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A BRIEF REVIEW OF THE THEORIES OF METALLOGENESIS.

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SUMMARY

A brief review of the nature of mineralizing solutions is presented.

An insight is gained into the nature and origin of mineralizing solutions by a study of the various types of naturally occuring thermal fluids of different origins. Volcanic hot springs generally deposit Sb, As, Au, and Hg, and are rich in CO_2, CO, H_2, NH_3, H_2O. They also contain alkalies, Ca, Mg, and Cl_2. Supper heated meteoric waters are generally rich in CO_2, H_2S, HCl. Other fluids, like the thermal waters, waters of metamorphic origin, connate waters, fluid inclusions in minerals and deep surface geothermal brines are always rich in metals and deposit minerals under different circumstances.

The solubility of metals in hydrothermal solutions in generally governed by pressure, temperature and the acidity of the solutions. The environment and availability of the metals also plays an important role. The lower concentration limit of metals in mineralizing solutions, enough to deposit minerals, is said to be 10^{-6} gm/l. Simple solubility of metals in solutions is, however, inadequate and recent work has shown that the occurence of different metal ions in the form of complexes plays a predominant role.

The nature of transporting fluids and the mode of occurrence of metals in these fluids is one of the most important controlling factors in the deposition of minerals from solutions. Various modes of transport as vapour, colloidal transport and simple non-ionized molecules are generally unimportant as they fail to satify many questions concerning field relation-ship of minerals. Transport as complexes is deemed to be the most favourable mode as it satifies many thermodynamic and field relations. Chloride complexing is thought to be a very important process in this respect as the stability and solubility of various metal ions, as chloride-complexes, is always enough under the generally existing temprature pressure conditions. Sulphide and bisulphide complexes are also supposed to play an important role. Under sulphur-rich conditions sulphide complexes usually predominate over chloride complexes, but under sulphur-deficient conditions chloride complexes predaminate. However, the occurence

of sulphide complexes is generally questioned on the basis of the sulphur deficiency of mineralizing solutions. Some researchers attribute this apparent dificiency to the rather high mobility of sulphur and believe that the original solutions usually contain enough sulphr to form complexes.

Deposition of minerals can be brought about by fall in tamperature, reaction of mineralizing solutions with the wall rock, mixing of ore-solutions with meteoric waters, changes in PH and a decrease in pressure.

INTRODUCTION

There are many kinds of ore-deposits and almost as many theories of their origin. The ancients believed that all the mineral deposits were formed by water. Agricola in Germany as early as the 16th Century seems to have laid the fonndations of Economic Geology. He is said to have proposed first the lateral secretion theory.

The Neptunian concept of Werner proposed that water was the main agent in the formation of all crystalline rocks and minerals. This pattern of thought was ultimately transformed by the plutonic concept of Hutton, and there was thus a gradual drift in favour of plutonism. This ultimately resulted in the concept that attributed most mineral deposits to some kind of magmatic activity. This concept ultimately laid the foundotion of the hydro-thermal hypothesis.

The word hydrothermal originally meant hot fluid emanations or exhalations from a magma which carried many dissolved elements, and ultimately deposited them at the sites of deposition. With the passage of time all the mineralizing solutions came to be known as hydrothermal. This resulted in much confusion, so much so that ultimately 'hydorthermal came to mean hot solutions irrespective of the source of origin.

The hydrothermal theory like its other counterparts fell out of favour from time to time with the accumulation of more and more data. It failed to explain all the aspects of mineral deposits. As data slowly accumulated about the solubility of many elements in hot solutions, it was realized that simple hot solutions could never have deposited such large quantities of ore-minerals. Moreover, the limited knowledge of the solubilities of minerals suggested that hydrothermal liquids could not satisfy the conditions of mineral zoning and paragenetic relations as observed in the field. Consequently the theory of ore-transport by high temperature vapours gained favour for a time.

It was observed during the industrial recovery of various metals in metallurgical processes, that metals separate in a definite sequence. The heavier elements usually sink to the bottom and the lighter elements float at the top in the furnace. The sequence of deposition of the heavier fraction, called matte, is similar to the sequence of elements in a zoned deposit. The sequence in the matte is in accordance with the volatilities of the elements, and also their density. Thus the lighter elements deposit at the top and form what is know as speiss.

On account of this correspondence of the actual occurrence of ore-minerals in the field and in a metallurgical furnace, Brown (1948) proposed the hypothesis of vapour transport. This hypothesis was rejected by Edwards (1956) and Krauskopf (1957, 1958, 1964) on the grounds that the volatile sulphide theory is inadequate to meet the geological requirements and also it does not satisfy the physico-chemical requirements.

Certain sulphide deposits occurring in sedimentary or metamorphic rocks exhibit all the characters of sedimentary structures, thus pointing to the possibility of their syn-depositional character. These deposits are thought to have resulted due to the precipitation of the ore-minerals in the sedimentary basin in which other sediments were deposited at the same time. The various geological features of these syngenetic stratiform deposts have been described by Brown (1967).

