I work in. And I think of it as a forgotten corner of chemical oceanography. And so I start out these two lectures admitting right off that I'm not going to make anybody a sediment geochemist in two lectures. So I have two real simple goals.

The first one is to make sure you remember that the ocean does have a bottom-- JGOFS aside, where they eliminated the sea floor-- there really is a bottom to the ocean. And second is that it has some important effects, that reactions in the surface of the sediments have some important effects. And I'd like you to look at surface sediments in the same way you look at the air/sea boundary as the interface between the atmosphere is the ocean, same way as you look at estuaries as the interface between rivers and the ocean, or as hydrothermal vent systems as the interface between the deep Earth and the ocean.

The sediments are the interface between-- the sediment-water interface is the interface between the water column and the accumulating sediments. So with that in mind I'm going to ask, why would we study this part of the ocean? After all, the ocean is a huge thing that's several kilometers thick. And the region that I focus on is about 10 to 20 centimeters thick. So it's a very small piece.

But it does have some-- the reactions there are important. And if we look at it in the way I've shown here, where the inputs for the reactions are the particle flux to the sea floor, you can think of the surface of the sediments as being a layer in which reactions occur. Those reactions can have a couple of important consequences.

The first is that they both use up solutes that are present in bottom water. And they produce solutes that can be returned to bottom water. So that solute exchange between the surface of the sediments and the deep ocean, and the water column, be it deep or coastal ocean, can have important effects on ocean chemistry.

The second way it matters is that, say you're a paleoceanographer, and you're interested in studying the record that's preserved in accumulating sediments. Well, then the particle flux to the sea floor has to pass through this layer where lots of reactions occur before those particles become part of the accumulating sediments. And as we'll see, the composition of accumulating sediments is very different from the composition of the particle flux to the sea floor. So if you're interested in interpreting the sedimentary record, it's important not to forget that there's this layer at the sediment surface that the particles have to pass through.

So with that little preamble in mind, we're going to start-- which I hope ties in with what you've been doing up to this point-- with a brief discussion of the composition of the particle flux to the sea floor. After that, we'll talk about the preservation-- we're going to focus on the biogenic components of the particle flux. After that, we'll talk about the preservation rates in a general way of biogenic components of the particle flux.

Once we've done that, I'll remind you of a couple of the consequences of early diagenesis, which we're not going to talk about in any detail, but I stick them in here as a motivation for the things I'm going to talk about later. And after we get through those preambles, we're going to get a little bit more specific, and I'll talk in turn about reactions that organic matter undergoes in the surface sediments. That will take up the rest of today. Then in the lecture on Tuesday, I'll talk about calcium carbonate and biogenic silica, the other two biogenic components of the particle flux.

And for each of those, we'll first talk about mechanism for decomposition or dissolution of the phase. And then we'll talk about what sort of measurements we make to quantify the reactions and to support our descriptions of the mechanisms. So first, the particle flux to the sea floor. And this is just a very brief overview.

On the left-hand side, these are all-- on the left-hand side are fluxes calculated from sediment trap data in milligrams per meter squared per day. On the very left-hand side is the total mass flux. And this range of total mass fluxes from about 50 to 250 milligrams of material per square meter of sediment surface per day is about representative of what you'll see over most of the ocean.

To the right of that, the flux is broken down into four components. The first three, calcium carbonate, organic matter, and opal are the biogenic components of the particle flux. And the fourth one on the far right-hand side in this picture is the lithogenic component. So that's the terrestrial material, which has a lithogenic origin, that falls to the sea floor.

I want you to notice a couple of things. First, in the Atlantic Ocean, which is the top-- well, before I get into that, on the right-hand side is the same data but plotted in composition terms. So it as weight percent of the different components of the flux.

So if we look now at the right-hand side, the thing-- first, if you compare the Atlantic Ocean to the central equatorial Pacific Ocean, you can see that the lithogenic component of the flux is much more important in the Atlantic Ocean than the Pacific, which is what you'd expect, because the central equatorial Pacific is far removed from any continental sources of material.

Again, looking at the lithogenic component, you'll see that this one marked eastern equatorial Atlantic, the lithogenic component is considerably bigger than the one that's marked North Atlantic. That's because this eastern equatorial Atlantic site is just west of the Sahara desert. And so there is a lot of input of Saharan dust at this site. And so the general take-home message is that lithogenic components of the flux are more important the closer you are to the continental sources of the lithogenic material.

The second thing to notice from all of this is that in the deep ocean, the majority of the flux of particles to the seafloor is made up of biogenic components of the flux. And on a mass basis, the most important component of the biogenic flux is calcium carbonate. Where calcium carbonate in these three examples makes up 50% to 60% of the mass flux to the seafloor, organic matter and biogenic silica are opal. Each make up about 10%, or a little bit more.

But I want to show you one more set of data. And the reason to show you this is so that you don't go away thinking that everywhere in the ocean, calcium carbonate is the dominant component of the particle flux to the seafloor. And the counterexample is in the Southern Ocean, where you may have studied already that south of the polar front, going towards the Antarctic continent, surface ocean productivity is dominated by diatom productivity. And as a result of that, close to the Antarctic continent, the flux to the sea floor is dominated not by calcium carbonate, but by biogenic silica.

And what I've shown here are some data collected by Sus Honjo on the AESOPS transect, which went along 170 degrees west from the Antarctic continent, across the polar front, and north into the part of the Southern Ocean that's north of the polar front. And this site, MS-5 here, corresponds to this left-hand point on the graph. It's south of the polar front.

And you can see that in this graph, which shows the components of the particle flux to the sea floor, it's greatly dominated by biogenic silica. But as you move further north, and eventually cross the polar front, the biogenic silica is essentially displaced by calcium carbonate. And calcium carbonate becomes the dominant component, as it is over much of the sea floor.

So the main messages from this are that in the deep ocean, away from the continents, the majority of the flux to the seafloor is made up of biogenic materials. And that over much of the ocean, with the exception of the Southern Ocean, the dominant component of the biogenic flux to the seafloor on a mass basis is calcium carbonate. So I'm just going to summarize here the preservation rates of biogenic components.

So if you go around and measure the accumulation rate of biogenic components in sediments, and compare that to the rain rate to the seafloor and divide the-- well, then you can use those two measurements to calculate what fraction of the flux to the sea floor for a given component is recycled, and what fraction is actually buried in the sediments. And what you find is that for organic matter in the deep sea, preservation rates are always less than 3%, and in many cases, are 1%. So the organic matter that falls to the sea floor is almost all remineralized. It's almost all recycled, with the carbon returned to the water column as CO<sub>2</sub>.

