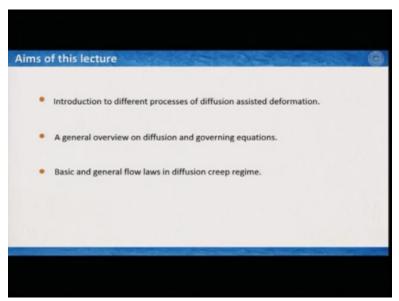
Structural Geology Professor. Santanu Misra Department of Earth Sciences, Indian Institute of Technology Kanpur. Lecture 16 Deformation Mechanism Part 4 Diffusive Mass transfer

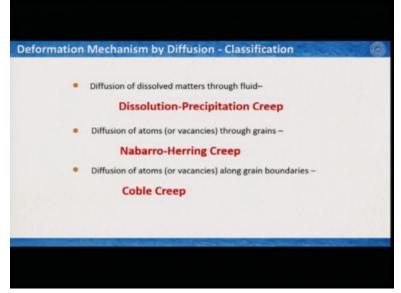
Hello everyone! welcome back again to this online Structural Geology, NPTEL course. We are learning deformation mechanism this week and we are in part 4 of this lecture series. Today, we will learn in this class diffusive mass transfer. We learn crystal defects in part 1, 'cataclastic part deformation' in part 2 and in part 3 went on 'intracrystalline plasticity' and this 1 is the last 1, where we learn diffusive mass transfer or diffusion creep.

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So we will mostly cover in this lecture, some sort of processes, different processes of diffusion assisted deformation. Then we will classify it and see some general overviews on diffusion and their governing equations. And then we also see the relationships between the strain rates, stress and if there are other parameters related to the flow laws in the diffusion creep regime. So these 3 are the major areas that we will cover in this lecture.

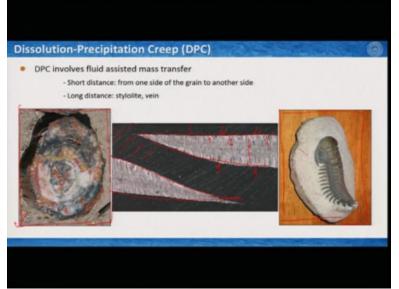
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First of all, let us classify, as geologists or any scientists does that classify the processes diffusion creep mechanisms are generally classified in 3 different classes. The first one is, Diffusion Precipitation Creep or DPC. This is diffusion of dissolved matters through fluid. When that happens, it is Diffusion Precipitation Creep then diffusion of atoms or vacancies through grains.

When that happens, we call it Nabarro Herring Creep. And the diffusion of atoms or vacancies happens along the grain boundaries, and then this is known as Coble Creep. So we will take 1 after another. First, we will look at Diffusion Precipitation Creep, then Nabarro Herring Creep, then Coble Creep.

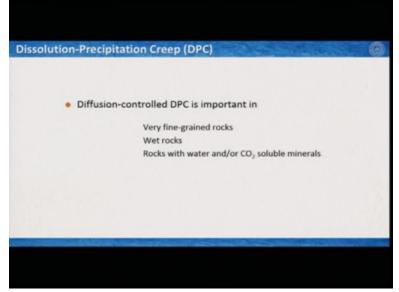
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So Diffusion Precipitation Creep is essentially a creep or diffusive mass transfer by gas strands of any fluid. So it can happen in a short distance, so from one side of the grain to another side. Or it can happen to a very long distance like stylolite, and some vein filling processes. There are two examples in this slide, you can see that these two are two fossils. So one is a petrified wood as you can see in the first image, and we know that initial composition of any tree trunk is carbon, but in a petrified wood is either replaced by silica or carbonates.

