

Mineral Resources: Geology, Exploration, Economics and Environment
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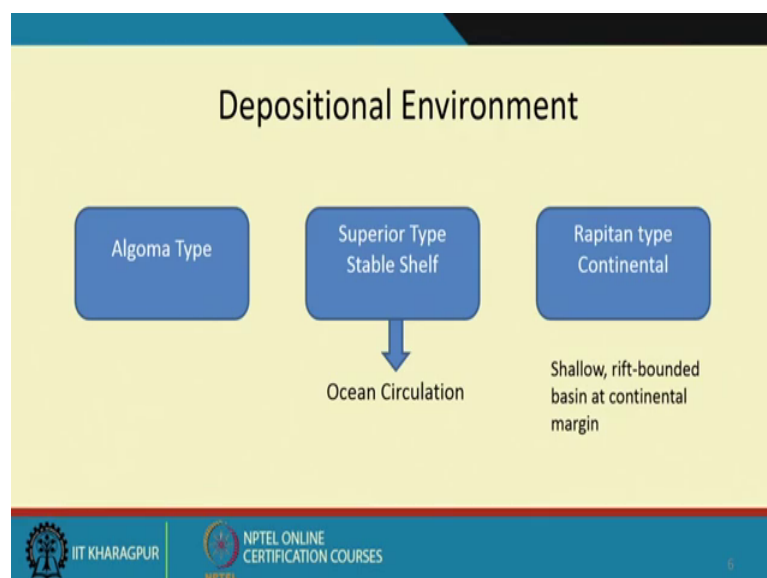
Lecture - 11
Sedimentary Processes and Resultant Deposits

Welcome to today's lecture. We have been discussing about the banded iron formations as a major source that constitute the major iron deposits of the world and in course of discussion, we just started to look into the hypothesis on the origin of such deposits and some of the intriguing aspects such as the depositional resource of iron.

And also in addition, we have to give an account to the source of silica solubility, which depends a lot on the chemical environment, in which the system is and we also take it that the silica is also derived from the continental sources, as well as the marine sources, the seafloor rocks of the sediments that are depositing there, through the interaction with the water which has a much more dissolving capability than the present the seawater and that is how we get them deposited in the form of alternating layers of iron and silica; the issue which will be coming to, in a while. But let us have a brief idea about the depositional environment.

We will briefly discuss that what is interpreted from this study of so many of deposits all over the world.

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So, if the depositional environment can be looked at for the different types, the Algoma type deposits, with their association with the older greenstone belts and then, the depositional environment also could be thought of in (Refer Time: 02:13) sea floor where, there has been exhalation volcanic activity, deposition of chemogenic sediments and the lava. So, they are the domain, which these iron deposits are supposed to have deposited during that time and later on modified, deformed and metamorphosed in the later time, as we see them in most greenstone terrines.

So, they can be thought of as environment very much checking to the sea - floor rifting environment, in which we have the volcanic activity and exhalations. The superior type are self stable, as we just discussed through the diagram, on which we looked into the hypothesis in which the bottom water, or the column of the seawater which had higher solubility of iron, because of the low pH and acidity that they have in them deducts and the condition being so low with iron, being mostly held in plus 2 state and there could be many possible ways in which the iron could be held in solution, either as plus 2 state in terms of Fe bihydroxide; soluble kind of compound or could be as bicarbonate. There could be many possibilities. Even the seawater could have had lot of iron in the form of chloride complexes, on which we are not going to get into details.

But the environment of deposition is somewhat a stable, continental, and self kind of environment, but then they are associated with some volcanic members, which sometimes, have to make some modification to the deciphered environment and then, the rapitan type which are the bounded continental basins where, they are deposited mostly in the fresh water conditions - in the inter - continental rift basins.

And they are in the type of area where they are associated with the glassiogenic sedimentation member representing the glassiogenic sedimentation, but that may not be quite genetically related to this basin, but they are dominance of the oxide phases, of the iron formation dominated by oxides. The situation is somewhat different from that of the other two and they are not associated with any volcanic member, representing any volcanic activity.