Sticking with organic matter for a minute, the fraction recycled can become somewhat smaller on continent and continental margin sediments, where the burial rates are faster. But in most instances, the recycling rates still are up in the 90% range, but in some cases, which are pretty rare, they can be less than-- the recycling rate can be less than 50%. But the overall message still stays the same, is that almost all the organic matter that falls to the seafloor is recycled rather than being preserved in the sediments.

For calcium carbonate, as we'll talk about on Tuesday, the picture is a little more complicated, where there's a depth in the ocean above which the predominant calcium carbonate mineral in the ocean, which is calcite, is preserved. And below that depth, the water is undersaturated with respect to calcite. And at those depths, calcium carbonate tends to be remineralized.

And that depth is called the calcite saturation horizon. So above the calcite saturation horizon, preservation rates of calcium carbonate in the sediment range from about 30% to 90% of the flux of calcium carbonate to the seafloor. Below the calcite saturation horizon, as you might expect, the preservation rate drops to zero. So that's a picture for calcium carbonate.

For biogenic silica, the median preservation rate throughout the oceans-- so if you compare the burial rate to the flux to the sea floor-- is only about 10%. In 80% of the areas where mass balances have been made, the preservation rate is less than 15%. And so throughout the oceans, the preservation rate of biogenic silica is very low. And so the recycling rate is very high. And so the overall message here is that the biogenic components of the flux to the sea floor are, to a large extent, recycled back. So only a relatively small fraction of the biogenic flux of particles to the sea floor is preserved in the sediments.

Now, I have one specific example, just to show the sorts of measurements that are made to make these mass balance calculations. And this is from a study that was part of the JGOFS project in the central equatorial Pacific. And as part of this study, they measured sediment accumulation rates and the accumulation rate of biogenic components of the sediments. They also measured remineralization rates by measuring fluxes of dissolved reactants and products of decomposition and dissolution reactions across the sediment-water interface.

So for instance, if calcium carbonate is dissolved, that results in a flux of CO<sub>2</sub> out of the sediments into the water column. So if you measure that flux, you can calculate the rate of recycling of the calcium carbonate at the seafloor. And the same sorts of arguments go for biogenic silica and organic matter. So you can measure burial, remineralization rate, and they also measured the rain rates of particles to the seafloor using sediment traps.

So if the system's in steady state, where the input to the sea floor equals the sum of the remineralization rate and the burial rate, then the remineralization rate plus the burial rate should be equal to the rain rate to the sea floor, because only when that's true will the concentrations in the sediments-- or the accumulation rates in the sediments be constant.

**AUDIENCE:** So how do you measure like a carbonate flux in the sediments? Just--

**PROFESSOR:** Which flux? The burial rate or--

**AUDIENCE:** Now, how do you-- the remineralization rate.

**PROFESSOR:** It's a little bit complicated. What you would do is measure the-- there's a few things you can measure. We'll actually talk about this more later.

**AUDIENCE:** Oh, OK. No, that's fine.

**PROFESSOR:** But just when calcium carbonate dissolves, it releases total CO<sub>2</sub> into the water and alkalinity into the water. You can measure the flux of those two across the interface and calculate the dissolution rate of calcium carbonate in the sediments. We'll talk about that more on Tuesday.

And so these guys, this group of investigators, measured burial rates for organic carbon in the black, calcium carbonate in the hatched bars, and opal in the-- or biogenic silica in the unfilled bars here. For burial rates, the burial rate of organic carbon was so small that it doesn't show up on this scale. And so what they did was they had separate measurements of burial, remineralization, and rain, and they added together the burial and the remineralization rate, and said in steady state, that should equal the rain rate.

And what they found was a balance for organic carbon and biogenic silica. And from this, they conclude that-- what I said before, which is that these components of the particles' flux are very nearly totally remineralized in the surface sediments is true. It held at this site. And for calcium carbonate, they actually measured a larger flux from dissolution of calcium carbonate than they measured a rain rate of calcium carbonate to the sea floor.

You can say two things from this, and I'd say the community is split. One is to say, well, these are close enough, and actually, they show that calcium carbonate is basically totally remineralized at this site. Or you can take it at face value and say, what this means is that the sediments aren't in steady state. And more calcium carbonate is dissolving now than it's falling to the sea floor now. But anyway, I include this just to give you an example of a specific case in which these mass balances were calculated, and tell you how the measurements were made, and the sorts of comparisons that are done.

Now, as I've said over and over again, the remineralization rate of these biogenic components of the particle flux to the sea floor tend to be very much greater than their burial rates. And the question is, should we care? Is that important to us? And to answer that question, I've said, well, suppose that you're a paleoceanographer, and you want to measure accumulation rates of some component of the sediments in the past and use that to infer rain rates to the sea floor in the past.

So in order to look at the problem, we'll assume steady state. And I put a star there because obviously, if we're looking about changes in accumulation rates over time, the flux to the sea floor, or the accumulation rate, isn't constant over time. So by assuming steady state, what we mean is that the flux is constant over a long enough time for the sediments to come into a steady state for that flux rate to the sea floor. And once that steady state has been reached, then the flux could change again, and the system would reach a new steady state. But we're talking about one of those periods of constant flux, which is long enough for the sediments to reach a steady state.

So if that's true, if the system is in steady state for a given component of the particle flux, the rain rate to the sea floor must equal the sum of the accumulation rate in the sediments plus the rate at which the component is remineralized. So if you write that in symbols,  $R$ , the rain rate, equals  $A$ , the accumulation rate, plus  $D$ , which I've called the diagenetic reaction rate. If you divide this equation through by  $R$ , and then rearrange it, you get rain rate equals some quantity multiplied by the accumulation rate.

So the way you might use this is if you're measuring accumulation rates at times in the past, and you want to infer past rain rates from that. You will need to multiply the accumulation rate by this quantity that's in the brackets here. So in order to make that inference of rain rates from accumulation rates, you need to know the quantity that's in the brackets.

So in looking at this equation, I've divided it into three cases. First is suppose that the recycling rate is very much smaller than the rain rate. This would be true, say, for the lithogenic flux, which is essentially completely preserved. It essentially doesn't undergo reactions in the surface sediments.

So in that case, this  $D/R$  term would be very small, and the rain rate would be essentially equal to the accumulation rate. If this  $D/R$  term were very small, then still, this quantity in the brackets would be essentially equal to 1. And you could make an easy inference of rain rate from your measured accumulation rates.

The second simple case is if this recycling rate were not insignificant compared to the rain rate, but it's constant. If that's true, then you could measure the ratio of the recycling rate to the rain rate, which would be a constant, and then this quantity in the brackets would be a constant. And it would again be easy to infer rain rates from measured accumulation rates.