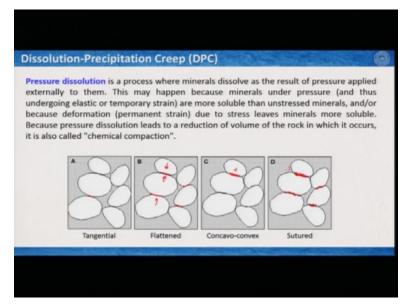
And mostly silica, it is replaced by silica. And therefore the entire thing gets transferred to the silicon and that happens atom by atom diffusion with the existence of some sort of fluid. And the same one is here. We have seen this animal before, this is a trilobite. It is not a carbon anymore. So each and every cells of this animal, each and every atoms of this animal is replaced by silicate materials.

And what we see in the middle; this is thin section of a shell, where you see that this shell has some sort of foliation. And these 2 things are the veins or the fractures that later, so fracture opened; then later got filled by some calcite rich or carbonate rich fluid. And these fluids sort of diffused from matrix, then slowly filled in the open space. So these are the processes; some sort of mass transfer through in assistance of some sort of fluid. (Refer Slide Time: 4:30)



Now diffusion controlled precipitation creep is important in very fine grained rocks and the rock has to be wet and mostly rocks with where you have the minerals in the composition which are soluble in water or carbon dioxide.

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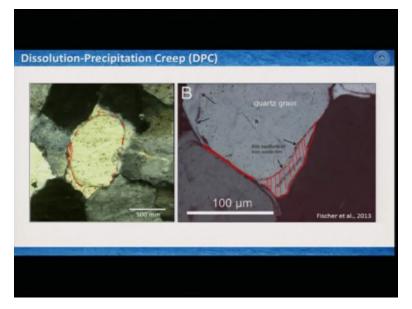
Fundamentals of the dissolution precipitation creep; now there are some ideas that we can think of. So dissolution can happen at a point and dissolution can happen on a surface. So whatever happens when the two points touch each other two surfaces touch each other than a pressure is generated on the surface. And if there are some fluids, then the process is known as pressure induced dissolution or pressure dissolution.

So pressure dissolution is a process where the minerals dissolve as a result of pressure applied externally to them. And this may happen because minerals under pressure and thus some sort of undergoing elastic or temporary strain are more soluble than unstressed minerals.

Thus, it implies if you have a mineral under stress, that has better solubility than a mineral that is not under stress. And because you have some sort of fluid that is helping the minerals to get dissolved, it is also known as mineral compaction. There are these 4 images; a, b, c and d. This is for illustration that tells you; you can imagine that these areas are some sort of sand grains and then they touch each other.

Slowly then, the force is generated on this side and then they dissolve here at the surface and finally this becomes like a sutured boundary; sutures, contact between these grains. So when this

happens, certainly some materials dissolved here, they get dissolved here and they get deposited on the sides of this grain.

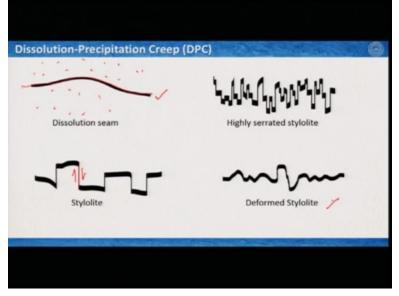


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What we see, these are some microstructure resulting from the dissolution precipitation creep. What we see here that this is certainly the grain you can see under microscope that people have snapped. And then this part, you can see that it had a contact with a grain this side and other side also. So this part of the grain got dissolved and then dissolved material got deposited in this region. This is known as overgrown of quartz. Now I just wiped it out so you can see it very clearly that this is your grain boundary.

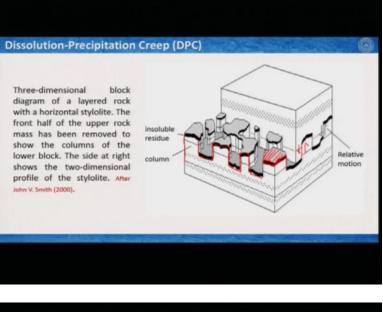
And the grain has overgrown due to precipitation of the dissolved material from this side. You can also see in the second example, here in this image, this is where the dissolution had happened and this was the original grain boundary and this is the overgrowth of this quartz. So if you see this kind of microstructures maybe this has happened due to dissolution precipitation creep.