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Mechanism of Deposition:

- Photo-oxidation (UV)
- Direct Oxidation with increased partial pressure of O_2

Banding

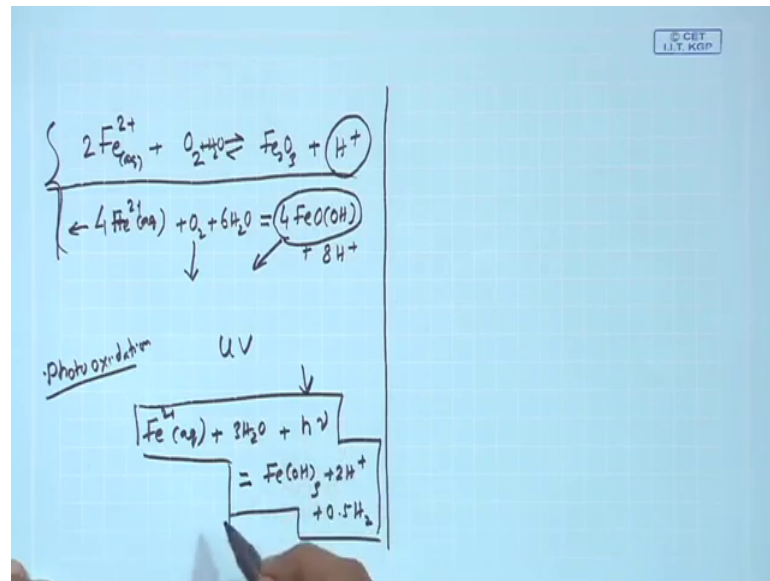
- Source
- Annual Varve
- Daily varve
- Isoelectric point at different pH

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We could now see that, if the ore lotion had a very high solubility of the metal iron, held in huge amount in plus 2 state, then what could be the possible mechanism by which, we could have brought about the deposition in the form of their iron oxides, that we see in the ores which are iron banded ore with alternating layers of silica and iron oxide.

So, we could think of possibilities such as a photo oxidation. There are situations in which it could be direct oxidation, or photo oxidation. Direct oxidation could be represented by a simple reaction, say, Fe^{2+} plus plus oxygen plus water, because we are taking these to be aqueous species. So, you will have Fe_2O_3 plus we can have H.

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So, it does indicate that such kind of mechanism which we proposed, can balance this out or we can even think of it as a process, where it could be 4 Fe²⁺ plus aqueous plus O₂ plus 6 H₂O, giving rise to 4 Fe(OH)₃ plus 8H⁺. It is this, as we have already stated, is more probable or more realistic initial process of the deposition of the iron, because we are getting then deposited in an aqueous environment and there is liberation of H⁺ plus ion, and it goes without saying that, this kind of a reaction will only proceed if this H⁺ plus iron is able to consume, that is the condition prevailing would be little bit more alkaline, which we can always visualize is happening a shallow self region.

So, this kind of mechanism would propose for direct oxidation, with increase in partial pressure of oxygen. We have already discussed that this oxygen with increase in its partial pressure, is because of the increase in the existence of the photosynthetic organisms, which liberated oxygen, with the gradual increase in the oxygen concentration in the aqueous environment. That is actually the prime mechanism by which the there has been extensive deposition of iron, in that particular period of time and which never happened again, because the conditions were not conducive for having that much of amount of iron held in solution by the ore lotion.

It could be a direct or a photo oxidation by the ultraviolet light. So, we could write Fe²⁺ plus aqueous plus 3H₂O. We will represent the ultraviolet light as HNU, giving rise to

FeOH_3 plus 2H plus 0.5H_2 . This reaction of course, will be still more schematic, but it will not require that much of a rise in the concentration of oxygen, but only the availability or increasing intensity of the ultraviolet light.

So, it would look to be as a mechanism less efficient, or more or less probable, than the mechanism which is shown to you, supported by the increasing oxygen content. This will only be interpreted in an ultraviolet way, because if a huge amount of iron 2 plus got deposited as hydride oxide of iron, absorbing the ultraviolet radiation from the sun, then it will enhance the growth of organisms in the aquatic environment, or on the land or during that early time and possibly that is how, the organism would start to proliferate, but that is pretty hypothetical. It could be one of the mechanisms by which, one can have this deposition.

Then, it is in our discussion about the origin of this very interesting and important class of deposit, given, the bulk of iron requirement is banding, which we saw in a photograph. They are very persistent. There are repetitive innumerable cycles of such kind of layers, which can be called as mezzo banding, because we can see them in hand specimen, in the scale of several millimeters to centimeters and their alternating silica rich and iron rich layers.