But what if you have a case, which is the one that seems to hold over much of the oceans for these biogenic components of the flux, where the recycling rate is very nearly equal to the rain rate? If that's the case, then small changes in this recycling efficiency, or the ratio of  $D/R$  in this equation, would lead to large changes in the rain rate that you'd infer from the accumulation rate independent of any changes in the accumulation rate. And so changes in this quantity in the brackets could mask changes in accumulation rates.

I've just shown that graphically here, where I've plotted the quantity in the brackets on the vertical axis, and the ratio of the recycling rate to the rain rate to the sea floor on the horizontal axis, going from the simple-- what I called case 1, where not much of the material is recycled. And then, in that case, this quantity varies a little bit, but not too much. So you're pretty safe inferring rain rates from accumulation rates.

But if you get to the case where the recycling efficiency,  $D/R$ , exceeds 80% then small changes in  $D/R$  lead to very large changes in the inferred accumulation rate. So this curve becomes very steep. And so if you're a paleoceanographer, it's probably a good idea to find some proxy for the biogenic components of the flux to the sea floor, because measuring those components directly is-- measurements of accumulation rates of those biogenic components directly are going to be difficult to interpret.

Now, some motivations for not pulling the plug on me now, and listening for a little bit longer, consequences of early diagenesis. First, we talked about-- we've just talked about low rates of preservation of biogenic components and what that means for interpreting the sedimentary record. Second, another long timescale-- in fact, a very long timescale process-- is how early diagenesis in marine sediments affects the atmospheric oxygen level. And here, it's a simple enough picture.

Oxygen is consumed on the continents by weathering. If the oxygen level in the atmosphere is to be constant, then the excess of photosynthesis, which releases oxygen to the atmosphere, over respiration, which removes oxygen, must balance that consumption of the oxygen from the atmosphere by weathering. Did I say that clearly enough?

For the oxygen level to be constant in the atmosphere, processes which consume oxygen have to be balanced by processes which produce oxygen. Oxygen is produced by the excess of photosynthesis over respiration. It's consumed by weathering processes. So those need to be equal.

In the ocean, photosynthesis occurs in the surface ocean. Much of the organic matter-- most of the organic matter that's produced is respired, is consumed by respiration in the water column, but a little bit is left over to accumulate in the sediments. And the fraction that accumulates in the sediments is determined, to some extent, by processes that recycle organic matter in the sediments.

And in addition to that, once oxygen is used up in the sediments, then other electron acceptors become important. And two of those, the most important, are sulfate and iron. When sulfate and iron are used to oxidize organic matter anaerobically in sediments, then the products are reduced iron and reduced sulfur. Some of that reduced iron and sulfur is buried as pyrite, as iron sulfides.

To the extent that those are buried, it represents a source of oxygen to the atmosphere in the same way that photosynthesis does. So processes in sediments, the burial of organic matter and the burial of reduced iron and sulfur, which are produced by sedimentary processes, are significant components in the long term atmospheric oxygen cycle.

If we move from these longtime scale things to the contemporary ocean, there have been studies of deep water oxygen consumption done. And when measurements of oxygen consumption in the sediments are included in those studies, what they show is that about half of the oxygen consumption below 1,000 meters in the ocean actually occurs in the sediments rather than in the water column. So sedimentary oxygen consumption is an important piece of the deep water oxygen balance.

And then the topic that has been of most interest to people in the last few years is that about half of the denitrification that occurs in the oceans today-- or actually more than half, even-- occurs in sediments. So you might ask yourself why that's true. What condition has to hold in the ocean for denitrification to occur? What has to be true of the water? I bet you've studied this already.

**AUDIENCE:** [INAUDIBLE] anaerobic?

**PROFESSOR:** Yeah. The oxygen has to be gone. So where in the ocean-- where in the water column does denitrification occur throughout the oceans?

**AUDIENCE:** Oxygen minimum zones.

**PROFESSOR:** OK, which are?

**AUDIENCE:** [INAUDIBLE]

**PROFESSOR:** OK, but there's only a very small number of places where the oxygen minimum is intense enough to actually have an anoxic water column. OK, I'll tell you. The Arabian Sea and the Eastern Tropical Pacific north and south of the equator. So there's a very limited number of very limited in extent places where denitrification can occur in the water column.

So why are sediments a better place for denitrification to occur? And what I've shown here is a picture, on the left, a profile of a continental margin. And continental margin has a continental shelf, which is very shallow and flat.

And seaward of the continental shelf, the continental margin slopes relatively rapidly down to the abyssal plain. So it goes from a depth of about 100 meters to a depth of about 4,000 meters over a horizontal scale of maybe 100 kilometers. So that's a region where the depth of the sea floor is changing a lot very fast.

And what I've shown on the right is a plot of the oxygen penetration depth in the sediments as a function of water column depth. So the thickness of the water column overlying the sediments. And I've done it for two continental margins. In the open symbols are the continental margins in the eastern and western North Atlantic Ocean. And the filled triangles are along the continental margin in the Eastern Pacific Ocean, the Northeast Pacific Ocean.

So the first thing to notice is that this oxygen penetration depth scale is in millimeters. And so say, at a water depth of 2,000 meters in the Atlantic Ocean-- so if you're a spot in this picture on the left, which is about where my arrow is there, if you go ahead and measure the oxygen penetration depth in the sediments, oxygen penetrates to a depth of about 5 centimeters. As you go up the slope, if you measure oxygen penetration depths in the sediments, it gets shallower and shallower, until when you get to about 400 meters, oxygen penetration depth in the sediments is less than a centimeter.

So that means only the top-- this much of the sediments actually have oxygen in the pore waters. If you do the same thing in the Pacific Ocean, you find oxygen penetration depths are much shallower. So why would oxygen penetration depths be shallower in sediments on the continental margin in the Pacific ocean? In the Eastern Pacific-- Northeastern Pacific? This has to be stuck in your brain somewhere, just waiting to come out.

What are the oxygen concentrations in the oxygen minimum in the Atlantic compared to in the Pacific? They're much higher. So oxygen concentrations in bottom waters at these Pacific sites are much lower than they are at corresponding depths in the Atlantic Ocean. So oxygen penetration depths in the sediments are much smaller.

So if you go along the continental margin in the Pacific Ocean, oxygen penetration depths vary from about 2 centimeters at a depth of 4,000 meters and decrease in the oxygen minimum to a depth of about half a centimeter. So this means in-- remember, in the water column, there's three places in the ocean where oxygen concentrations in the water get low enough for denitrification to occur. In the sediments, oxygen penetration depths along all of the continental margins are ranged from 5 to half a centimeter.

So there's this region very close to the water column that's anoxic. And as long as the flux of organic matter to the sediments is high enough, denitrification can occur there. And the result of that is that over half the denitrification in the oceans occurs in the sediments. So if you're interested in oceanic nitrogen balances, you shouldn't forget about the sediments.