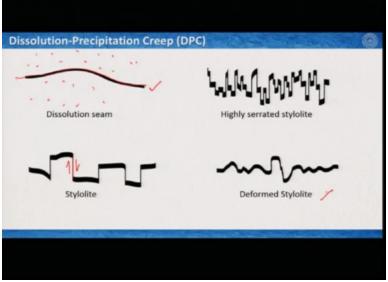
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Now if it happens on the surface; so initially we develop some sort of plane which is known as dissolution seam. So you have 1 grain here or 1 area here. And then you have another area here. They just compress each other here and then a dissolution seam along which the materials get dissolved. You form this dissolution seam and sometimes when you do; you go with higher pressure then this seam tries to slip along this line. and then it develops a structure; we call it stylolite. And if it can happen in a very dense way, so this we call highly serrated stylolite. And this stylolite can also get deformed and then we call it deformed stylolite.

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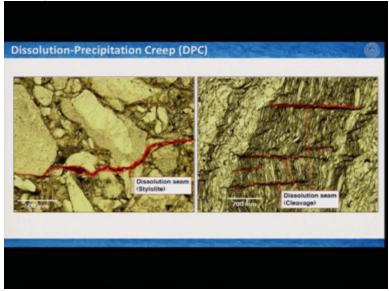




So in 3 dimensions you can see the stylolites. They look like this. In the previous image, you may or in the previous slide you may have seen that these parts are little thicker compared to this part and these parts are thicker because you always have some materials which do not get dissolved in the fluid. So they stay here as a residue and if we try to look at it in 3 dimension, this is how it looks like in a 3 dimensional block.

So you see, these are the columns of the stylolite. And here, in this area, you have this soluble residue. This stays like that and of course if you it from the side, these are your places where you

have some sort of relative displacements of the initial dissolution seam. So this is how the stylolites deform through the process of dissolution precipitation creep.

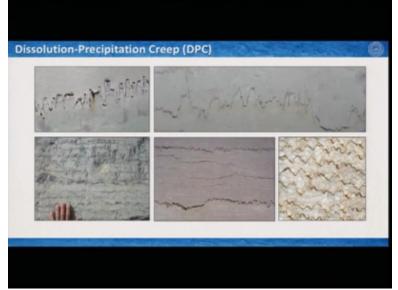


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Now, there are some examples in this image. So the first 1, you can clearly see that something has happened along this and if you can match the illustrations of the previous slides, this is essentially or you can nail it as a dissolution seam or initiation of stylolite. You can also see here, dissolved seam here, and that happens in a regular manner, regular arrangement then it also develops some sort of layers in the structure or repetitive layers in the structure.

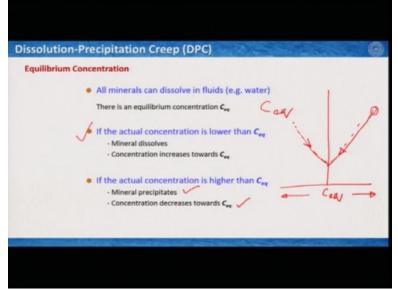
So therefore, you can also call it a cleavage or folliation. So this is the mechanism or this is the process how you see dissolution precipitation creep and this is how they look like under microscope.

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Now I have 5 images which I collected from different web pages or different papers. And I present these 5 images to you to interpret which one is dissolution seam, which one is stylolite, which one is highly serrated stylolite and which one is deformed stylolite. So you can look at these images in detail. Go back to the previous slides and check them and match them and identify by yourselves which 1 is what.

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Now, if we try to theorize this dissolution precipitation creep, then it is important to understand that the solution or the fluid that you have in your system must have the concentration less than the, the concentration has to be less so that the materials dissolve within this and if the concentration is high, then the material would not dissolve into it further; it would precipitate. So there must be some sort of an equilibrium concentration.