So, one of the things to be explained about these banding deposits is something which is needed to be understood. So, we can consider many possibilities. First, is that the source could possibly be that, they have been alternately iron rich and silica rich input into the ocean, because of fluctuations in the climatic conditions, or the oxidation state at the very beginning it might have caused the quantum of the magnitude of input of iron and silica to vary.

The other possibility could be most on the depositional site. Each individual pair of layers of iron and silica rich layers are ferruginous, they are just the bursts of the cherty layers known as cherts. So, if we take them, then the iron rich and silica rich pair of layers would constitute to one year.

Then there has been suggestions that possibly represent the annual time taken for this kind deposit, comparing to years, which form in the different lakes and we see them present in the time, when they were interpreted as annual years. Even it was proposed that it could also be presenting the daily years, means, during the day time, when there is

ability of the ultraviolet radiation from the sun, the iron oxide in these layers will precipitate and during the night time, when there will be dearth over there, no much of ultraviolet light would be coming from the sun at the night time. So, it will be with the time during which, the silica would precipitate in the form of the crept crystal line, silicon layer which we call it as jasper.

But then, they will also have their shortcomings in this kind of explanations, because they are being deposited in an ocean basin. The other possibility is that both the iron, when we are considering the iron to be precipitated in the form of the hydroxides, they do essentially form in the form of gel, or the colloidal kind of precipitation. As we see them, many of the preserved samples where, the colloidal precipitation of iron oxide, in the form of growth, height and many alteration zones, which we see are essentially colloidal precipitation.

So, there could be that, since both silica and iron are precipitating as colloidal precipitates, but they require different conditions for an isoelectric point, means, that the Ph, at which the coagulation of this colloidal particle will take place. So, this isoelectric point for iron oxide and silica are different, and then it could explain that at particular pH value, occurring in the aqueous environment, because of the fluctuations, could result in the alternate precipitation of the silica and the iron rich layers.

So, we could discuss about all these interesting deposits, in a very important class, which are our banded iron formations. As I told you, that these are the classes of deposits which have been extensively studied and the older deposits, when, there are many features like many subtle - chemical characteristics such as, the rare - earth element distributions and several other chemical parameters. Many times, many of the superior types of ores, are the signatures of the sea water signatures, which come from them and also volcanic exhalation signatures, that how many of the depositional environment are thought to be of mixed type, or hybrid type environment. But the fact remains that, they are a very interesting class of deposits and the steel generate many issues which still need to be resolved.

So, that is all we could discuss about banded iron formations. As a basic knowledge, that we need to have, we will discuss about them a little bit more, where we see them about the enrichment process, because as I told you that these are ore bodies that do undergo in

order to be mined, as high grade ores, which generally is done in many of the countries including India.

So, the high grade or the corners, where the iron is more concentrated of the order of 55% or 60, reaching to 60% driven more that, it requires some later modification enrichment processes by which, we could possibly remove the silicon layers and which in the mining geology term, there are many ways. They are called as lumpy ore or blue dust and this blanket type of situation is where the high grade ores are exploited. So, that is all about the banded iron formations.

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Iron and Manganese

- Similar geochemical affinity (Mn exhibits wider range of oxidation state and forms a larger number of oxide minerals)
- Both exist as oxide, carbonate and silicate facies (No sulfide facies for Mn)
- Comparable stability in surface environments (Mn only has a higher solubility)
- Older deposits occur in close proximity while young (Cenozoic) Mn-deposits are Fe-free (Black Sea Situation)

Fe – Mn Stability Compared

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Now, let us move on to a brief discussion to have within the constant of time. So, we do have manganese. We all know that manganese has a very similar geochemical affinity with the iron, and manganese also forms oxides. The only difference that manganese has with iron, is that the manganese does not form a stable sulfide even though, its name is all abounded, but it is generally not observed or not seen in nature, in any of the ore deposits of manganese, but manganese exhibits the wider range of oxidation state from plus 2 to plus 7 and occurs at the mineralogy of the manganese ore, which is far more complicated. I mean, lots of oxide mineral phases are present for manganese as compared to iron.