So now that we've talked in general about reactions in the sediments, we'll get a little more specific and focus on, for the rest of today, the oxidation of organic matter in the sediments. So you might ask how sedimentary processes are different from water column processes. Well, they must be different.

Remember that-- I'm sure you've studied this-- that most of the organic matter that's fixed by photosynthesis in the surface ocean, something like-- well, well over 90%, is respired in the upper 1,000 meters of the water column. So relatively little gets to the seafloor, and what's left is presumably the relatively unreactive components.

So the question is-- and I've already told you that these are almost completely remineralized in the sediments. So they're unreactive in the water column, but they hit the seafloor and conditions have changed so that they'll react. So how are processes in the sediments different?

First is the really obvious one, that there's a lot more particles in sediments than there are in the water column. So the concentration of particles in the water column is on the order of a milligram per liter, but surface sediments are 40% to 70% particles by weight. So they're 30% to 60% water, 40% to 70% particles. So there's a lot more particles. And along with those particles are a lot more bacteria. So it's a great place for reactions to occur.

The second is a question of time. So if you consider a water column that's about 3,500 meters long, and if you consider the large particle flux, which falls at a rate of something like 50 meters a day, then those particles will reside in the water column for about 70 days. Now, if you consider the surface sediments, and here, I've taken as the layer of the sediments in which these "rapid" reactions occur-- "rapid" in quotes-- to be what we call the mixed layer, which is the layer at the surface of that live in the sediments, in the deep sea, in the pelagic ocean, away from the continents, the depth of the mixed layer is about 8 centimeters. And in the open ocean, sedimentation rates are about a centimeter per 1,000 years.

So a particle will reside in that mixed layer where reactions occur for about 8,000 years. In the coastal ocean, mixed layers are thicker, say 20 centimeters. Sedimentation rates are faster, say a tenth of a centimeter per year. So a particle will reside in that mixed layer for about 200 years.

So whereas a particle resides in the water column for on the order of months, it resides in that surface layer of the sediments for hundreds to thousands of years, so there's a lot longer for reactions to occur there. Reactions that are too slow to occur in the water column have plenty of time to happen in the sediments.

And a final way, and this is actually a key to the occurrence of denitrification in sediments, is that the reactants for the processes that occur in the sediments are supplied from above. So the particles fall to the sediment surface. Once they fall there, they can be mixed through the surface sediments. But they arrive at the sediment surface and they react with solutes, and in particular, you can think of oxygen, that diffuse from the water column into the sediments.

So you can see that reactions-- there tends to be a layered structure to zones of reactions that occur in sediments, where first-- that's as far as-- reactants are supplied from above, and the sequence of reactions that occurs tends to make a sort of layered structure in the sediment column-- to a first approximation. So why is that important? When you think about how organic matter is oxidized, and in writing the equation in this funny way, I've assumed that you've already written out equations for the oxidation of organic matter by oxygen, nitrogen, by nitrate.

**AUDIENCE:** Only [INAUDIBLE] respiration.

**PROFESSOR:** OK. Well, then--

**AUDIENCE:** Carrying sea nitrate per [INAUDIBLE] comes after [INAUDIBLE].

**PROFESSOR:** Well, then this equation will look a little odd to you, but it's--

**AUDIENCE:** But it'll be very useful for your homework.

**PROFESSOR:** And anticipating that you've already seen these, I didn't include any stoichiometric information at all. So you're going to have to go somewhere else to get stoichiometry of these reactions. But what I've done is written the reactants on the left-hand side here, and products on the right-hand side, where the reactant obviously is organic matter. And that can react with oxygen.

When organic matter reacts with oxygen, the nitrogen in the organic matter is-- the carbon is oxidized to CO<sub>2</sub>. The nitrogen is oxidized to nitrate. And just to give one more example, the reason I'm going through this will become clear, I hope.

If organic matter is oxidized by nitrate, then the nitrogen in the organic matter ends up as N<sub>2</sub>. And the same for the nitrate-- for the electrons-- nitrate that's used as an electron acceptor, it ends up as N<sub>2</sub>.

When manganese, iron, and sulfate are used as electron acceptors by anaerobic bacteria for organic matter oxidation, then the nitrogen in the organic matter is released as ammonia. It's not further oxidized. And in addition, the manganese oxides are released to the water as dissolved manganese. Iron is dissolved iron. And the sulfur is released as sulfide.

And the reason for going through this is that you can use measurements of solutes in pore waters to tell you which of these reactions is occurring where in the sediment column. You can measure oxygen profiles to tell you the rate of consumption of organic matter by oxygen, and to tell you where in the sediment column oxygen is being used.

You can use nitrate as an indicator of oxic respiration because nitrate is produced, and a denitrification because nitrate is consumed, and so on down the list. And the one thing I'll point out is you can use ammonia profiles in sediments as an indicator of the combined effect of oxidation of organic matter by manganese and iron oxides, and by sulfate sulfur, because it's a product of each of those reactions.

Now, I've written a very simple-- well, simple. If I wrote out one of these equations on its own, it would be a simple picture of a reaction with organic matter plus electron acceptor equals oxidized products. But in reality, you have to be aware that the true mechanisms for these reactions are much more complicated. Bacteria don't bite off pieces of particulate organic matter. Instead, they release enzymes which break down the organic matter into pieces that are small enough for them to incorporate in their cells.

And anaerobic bacteria, at least, can't take organic matter and oxidize it all the way to CO<sub>2</sub>. So it's not a single bacterium that's carrying out the whole process, but it's a consortium of bacteria. But the overall effect is these overall reactions with organic matter plus electron acceptor goes to oxidized products.

And the reason for writing them in that way is that writing them that way allows you to calculate the free energy yield of each of the reactions. And what you find is that the order in which these reactions occur is the order of decreasing free energy yield for this overall reaction. And I was assuming you had done this already, but you haven't. But if you do this calculation, you'll find that the free energy yield for the oxidation of organic matter by oxygen, to CO<sub>2</sub> plus nitrate-- to CO<sub>2</sub> plus nitrate has a higher free energy yield than for the reaction of organic matter with nitrate, which in turn has a higher free energy yield than that of organic matter with manganese oxides, and so on, going down the ladder to iron oxides and sulfate.

So the order of reactions that you would predict based on the free energy yield of the reactions is oxygen first, nitrate second, manganese oxides, iron oxides, sulfate. And if all those electron acceptors are used up and there's nothing left but smaller organic molecules, then organic matter-- carbon reacts with organic carbon and produces methane, actually.