So we can think that all minerals can dissolve in fluids. It can be dissolved in water. It can be dissolved in carbon dioxide, or so on and therefore, as we talked about, there is a equilibrium concentration. Let us assign these as Ceq. If the actual concentration is lower than this equilibrium concentration, Ceq, then the minerals do dissolve and then the concentration of this fluid increases towards the equilibrium concentration.

This is very simple because if you are adding more materials to the solution, it would slowly try to saturate and achieve the equilibrium concentration. Otherwise, the actual concentration is higher than the equilibrium concentration. Then the minerals would precipitate and the concentration would decrease towards equilibrium concentration. So that means if I have, this curve, this line as Ceq, then does not matter where I am. It would always approach towards the equilibrium concentration. If this is, this is high and this is low, so if this is low concentration, that means here, then it would dissolve more material and try to achieve the equilibrium

concentration. If in this side, it is over saturated, then it would precipitate materials and it would try to reach the equilibrium concentration as well.

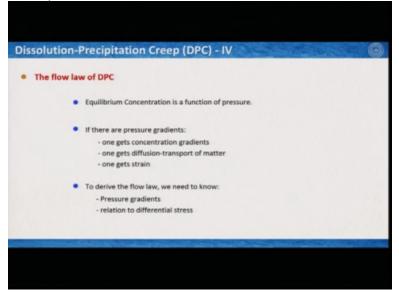
Chemica	Potential and P	ressure			
The	chemical potential ((ψ) is a function of	pressure (P)	$\frac{\partial \psi}{\partial P} = \Omega P$	
Con	centration (C) is pro	portional to	$C = \psi \Leftrightarrow \frac{\partial C}{\partial I}$	$\frac{\partial \psi}{\partial P} = \frac{\partial \psi}{\partial P} = \Omega P$	c=52
The	Equilibrium Concen	tration	$C_{eq} = C_0$	+ 20	
The	Equilibrium Concen	tration	$C_{eq} = C_0$	+ΩP	

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So some equations; these are very simple, do not worry about it. So the chemical potential if we consider as phi is a function of pressure, so you can write this equation. And then concentration is also proportional, is a function of this chemical potential or phi and this is proportional so you can write like this.

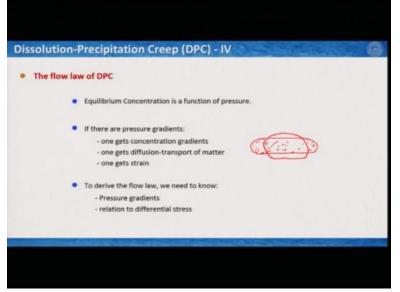
And then by replacing these two equations, I can come to this one equation; C equal to sigma p. Sigma here and here is a constant. So at equilibrium concentration therefore we can come out with this equation which is a function of Pressure, a constant and initial concentration or threshold concentration which is C 0. And this is your equilibrium concentration. This equation is important and we will come back to this soon.

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So if we have to derive the flow law, we are not going derive, we will state it but I am trying to give you some sort of ideas that how these are being derived. So functions that we need to take care of, or parameters that we need to take care of are equilibrium concentration, pressure, chemical potential and so on. And we have seen that equilibrium concentration is function of pressure

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And if there is some sort of pressure gradients, then you also generate concentration gradient. And you also generate diffusion transport of matter and if you diffuse material or if you move material from one end to another end, you change the shape of the material, the block and therefore you generate strength. What I mean by that; if I have a shape or a crystal like this and then I dissolve materials from here and here. These materials get dissolved and if they are being deposited here and here and if I remove this part, so actually achieve something like this.