But the fact is that, since iron and manganese are both geochemically very similar. So, they would have also followed the similar type of geochemical cycle from the very

beginning, and they also are likely to have been transported, remained and acquired by the solution and also to have been deposited in the basins, much like the banded iron formations and that is what exactly we see them.

Most of the older, because we know that in the in the greenstones, we do get manganese deposits in close proximity with iron deposits. In superior type provinces like the superior province or in the iron ore (Refer Time: 18:43) in India and many other basins where, we get the superior type of iron deposits. We get manganese in very close association and the way we describe the manganese to be occurring in different species as oxide – carbonate, and oxide carbonate species just the sulfide, will be missing. We also, do get them as oxide and the carbonate ore which is carbonate is rhodochrosite

So, what exists is oxide, carbonate and silicate species, also in addition to the sedimentary iron, sedimentary manganese deposits. Manganese also transforms rich deposits by residual concentration process, from many high grade metamorphic terrains where, there are metamorphism of the manganese rich sediments and later enrichment process, that have given rise to very rich deposits, which we are not discussing here. Maybe, we will take them up in the discussion on the mineral deposits of the Indian subcontinent.

As far as this particular issue is concerned, whenever we are discussing them together, it would be worthwhile to see the characteristics of these. Here, by looking at these two diagrams which are just nearby. So, if iron and manganese have got similar geochemical affinity, then it would be worthwhile to see how their oxides, or how their species plot on the pH diagram, that we generally and extensively use for iron and we also, do use it for manganese.

What we see, when we compare these two is that this pyrite field, which I showed in the diagram, which I just drew in hand, there stability field. This is iron 2 plus iron 3, and this is hematite, this is magnetite. Magnetite, when it is a silica rich situation, it might be a magnet iron (Refer Time: 20:43) silicate, and the area that this pyrite stability field has in iron 2 plus and carbonate depending on what are the dominant sulfurous species here, whether it is a sulfate or a sulfide or a bisulfide and we see this in the stability fields.

So, what we see is that they are more or less comparable. This is the stability field of manganese 2 plus, this is rhodochrosite and this is the stability field of hematite, which

very much coincident with that and this is the pyrolusite field. So, what essentially is observed in this is that manganese only requires a little higher because this is the hematite field and this is a manganese field is could be compared.

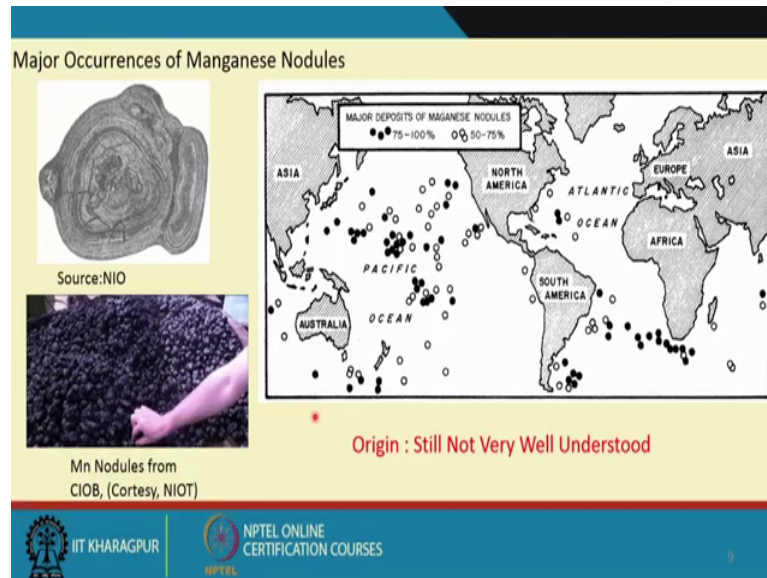
So, manganese only requires a little higher oxidation state to form its oxides and under any given situation, iron is much less soluble than that of manganese. Manganese persists in the solution for longer time and also in higher pH conditions. So, that is the reason why in most of the basins, we find that the manganese bearing halogens, generally succeed the iron bearing halogens, who which occupy the lower part of the stratigraphic column.

So, this is the reason for, as we see that there are comparable stability in surface environment, for the manganese is only as a higher solubility, older deposits which occur in close proximity, find the young synergic deposits like, the ones which are occurring in the black sea, which is a very interesting situation; where black sea is a stratified sea, because of the salinity difference and is lower at the bottom part of this pretty low pH and acidic uremic conditions.