So I've essentially asserted that that's the order in which these reactions occur. So how do we know? We can find out the rates of these reactions and where in the sediment column each of the reactions occurs by measuring benthic fluxes, so exchanges across the sediment-water interface of dissolved reactants and products of these different processes. And we can measure pore water profiles of both reactants, those being oxygen and nitrate and sulfate, and products of the reaction, which can be CO<sub>2</sub>. They can be nitrate or ammonia. And we can also measure the reduced electron acceptors, especially manganese, iron, and sulfide.

Don't use solid phase measurements as a rule to determine these reactions, because, one, they're-- concentrations in the solid phase tend to be quite high. So solid phase profiles are very insensitive to the occurrence of these reactions. And second is that solids are mixed by very complicated particle mixing processes, so it's very difficult to interpret the profiles. So we measure solute profiles as sensitive indicators of these reactions' occurrence and their rates.

So what do these pore water profiles look like? What I've shown here is pore water dissolved oxygen profiles at three places in the ocean, which were intended to show the range of oxygen profiles that you would observe. And all these measurements were done by in-situ microelectrode profiling.

These in-situ instruments measure oxygen electrochemically. So you have an oxygen-sensitive electrode that's mounted on an instrument that sits on the sea floor and has a plate that lowers down by very small and well-controlled steps into the sediments. So you can use the electrode that's attached to that plate to measure dissolved oxygen profile in the pore waters on a very, very fine depth scale of millimeters or even less than millimeters.

So I've shown pore water oxygen profiles at three locations. One is an open ocean place. It happens to be in the Atlantic, at a water depth of 3,200 meters, where the total organic matter oxidation rate, which is essentially equal to the rain rate of organic matter to the sea floor, was 14 micromoles per centimeter squared per year.

And under these conditions, you can see that over a depth of 7 centimeters in the sediment column, oxygen dropped from its bottom water value of about 250 micromolar, down to about 100. So there was lots of oxygen left even at a depth of 7 centimeters in the sediments, these are what we would call deep sea oxic sediments.

The next one, moving to the right, is at a water depth of 600 meters on the Northwest Atlantic continental margin. And here, the rain rate of organic matter to the sea floor was about three times what it was at that deep water site, about 45 micromoles per centimeter squared per year. And here again, this is an oxygen profile measured with an in-situ microelectrode profiler.

Starting in bottom water, hitting the sediment-water interface, and then the oxygen concentration in the pore waters of the sediments drops off to zero at a depth of a little less than 2 centimeters. So now, with three times the flux of organic matter to the seafloor, there's enough organic matter so that the oxygen is completely consumed by a depth of about 1.5 centimeters in the sediments. This would be the oxygen penetration depth that I showed on that earlier plot.

And if we go to a more extreme case of a shallow water coastal sediment, where the organic matter flux to the seafloor is about-- well, 10 times what it was at the margin site. So now, 350 micromoles per centimeter squared per year. This is another in-situ microelectrode oxygen profile. The oxygen penetration depth is about 2.5 millimeters. So here, the sediments become anoxic very close to the interface, because there's a very large flux of organic matter to the seafloor.

So that's what pore water profiles in general look like. So that you have a measurement of the solute concentration in the pore waters that are included in the sediments, and the concentration changes with depth going from the sediment-water interface down. How do you interpret profiles like that? First, we'll talk a little bit about a qualitative interpretation.

If we assume that the system is in steady state, so that the concentration profile is not changing over time, then-- well, also assume constant porosity and diffusivity, but we won't worry about that. So what I've shown on the left-hand side is a hypothetical solute profile of a solute that happens to be increasing with depth below the sediment-water interface. And we'll consider what happens between depth XA and depth XB.

If we draw a straight line between the concentration points corresponding to those two depths-- it's shown in the dashed line here. And what you can see is that at every depth over that interval, the actual concentration of the solute is greater than the concentration along that straight line. Now, the concentration along that straight line is what you'd get if you just mixed water from point A and from point B. The fact that the concentration is higher at every point tells you that over this interval, the solute is being added to the pore waters over that depth interval.

If we take the opposite case, and here, a solute that happens to be decreasing with depth below the sediment-water interface. Again, point A, depth A to depth B. And if we connect the points on the concentration versus depth profile by a straight line, we find that the concentration of this solute is less at every depth than it would be along that straight line. The straight line is the mixing line, which is the line that you would get if the water were being mixed with no reaction. And since the concentration of this solute is less at every depth than the concentration along this mixing line, then the solute must be removed from pore waters over this depth interval.

The reason for going through of complicated picture, rather than just saying, oh, the solute is increasing with depth, therefore, it must be produced, is because you can have situations where the solute is increasing, but over some depth range in its profile, it's actually being consumed. And in that case, you could apply this same criterion. Draw a straight line between the points bounding the interval you're interested in.

If the concentration profile falls above that straight line, then the solute must be added over the interval. If it falls below that straight line, then it must be consumed over the interval. So that's the basis for qualitative interpretations of pore water profiles.

Why are these useful? Well, I've shown you what pore water oxygen profiles look like. Here's a hypothetical picture of what some other solutes might look like as well. So in the dashed line up here is a hypothetical pore water oxygen profile. And over the whole range of this profile, if you apply that straight-line test, you'll find that oxygen is consumed over that interval.

Over this interval where oxygen is consumed, if you apply that same straight-line test to the nitrate profile, you'll find that in the region where oxygen is being consumed, nitrate is produced. Remember that I said that when oxygen is used as an electron acceptor for organic matter oxidation, the organic nitrogen is oxidized all the way to nitrate. So nitrate is produced.

Below this interval, the nitrate profile in this case has a straight line component. That means that over that depth interval, the nitrate would be neither consumed nor produced. It's just diffusing down. It shows manganese profile where if you apply the same tests, manganese is produced over a depth region in the sediments.

But at the very top of the profile, you note that manganese doesn't go all the way to the sediment-water interface. Instead, there's a region at the top of the profile where the manganese that's diffusing up from below is removed from the pore waters by oxidation to manganese oxides. And you can apply these same tests. But the main point of this is that you can look at a suite of pore water profiles, analyze the depth intervals over which the solutes are either produced or consumed, and use that to infer the depth in the sediments over which the reactions that either produce or consume those solutes occur.

So if we go on from that-- we're going to do that in just a minute. But before we do, you should know that people don't just look at them and infer reaction zones. They also use pore water profiles of solutes to calculate reaction rates. And they do that by calculating fluxes.

And in this case, we've assumed it's a simple sediment where the transport process is diffusion of solutes in the pore waters. And the diffusion occurs perpendicular to the sediment water interface. So it occurs up and down

Now, you probably haven't seen Fick's first law. So this is how you calculate a diffusive flux. There is a diffusive flux if there is a concentration gradient. So in this case, the concentration gradient is the change in concentration with depth.