So clearly, my initial shape was like that; so I certainly have achieved some sort of strain in the crystal. And how it happens and to derive the flow law, you need to know what is the pressure gradient and what is its relation to the differential stress

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Dif	fusion-controlled DP creep DPC involves three sequential steps –
	1. Dissolution reaction
	2. Transport through diffusion through grain boundary fluid
	3. Precipitation reaction
	Gr A ler
• T	te flow Jaw 20 20 a3
	• $\dot{\varepsilon} = A_{\pm} D \frac{\Delta \sigma}{\Delta \tau}$ A_{\pm} : Constant
	• $\dot{\varepsilon} = A_{dc} D \frac{\Delta \sigma}{g^3}$ A_{dc} : Constant D: Diffusion co-efficient
	Linear viscous (Newtonian) creep & Strongly grain size sensitive
	inear viscous (Newtonian) creep & strongly grain size sensitive

And it happens in 3 different stages which are in sequence. First you have to have a dissolution reaction, which means you have to dissolve your materials. Then you have to transport it through the mechanism of diffusion either or in this case, most are on the grain boundary through an open space and then it has to precipitate somewhere. So first one is dissolution reaction, then transport through diffusion grain boundary fluid and precipitation.

The flow law is given in this form: strain rate is equal to a constant Adc, multiplied by diffusion coefficient delta sigma stress and this part is very important G is grain size or sort of length of the grain which is Q. Now, this tells you very clearly that first thing we need to observe is what is the relation between strain rate and stress. If we see this equation - strain rate is proportional to stress, so this is linear. So the flow is Newtonian, we can clearly see from equation. And what is important that strain rate inversely proportional to grain size and that even to the power of cube.

So that means it is extremely grain size sensitive. That means lower the grain size, faster the dissolution precipitation creep will happen or these are the take home messages from these equation, that is this is a Newtonian flow that is the strain rate is linearly proportional to the stress and it is extremely grain size sensitive mechanism where lowering the grain size could make the deformation faster.

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+Δσ.	$\frac{12}{77^2}$		
	$-\Delta \sigma_n/2$	Pressure = Mean stress	1 171
g	A	Compression	Extension
	stress, the grain boundaries $\sigma s_1: P_{eff} = P + \Delta \sigma_n / 2$	s have different effective pressures	
- Perpendicular t	osp: Por P- Ar /2		

Here, we try to see what is the role of the pressure and concentration in activating the dissolution precipitation creep. Now what I see here, if we consider that this cube is a grain where one arm of this grain is has a length of G. And if I apply some force here on this surface, this surface, this stress which is a positive stress, compressive stress. And then therefore on the other side we have a negative stress, a tensile stress on this side. So this surface is under compression and this surface is under tension.

Now under differential stress, at least in this condition the grain boundaries have a different condition. So if I have my initial pressure P which is a confinement of a grain. You can imagine then on this surface you have initial pressure plus this one. And on this surface, on this tensile surface you have P, initial pressure minus this one and if we have to find a mean stress in this illustration, which is this one, then clearly at stress level we have surface somewhere here and on this surface, on this tensile surface we have stress level somewhere here.

So if we now can imagine the time which would try to dissolve the material here. And which would be precipitating on this side here. So therefore the compressional side would dissolve and it would add on the extensional surface. So this drives the transport from compressional grain boundaries to the extensional grain boundaries.

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	um concentration + $\Delta \sigma_n/2$	on the surfa	ace of the grains		
		2 J	Acorago C _{ite}		
		_	Compression	Extension.	
	ntial stress, grain bound of $\sigma_{\mathbf{I}} = C_0 + C_{sq^*} = C_0 + C_{sq^*}$		different equilibrium	concentrations	
- Perpendicu	alar to σ_3 : $C_{ag^*} = C_0 -$	ΩΔσ			

And if we try to look at in terms of equilibrium concentration, and we can think of in a very similar way that we have this side applying some stress and this side we have the tensile domain, so compressive domain, this is tensile domain. So perpendicular to this one, we have very similar equation we have derived. So we have plus 1, minus, so they will be less.

And then we would have higher equilibrium concentration at the compression surface and lower equilibrium concentration at the extensional surface. And these would also drive your transport from compressional grain boundaries to extensional grain boundaries. That means materials would move from this side to this side.