And it is exactly the basin where, the present day situation can be studied. The concentration profile of the two iron and manganese where, the bottom water is very rich in manganese and the same situation is visualized when the bottom water is upheld periodically and encounters higher pH oxidizing conditions, where they get deposited in the basin rims or the edge of the self part of the basin, that has reached manganese deposits. As we see, then in the famous Nikopol deposit the Ukraine, just around the Black sea - the Cenozoic deposits, but these deposits are not associated with any rich iron deposits, which comes out as one of the major point of distinction. There is possibly explainable on the basis that iron is not as soluble as manganese. In the present day revealing physicochemical conditions that the sea water oxidation in the pH and the oxidation in the partial state pressure of oxygen in the atmosphere.

And that is the reason why any amount of iron, which will be there, dissolved in the situation like a Black sea stratified Black sea will be deposited on the floor of a sulfide, where the condition is very - very reducing and we will only be getting the manganese deposits in the upper halogens. So, we go to a very interesting situation.

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Here, is also the manganese situation which would have rather been incomplete, if we do not discuss something about a very interesting occurrence, a manganese in the form of what we call them as – ‘nodules’. They have essentially ferromanganese nodules and they do have a latitudinal restriction. If you could see here, they are distributed in almost all the seas - the Atlantic, the Indian ocean, the pacific where, we could see that they are essentially ferromanganese nodules and the concentration at the black dots are representing higher value than the open dots.

These in the ferromanganese nodules as they call, are more richer or are considered as a more important resource of nickel, cobalt kind of metal and sometimes even some of the radioactive metals like - radium and uranium rather than the iron and manganese, because compared to the iron manganese which we have, the land based resources are in plenty.

So, these manganese nodules are definitely very intriguing, because 1, that they are observed on the open ocean sea floor in their depths and only precondition personally is that they are in areas, in the open ocean where, the rate of sedimentation has to be low for the manganese nodules to grow.

Here, is a picture of a cross section or a poly as a section of the manganese nodule, that is what they are called as the nobles of the concretions, at the core of it will be any particle

either an older nodule, or any kind of a data to particle, from the ocean floor have any animal teeth at any part or any hard part of any organism.

On which, we will have this kind of a constantly colloidal precipitation of the manganese, mostly manganese oxides with variable concentrations of iron, with the also observed on the flanks of the (Refer Time: 26:20), they are also observed on the sea quartz, on the sea mounds and there is a bit of a correlation on the cobalt content, when they occur on the cobalt continent, generally, on the flanks of the mid oceanic ridges or on the ocean seafloor, manganese or the sea quartz.

The global concentration is higher compared to the ones which are found in the sea floor and they kind of can be projected as the resources that are there for future, because right at this point of time, the technology to mine them out from the seafloor has not very well been in place, but they do have a substantial amount of the metals, as result of the metals available as a resource of the seafloor, which we will also be discussing a little bit, when you go to the seafloor resources .

So, they have been pretty interesting and still not very well understood, as far as the origin is concerned. The metal, the obvious source for this metal like manganese, could be the seafloor rock on the seafloor itself. Exhalation coming from deeper and the regions in which there are higher temperature, in which the sea water is reacting with the seafloor rocks and getting enriched with respect to manganese and some very special situations in which, they may be depositing because otherwise in general, the seafloor situation would not be that very oxidizing in nature, to favor the growth of this kind of nodules.

There must be some additional factors, even some biogenic factor can also not be ruled out and people have also attempted to calculate the rate of growth of these manganese nodules, with a pretty slow. Here, there is a picture of the manganese nodules which are recovered from the Central Indian Ocean Basin by N.I.O.T. (National Instruments Ocean Technology).

So, they do constitute the modern day, I mean they do give us an idea about the present day formation, when we talk about whether ore deposits are forming in the present day. There are very good examples for us, in addition to the fact that they remain as a very rich resource, not only for iron and manganese, but for rare metals like – nickel. I think

the total nickel resources that might come from this manganese nodules, possibly will outweigh the resource that is available on land as far as discovered so far.

So, that is all about the iron, manganese and they are of course, essentially chemogenic and they will be classified under that category. So, we conclude our discussion on the chemogenic sedimentary process, giving rise to the important metals like manganese,

Thank you.