And there's a proportionality constant that you multiply that gradient by to calculate the flux, and that's the diffusion coefficient. So the diffusive flux in water equals diffusion coefficient multiplied by the concentration gradient. And this minus sign means that the diffusive transport is down the concentration gradient.

So for instance, if you look at this profile, from that point there is this point here, the concentration decreases going toward the sediment-water interface. That means the diffusive flux is toward the sediment-water interface. There's an additional thing you have to worry about in sediments, which is, How much of the area actually of sediments is water compared to how much is solids? which are sediment grains, because the solutes are only diffusing through the water.

There's a factor called the porosity that you have to multiply this flux by to account for the fact that part of the path is blocked by sediment grains. So the solutes that are diffusing through the water can only diffuse through part of the cross-sectional area. Is that clear? So the diffusive flux of a solute in sediments is equal to the porosity, which is the volume fraction of water in the sediments multiplied by diffusion coefficient for the solute multiplied by the concentration gradient.

And to take this just one step further, this is actually a typical profile for the nitrate concentration in sediments, where, in the surface of the sediment, organic matter is oxidized by oxygen, and it continues to be oxidized by oxygen until all the oxygen is used up. When the organic matter is oxidized by oxygen, nitrate is released into the pore waters. So if you first do that quantitative interpretation I talked about, you find that this dashed line here is the layer in the sediments in which nitrate is being produced. It's actually important to realize that it goes a little bit below the nitrate maximum.

And the layer below that is the layer in which nitrate is consumed by denitrification. We can calculate the rate at which nitrate is produced in this oxic layer by using a mass balance, where we say the rate of production in the layer has to be equal to the net flux out of the layer. If the concentration is constant within that sediment layer, then the fluxes out have to be exactly equal to the rate at which the solute is produced.

So if we calculate the diffusive flux up out of the sediments at point 1, we calculate the rate at which nitrate is consumed by denitrification at point 2, then the sum of-- the absolute values of those two fluxes has to be equal to the rate at which nitrate is produced in this oxic layer. And we can use stoichiometry from that calculated nitrate flux to tell us the rate of organic matter oxidation by oxygen. But the point of this is just to show you how it's done. And if you're really lucky, Scott will come up with a problem that makes you do it.

**AUDIENCE:** [INAUDIBLE] on your own problem.

**PROFESSOR:** So I've essentially asserted that the order in which electron acceptors are used for oxidation processes in the sediments is oxygen first, nitrate second, and manganese, then iron, then sulfate. So is there evidence that this sequence is actually followed? First, you have to go to a place where the organic matter flux is large enough so that the oxygen is completely consumed in the sediments. That's the first thing that you have to do.

If you go to such a place with a large enough flux of organic matter, you could measure an oxygen profile, like here, and you find that the oxygen decreases from its bottom water value and goes to zero at about 1 centimeter depth. If, at the same place, you measure a pore water nitrate profile, and here, zero is the sediment-water interface. And that's measuring the concentration of nitrate in the pore waters as you go down into the sediments. And the depth scale here is from 0 to 5 centimeters.

See that nitrate is produced in this upper layer, and then immediately below that layer in which nitrate is produced, the profile shape tells you nitrate is being consumed. So just below this oxic layer of the sediments is a layer in which nitrate is used by denitrification to oxidize organic matter. If you go a little bit deeper, and here the indicator is pore water dissolved ammonia concentrations-- remember, ammonia is a product of the oxidation of organic matter by manganese, iron, and sulfate.

You see that the pore water ammonia profile shows that ammonia is actually consumed in the sediments above a depth of about, oh, 3 centimeters or so. But below that, the profile shape tells you that ammonia is produced. If you look at where nitrate goes to zero up here, it's right about at 3 centimeters. So you have a pretty distinct sequence where oxygen is consumed first, then nitrate is consumed, then reactions which release ammonia into the pore water occur. So that's some evidence for the sequence of reactions which I asserted earlier.

And for completeness sake, I'll show you an extreme example of a coastal sediment. Now, remember the rates of organic matter oxidation, or the flux of organic matter to the seafloor, at a deep sea site, is something like 15 micromoles of carbon per square centimeter per year. On a continental margin site, it might be as much as 50. But here, these are results from a site which is actually in Boston Harbor, where the rain rate of organic matter to the sediments is about 850 micromoles of carbon.

So the oxygen penetration depth at this site is on the order of 2 millimeters. It's very shallow. Below that, there's essentially no nitrate visible, because first, this is a very shallow water. It's in about 5 meters water depth. So there's very little nitrate present there, because it's in the euphotic zone. And second, because denitrification is so fast that the nitrate that's produced by oxic organic matter decomposition is essentially immediately used up.

And so you go right into the use of manganese as an electron acceptor. And you can see that manganese-- there's the bottom water value. If my arrow wouldn't keep going away, I'd show it to you. The bottom water value is very close to zero. And right away, in the first pore water sample, there's dissolved manganese present. So manganese is used as an electron acceptor right near the sediment-water interface.

If you look closely at this iron profile, see there's a very thin layer-- it's very hard to see. But if I expanded it, you'd see there's very thin layer where iron is consumed, diffuses up, and is oxidized. It can be oxidized by manganese. And below that, iron is released into the pore waters by decomposition of organic matter using iron oxides.

One point of interest, if you're used to looking at water column data, you think of manganese and iron as trace metals with nanomolar concentrations. If you look at these reducing sediments, manganese concentrations are in the tens of micromoles per liter, and iron actually reaches very nearly millimolar concentrations. So they're not trace metals in these sedimentary pore waters.

We go down here and look at the sulfate profile-- don't look at the open circles. That's a different place. If you look at these triangles, see, sulfate reduction begins at a depth of about 2 and 1/2 or 3 centimeters, which is right about there. So sulfate reduction and iron reduction actually occur in overlapping regions of the sediments, which is actually what you would predict if you calculate the free energy yield of the reactions.

And you see an interesting thing-- so again, the sequence is followed, where you have oxic decomposition, nitrate's not important here-- then decomposition using manganese oxides and iron oxides and sulfate. But you see an interesting thing, if you look at pore water dissolved sulfide profiles, where I've said that sulfide is the reduced product of sulfate reduction. But if you look at this, you see sulfide concentrations are pegged at zero until the depth at which the iron disappears from pore waters. And then sulfide concentrations increase pretty dramatically.

The reason for that is that sulfate reduction and iron reduction occur over pretty much the same interval in these sediments. And that iron, reduced iron, has very insoluble sulfides. And so the sulfide is produced by sulfate reduction reacts with the iron and precipitates out as iron sulfides until all the iron is gone. And then sulfide starts to be released into the pore waters.