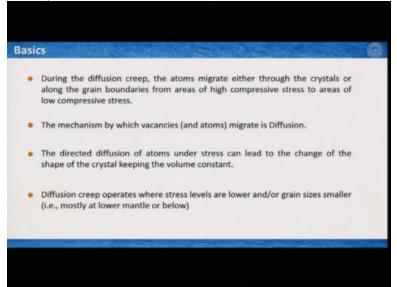
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Equil	ibrium concentra	tion on the su	rface of the gra	uns	
	+ \Delta \sigma_n/2	-Δσ./2	75		<u> </u>
	tion tries to equalize the		Compression		e > Ca
	pressional faces are un sional faces are over s		PRECIPITATION	-00	

Now if I try to combine both then things would move from this side. So if I look only on the surface I clearly can see that this was the square this G and then this side is getting dissolved and is being precipitated here. So I am just showing it in one way. Eventually you are getting something which is greater than G say G prime so clearly G prime is greater than G. And therefore you achieve some sort of strain and slowly you also approach the equilibrium concentration from this part to this part.

So diffusion then tries to equalize the concentration. If that happens then you are doing the transport. Compressional faces are under saturated most of the cases so therefore you would have dissolution. So material will dissolve on compressional surfaces and extensional faces are over saturated therefore you would have precipitation on the surfaces. So these are the 3 basic mechanisms. First you have dissolution, then you have transport and then finally you have precipitation.

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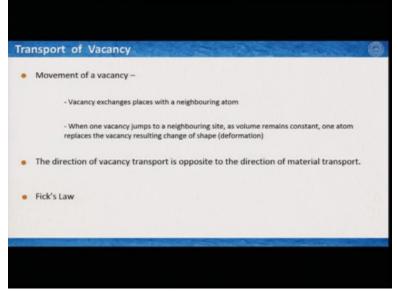


Now let us have a look on the other two processes that is Nabarro Herring Creep and Coble Creep. But before going into the details of this, we will have a look at the basics of the Diffusion Precipitation Creep. So, during these types of Creeps, the atoms move from one side to another side of these grains. The atoms migrate or they can migrate have option to migrate either through the crystals or along the grain boundaries from again the areas of high compressive to areas of low compressive stress.

And therefore, when the atoms move from one end to other end, the vacancies also move from one end to the other end on the other side you have understand it when you have learned the crystal defects. So the mechanisms by which the vacancies and the atoms migrate are known as diffusion. Now the directed diffusion of atoms under stress, that means all the atoms if they are moving to a particular direction and the vacancies to the opposite directions, then this can lead to the change of the shape of the crystal where the volume remains constant.

Characteristically, these diffusion creeps, Nabarro Herring Creeps and the Coble creeps; they do operate where the stress levels are very low and also grain size is extremely smaller. And this we generally get at lower mantle or below of the earth and we will see why the grain size should be smaller. And even between these 2 processes, we need the grain size sensitivity is also different in Nabarro Herring Creep and Coble creep.

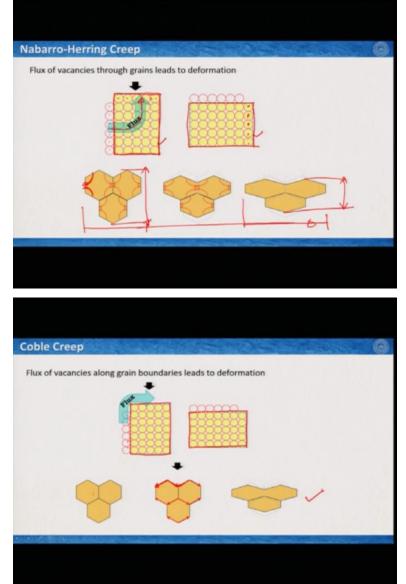
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Now transport of the vacancies, we know that it happens. The vacancies changes places with a neighboring atom. We learnt about it. And we know 1 vacancy jumps to a neighboring site, the volume does not change. The density remains constant. So one atom replaces the vacancy resulting to the change of the shape and therefore we achieve the deformation. We talked about it a many times.

The direction of the vacancy transport is opposite to the direction of material transport. This we also have learnt. And here, Fick's law is somehow important, where Flux is directly proportion to the direction and indirectly proportion to the chemical concentration of the fluid or the material we are talking about.