Anyway, this is an example-- so I've shown you two examples. One continental margin site and one extreme coastal sediment example, showing you the range of conditions you'd observe. And if you remember back to the very first oxygen profile, I showed you an oxygen profile in an oxic sediment where it never even got close to going to zero. That's a deep sea condition.

To summarize this little section about electron acceptors that are used for organic matter oxidation, I've put together a table which shows, for, first, this table up here, electron acceptors in pelagic sediments. So those are away from the continental margins, out in the open ocean. And these are all examples from the top tour from the equatorial Pacific and the last ones from the equatorial Atlantic, with organic matter oxidation rates that are pretty low, 12 to 20 micromoles of carbon per centimeter squared per year. So those are typical values for the deep sea.

And you find that under these conditions, essentially all the organic matter oxidation occurs using oxygen as an electron acceptor. It's the first one used. There's plenty of it in the bottom water in all these locations. And essentially, what happens is the supply of organic matter runs out before the oxygen runs out. So nearly all the organic matter decomposition uses oxygen as an electron acceptor, just like in the water column.

But if you go to places on continental margins where the supply of organic matter to the seafloor is great enough so that all the oxygen is used up, then you get a little bit different story. And here, I've got examples from the North Atlantic Ocean and from the North Pacific Ocean. In the North Atlantic Ocean, oxygen still accounts for 70% to 95% of all the organic matter oxidation in the sediments. Nitrate accounts for a little bit, and of the remainder, most of it is accounted for by sulfate reduction.

So under these continental margin conditions in the Atlantic, oxygen is the main most important electron acceptor, followed by nitrate. Manganese and iron have a very limited importance, but sulfate reduction can be significant. If you go to the Northeast Pacific Ocean, the story is a little bit different because-- why would it be different?

**AUDIENCE:** [INAUDIBLE]

**PROFESSOR:** I didn't hear you, but I'll bet you said because oxygen concentrations in the bottom water are much lower in the Northeast Pacific. And in fact, there's an intense oxygen minimum. And so in the oxygen minimum-- that's what's shown in this line in the table here-- oxygen only accounts for 5% to 50% and nitrate accounts for most of the rest. Iron and manganese again are not very important, but sulfate reduction is significant.

The Northeast Pacific deeper than the oxygen minimum, you get a picture that's much more like the Atlantic. Oxygen is the most important. In this case, nitrate is second, and sulfate reduction can also be important. So why would nitrate be more important under these conditions in the Pacific than the Atlantic?

**AUDIENCE:** [INAUDIBLE]

**PROFESSOR:** What else is there in the bottom waters? There's more nitrate. So nitrate can diffuse in from the bottom waters. Actually, if you look at-- I showed you a nitrate profile from the Atlantic earlier, where there's actually a nitrate maximum in the sediments, meaning that some of the nitrate that's produced by oxic organic matter decomposition leaves the sediments and isn't used for denitrification.

If you look at nitrate pore water profiles in the Pacific, you see there is no subsurface maximum. Concentration decreases right from the interface, which means that bottom water nitrate is diffusing into the sediments. So that's an added source of nitrate. So nitrate is a little bit more important in the Pacific.

But anyway, all these deep ocean and continental margin sites, oxygen is the most important electron acceptor, except in the oxygen minimum, followed by nitrate and sulfate. Now, in coastal sediments, very shallow water sediments, is a different story where the dominant electron acceptors are iron and sulfur. But there's a catch. And the catch is that the reduced products-- so reduced iron sulfides-- can be mixed back up to the sediment surface. And at the sediment surface, what happens to them? They're oxidized by oxygen.

So even though the pathway for organic matter decomposition is mostly anaerobic, where iron and sulfate are the electron acceptors used by the bacteria, actually the ultimate electron acceptor is still oxygen, because very little of the reduced iron and sulfur are buried. They're mostly mixed back to the surface to be re-oxidized. So they're used over and over again. And oxygen is the ultimate electron acceptor.

Now you've heard more than you ever wanted to know about pore water profiles. So we'll talk for a minute about organic carbon burial in marine sediments. I said way back at the beginning, what the long-term importance of organic matter burial in sediments is, and that's that it represents the net-- the excess of photosynthesis over respiration in the ocean. And so it's a part of the long-term oxygen balance. So there's good reason for studying organic carbon burial in marine sediments, and to understand what makes it change from place to place, and what may make it change over time.

So what's written in this table are three summaries of organic matter burial in marine sediments. The first one is an old one, and it actually doesn't tell you much. The second one, the point of these is to show you that of the total organic carbon that's buried in sediments, by far, the majority of it is buried in the Berner compilation terrigenous deltaic shelf sediments.

And when those were broken down by Hedges and Keil into deltaic sediments plus sediments on the upper shelves and slopes. So what that tells you, if you want to understand organic carbon burial in marine sediments in the locations that are most important, you need to understand organic carbon burial in continental margin sediments, because that's where most of the organic matter burial occurs.

So you could ask yourself, what determines the organic carbon accumulation rate in sediments? And way back when, two camps arose. One camp said, well, what determined-- I think of these as the wishful thinkers-- that what determines the organic matter burial rate in sediments is the productivity of the overlying waters. So if you measure organic carbon burial rates in sediments, that'll give you a picture of productivity in the overlying waters.

The others say, no, that's not true. And they go back to what I discussed earlier, which is the fact that in marine sediments, most of the organic matter that falls to the seafloor is remineralized. So variations in the inputs can be masked by variations in the remineralization rate, or the recycling efficiency of the organic matter.

So how did these two camps, one that says local productivity determines organic carbon accumulation in sediments, and one that says variable preservation determines variations in organic carbon accumulation. And there's actually an important piece to the variable preservation story. And that is that when this argument first arose, the variable preservation was attributed entirely to variations in bottom water oxygen concentration.

They said that if the bottom waters are anoxic, organic matter is preserved to a much greater extent than if bottom waters are oxic. So you could simplify this discussion into pictures like this. The top one is a picture of the organic carbon concentration in sediments around the world, where the darker the color, the higher the organic matter concentration. I put a star there because, remember, up until now, I've talked about organic matter accumulation rates. And that's what I really want to know. I want to know the accumulation rate.

It turns out that if you're looking at gross large-scale features, the concentration variations give you a reasonable picture of accumulation rate variations. But there's a catch, and you can see the catch if you look at these areas of lightly hatched low organic carbon concentration. Have you had your hydrothermal lecture yet? So you know that those follow mid-ocean ridge system. Those are all shallow places in the water. And as we'll see later, those are places where calcium carbonate accumulates.

And so what these low organic carbon concentrations tell you is that the organic matter is being diluted by a lot of calcium carbonate. It doesn't tell you that the accumulation rate of organic matter is lower there. That's an aside. The main point here that I want you to be aware of, because I don't want you to get trapped into equating concentrations and accumulation rates. You can run into problems.

And I used to be an economist and mixing stocks and flows was grounds to get you failed out of all your classes. So I don't want you to do that. But having said, that I'm going to proceed to mix stocks and flows. So these regions--

**AUDIENCE:** You can still do that in fisheries research.

**PROFESSOR:** Oh, can you?

[LAUGHTER]

So anyway, the point here is that the black spots, the black ones, which are high organic carbon concentrations, are along the continental margins. And I've highlighted three spots. Number one is the Arabian Sea. Number two is the Eastern Tropical Pacific. And number three is the West African Coast.

What's shown in the next plot down is a map of oxygen concentrations at the oxygen minimum in the water column, where the black ones are very low oxygen concentrations. And you see that I've labeled the same spots, the Arabian Sea, the West African Coast, and the Eastern Tropical Pacific. And they're not only areas of high organic carbon concentration and accumulation rates, they're also areas of low bottom water oxygen concentration. Well, it turns out that if you take this one step further and look at a map of primary productivity-- this is an ancient map, which I'm sure will make Scott cringe, but it does the purpose here-- see that those same spots labeled 1, 2, and 3 are also areas of high primary productivity.

And so what you see is there's a correspondence between regions of high productivity and high percent organic carbon in sediments. So that bolsters the argument of the overlying water Productivity is what counts. But those are also regions of low bottom water oxygen. And so that also bolstered the argument of the variable preservation rate camp.

And in addition, it's been shown by a number of studies that some naturally occurring molecules require oxygen for decomposition. And so you might reasonably ask yourself, does the sedimentary organic matter accumulation rate actually depend-- the variations, are they determined by variations in overlying water productivity or variations in the preservation rate of the organic matter, or both? What I'm going to show is not an answer to that question. I think I've already made clear where I stand on the issue. I think preservation is important.

But is actually a recent-- well, fairly recent improvement of the argument of how bottom water oxygen concentrations affect organic matter preservation in the sediments, where it used to be just oxic versus anoxic. This reaches a middle ground, this interpretation that I'm going to show. And what these people did was study-- was come up with an idea that they called oxygen exposure time. And in their original work on this, they studied two areas, which were actually very good for this purpose because of their contrasting properties.

They studied the Washington margin, so that's in the Northeastern Pacific off the coast of Washington. And the Mexico margin, so that's, again, Northeast Pacific, but off the coast of Mexico. If you compare these two regions, the Washington margin, which is shown by the squares in these plots that I've shown below it, is a region that has higher productivity than the Mexico margin, but a less intense oxygen minimum. The Mexico margin, which is shown by the circles in these plots, has lower productivity, but a very intense oxygen minimum.

So on the left here is a plot of profile of oxygen in the water column in these regions, where the Washington margin, there is an oxygen minimum, but it's deeper and not as intense in this region from zero to 600 or 700 meters as it is in the Mexico margin, where the water column is anoxic. What's shown on the right are concentrations of organic carbon in the sediments. So on the Washington margin, the organic carbon concentrations are around 2%. In the Mexico margin, the concentrations of organic matter in the sediment run around 10%.

So you can already see where this argument is going in the simple productivity versus preservation discussion, where the site that has an intense oxygen minimum, but lower productivity has a much higher oxygen concentration in the sediments than the site with higher productivity, but a less intense oxygen minimum, saying that preservation rate is a key in determining organic carbon distributions.

What these guys did was, in addition to measuring organic carbon concentrations in the sediments, they also measured oxygen profiles in the sediment pore waters. And with each of those oxygen profiles, they determined the depth below the sediment-water interface at which the oxygen goes to zero. And they called that depth the oxygen penetration depth.

What they were interested in doing was calculating how long a particular particle would be exposed to oxygen after it reaches the sea floor. And they did that by also measuring the sediment accumulation rate at all these places, and dividing this oxygen penetration depth by the sedimentation rate. And the result of that would give you, on average, how long a particle spends in the oxic part of the sediment column. And they called that quantity the oxygen exposure time. So the longer the oxygen exposure time, the longer a sediment particle, or a bit of sedimentary organic matter, is in a region where it's exposed to dissolved oxygen.

And once they made these calculations, they compared the oxygen exposure time for particles at a given site to the organic carbon burial efficiency at that site. And the burial efficiency is here equal to the burial rate divided by the rain rate. And the prediction would be that if oxygen matters-- so if organic matter is oxidized more readily by oxygen than by other electron acceptors, then the longer the oxygen exposure time, the lower the organic carbon burial efficiency will be.

And they came up with a compilation of data that looked like this, where they plotted organic carbon burial efficiency. And here the range is from 0 to 60% versus oxygen exposure time. The vertical axis is linear scale. So burial efficiency is on a linear scale. Oxygen exposure time is on a log scale.

And a very important piece of their conclusion is that they measured oxygen exposure time over a five order of magnitude range. And it's safe to say they wouldn't have come to any conclusion if they'd measured a much smaller range. They're actually very upfront about that, because in this inset here, they plot both on linear scales, and you see that all their data fall in a big clump. They don't start to separate out and let you see a pattern until you plot it on a log scale and look at this very large scale, this very large change in oxygen exposure time.

What you see, if you look at this overall picture, is that there is indeed, over this large range of oxygen exposure times, a decrease on average in organic carbon burial efficiency the longer the oxygen exposure time is. But if you look at any particular spot, the variations are really big. So my conclusion from this was that it's a promising idea that oxygen does matter, and that you can determine how much it matters by measuring this oxygen exposure time thing, but that you really need more information, because there's a lot of variability in the results that isn't explained by this simple model. And in fact, they've gone on in subsequent years to make it a lot more complicated.

One interesting note is that this actually provides a feedback between atmospheric oxygen levels and the organic carbon burial rate. When you get into these arguments, they're very hand-wavy, but they're interesting to think about. If you suppose oxygen exposure time matters, and, say, there's an increase in weathering rates on the continent, or something that increases-- that tends to decrease the level of oxygen in the atmosphere, the level of oxygen in the atmosphere decreases, then less will be mixed down into the deep ocean. So the bottom water oxygen will have lower-- bottom water will have lower oxygen concentration. And other things being equal, the penetration depth of oxygen in the sediments will be smaller.

If that's true, and if this argument is true, then oxygen exposure times will be smaller. So the preservation rate of organic matter will increase, which, remember, means a larger excess of photosynthesis over respiration, which tends to increase the atmospheric oxygen level. So there's a feedback between these inorganic carbon burial and continental weathering. So with that, I'll quit my discussion of organic matter decomposition in sediments.