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Now we will have a look to the two different processes that we have learnt; one is Nabarro Herring Creep and the other is Coble Creep as we have classified in Nabarro Herring Creep flux is to happen through grains and that leads to the deformation. So you can see here, this is a grain with this yellow atoms inside and outside there are some white vacancies. Now in Nabarro Herring Creep the flux happens through the grains.

So inside the grains, so the vacancies could move through the grain to here and they will appear somewhere here and they displace these 5 atoms and they come here and therefore, the shape actually change from this to this and therefore you achieve a deformation, you strain the material, you change the shape of it. Here, you have somehow the same example we have shown here with 3 grains. So this is how atoms are moving from here to here vacancies on the opposite side. Therefore, you continuously strain the grain and you can see here.

If I consider, this is the initial distance, then here, this is the final distance or final height. It essentially got shortened and on the and on the other side, it also got extended. So elongation on this side and shortening on the other side happened through the process of Nabarro Herring Creep where the fluxes happened through the crystal. Now in Coble creep, instead of moving this atoms or vacancies through the crystals, they move along the boundary of the grain.

And does not matter how they are moving, we more or less achieve the similar shape but the mechanisms are different. Again this is the size of the grain, you can think of with the yellow atoms inside and the vacancies outside and these grains, these grains particularly take the shape in a very similar way. And here, instead of moving through inside the grain, the movements do happen along the grain boundaries but the result is very similar.

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	Nabarro-Herring Creep	Coble Creep	
Flow Law	$\dot{\dot{s}} = A_{NH} e^{\left(\frac{-Q_{NH}}{RT}\right)} \frac{\Delta\sigma}{d^2}$	$\dot{\varepsilon} = A_c e^{\left(\frac{-Q_c}{RT}\right)} \frac{\Delta \sigma}{d^3}$	7.
Newtonian Flow	$\dot{s} \propto \sigma$	έ∝σ	-
Grain Size Sensitive	Ė 🗶	Ė ∞ 1	
Temperature Sensitive (faster at high T)	$\dot{\varepsilon} \propto e^{\left(\frac{-Q_{MT}}{RT}\right)}$	$\dot{\varepsilon} \propto e^{\left(\frac{-Q_{\rm C}}{RT}\right)}$	

Now it is interesting to note that the flow laws of the Nabarro Herring Creep and they Coble creep, they look very similar. So for Nabarro Herring Creep it is exactly like this. And for Coble creep, it is like this. What we see here is that both of them are Newtonian flow laws. The strain rate is proportion to grain size. Both of them are grain size sensitive. In Nabarro Herring Creep is squared, and Coble creep it is cubed.

Here the, in this equations, here the d is the grain size. So in previous slide, g has defined, g was the sign of grain size but in these slides, I have defined as d. I should correct it but now you know that d means grain size here. Now, why it is so? That one is, clearly this is less grain size sensitive than this one so you know in coble creep it has to move along the creep, along the boundaries. So shorter the grain size, faster is the process.

But if it is happening within the grains then it has to pass through the grains, so it is not that grain size sensitive compared to the Coble Creep. Therefore, it the equation, it is cubed and it is squared and as we have learned that both of them are temperature sensitive and generally it happens at very high temperature.

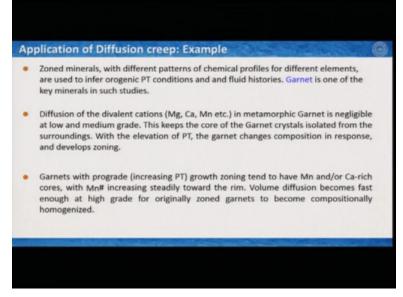
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So the microstructures of diffusion creep, it is not easy to identify under optical microscopes. But when the diffusion creep is active, stresses are too low to move the dislocation which is why it happens. There is no major driving force for dynamic crystallization so therefore you do not achieve some sort grain migration and so on. Therefore, you have to have the diffusion creep. Now only force for recrystallization you have is surface force and therefore it develops a very strong shape preferred orientation.

So you do not have any dynamic recrystallization, that means that there is no deformation or there is no thermal overprint and also very interestingly diffusion creep is essentially movement of the atoms, so it is used heavily by petrologists and metamorphic petrologists for mapping the movement of major and trace elements and this also gives you an idea of the pressure and temperature of the deformation and metamorphism as well.

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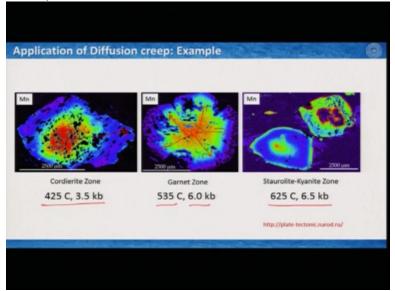
Now if you think of application of diffusion creep, there are many but I will give you one. As I talked about it that it can, you can use it for mapping the movement of major or trace elements. So the zoned minerals, particularly we see in nature very frequently with different patterns of chemical profile for different elements sometimes are used to infer the orogenic pressure temperature conditions and yeah most of the times fluid histories.

And Garnets in particular is one of the candidates for such studies. So what happens here, the diffusion of particularly divalent cations, for example, Magnesium, Manganese, Calcium and so on in metamorphic Garnet is negligible at low, medium grade. So if I have some distribution of these elements inside the Garnet at low or medium grade metamorphism, then they stay there. So therefore, if I have a large Garnet crystal, core of this Garnet is undisturbed.

It is some sort of isolated for the surrounding, but if the temperature is high, diffusion starts operating and then the elements, particularly the divalent cations they move within the Garnet following a typical pattern. What has been shown by several studies that Garnets with prograde growth zoning tend to have manganese or calcium rich cores with manganese number increasing steadily towards the rim.

So volume diffusion becomes very fast process enough at high grade for originally zoned garnets to become compositionally some sort of homogenous. So you have initially a very heterogeneous

rimmed or zoned garnet in terms of a particular element but when you have high temperature, then the volume diffusion starts of this element and then the entire garnet becomes homogeneous in terms of the distribution of these elements.

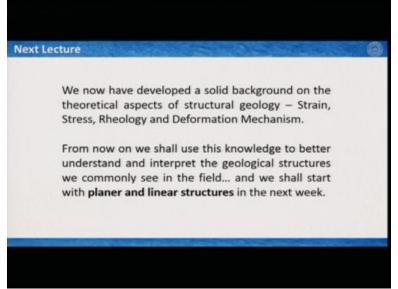


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So here is an example, as you can see here, the 3 different garnet grains mapped with microprobe or epma. The different elements I have here are manganese. The warmer colours, the red colour means you have higher concentration and colder colours, blue, that indicates you have lower concentration. So in this, in cordierite, the temperature was estimated 425 degree centigrade and pressure, 3.5 kilo bars.

Here you see that manganese has higher concentration at the core and slowly it is decreasing towards the rim. When temperature is elevated to temperature 535 centigrade and pressure to 6 kilo bars in the garnet zone, you see that these manganese elements are diffusing towards the rim. And even at higher temperature and pressure at staurolite kyanite zone, you see that this manganese are more or less homogeneously distributed and even there concentration has somehow increased at the rim and also, this is the rim and also at the inclusion boundaries. So this is how the diffusion do happen. Process is extremely slow so geologists, or particularly, metamorphic petrologists do use it for calculating different types of geobarometry and geothermometry.

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So we are done with this lecture of deformation mechanism. The entire week might be little long for you with this lecture time in particular. But it is important that we now interestingly have developed a solid background on the theoretical aspect on the structural geology.

We have learnt strain in detail, you have learnt stress in detail, you have learnt rheology and now you have learnt deformation mechanism in detail. So from now on, we will use all this knowledge of strain, stress, rheology, deformation mechanism and so on to understand and interpret the different geological structures that we commonly see in the field and we will start in the next week with planer and linear structures. So thank you very much. I will see you in the next week.