In order to account for the sedimentary character, Knight (1957), forwarded the hypothesis of source bed concept, which claims that these deposits are syndepositional with the sediments in which they occur. His ideas, however, have been criticized by Walker (1958) and Chamberlain (1958) etc.

From the study of the different theories of origin, it has become clear that ore-deposits can form under very many diverse conditions and that most of these deposits are laid down by fluids which in turn may exhibit extremely diverse characters in chemical composition and pressure temperature-conditions.

Smirnov (1968) has given a broad classification in terms of the source of the ore matter. He classifies the source of the ore matter as (1) juvenile, related to subcrustal basaltic magma, (2) assimilated, related to palingenic granitic magma of crustal origin, and (3) filtrational, related to the circulation of non magmatic uderground waters.

The nature and Origin of Mineralizing Solutions.

The various aspects of ore-genesis have been reviewed in great detail by Edwards (1956). White (1968) has reviewed the origin and nature of mineralizing solutions on the basis of the data that has accumulated from the study of the chemical composition of thermal waters, fluid inclusions and deep seated hot brines and has postulated five major limiting types of mineralizing solutions.

From these studies a clearer picture as to the nature of the mineralizing solutions has developed. It now seems probable that the mineralizing fluids cover a very broad spectrum of compositions, temperatures, pressures, and various other conditions, Barton (1958). No one theory of ore-genesis can possibly have a universal application.

An insight into the composition of the possible mineralizing fluids can be gained from a study of natural waters. These waters can be discussed under various headings depending on the mechanism of their generation.

In areas of recent volcanic activity one usually finds hot volcanic springs and fumarolic gas. These gases are usually very rich in water vapour (above 90%), CO_2, H_2S, SO_2, HCI and many other constituents. Amongst the sulphur gases, SO_2 is usually predominant over H_2S in high temperature areas, though there are many exceptions to this rule. These gases can and do transport metals as volatile complexes, and are thought to be possible contributors to mineralization.

Heating of various kinds of rocks can release highly complex charged gases, which can be important in mineral and recrystallization processes in near surface conditions, a situation which is somewhat similar to volcanic emanations, Walker and Buchanan (1969),

Volcanic hot springs are usually thought to be heated meteoric waters which may contain from 5% to 10% waters of purely magmatic origin. They usually contain the common ore forming elements in various amounts. These hot spring waters are also very rich in gases. CO_2 is the most abundant, while CO, H_2, NH_3, H_2O and Ar occur in varying amounts. Some of these springs are at present depositing many elements, for example, Sb, As, Au, at Steamboat Springs, Nevada, and Hg at Boiling Springs, Idaho. Many springs all over the world are known to deposit sulphur. Most of these springs are usually rich in alkalis, calcium, magnesium and chlorine.

The mineral and thermal waters in many parts of the world are rich in Na-K-Cl; Na-Ca-Mg-SO_4. These waters are known to carry many metals in varying amounts.

Edmonds et al (1969) in a recent review of the mineral and thermal waters (spa waters) of Britain have shown that these waters exhibit characteristic compositions depending on their geological environment. For example, most of the thermal waters in the paleozoic and Triassic formations of Great Britain are predominantly Na-K-Cl type, while those in Jurassic formation are predominantly Ca-Mg-SO_4 type. Mineral and thermal waters in Tertiary formation are more variable in composition, and this is attributed to variation in lithology and mineralogy of the rocks. Some of these waters contain unusual amounts of certain elements. For example, the waters at llandrindod Wells contain lithium from 1.0 to 26.0 mg/lit., while the waters in Builth Wells are richer in flourine. In overall composition these waters are similar in composition to the recent Red Sea and other brines.

It has been suggested that metamorphic waters which result from the breakdown of hydrous minerals during metamorphism are able to dissolve metals and thus slowly build up to metal enriched fluids, White (1957).

Sediments usually retain a lot of the original seawater in their pore spaces during their burial. During diagenesis these connate waters might evolve into saline brines and escape along with some other mobile constituents in solution, White (1965). During this process the magnesium is usually fixed in the sediments while calcium and sodium may be dissolved. The escape mechanism of connate waters has been attributed to be due to semipermeable membrane filtration by Berry (1966), 1967, in White). These pore-waters in the neighbourhood of salt deposits show unusual enrichment in many different elements. Zatenatskaya et al (1969) have shown that interstitial waters in the Devonian argillaceous marly sediments near the Starobin potassium salt deposits are highly entriched in Na, K, Mg, Cl, SO_4 and HCO_3.

Meteoric waters of surface origin usually get enriched in many elements during their dewnward migration in rocks. These waters are usually very rich in CO_2, O_2 and N2, and therefore, are always slightly acidic. These meteoric waters may react with the rocks or ther waters and can be responsible for mineralization. Gurevich (1964) has suggested that the accumulation of Cl_2-Ca waters in ore-bearing veins owe their origin to mixing of hydrothermal solutions and ground waters during the late stages of mineralization of the veins, or to an independant influx of water under head from underlying sedimentary deposits.

Ivanov (1964), on the other hand, has shown that in regions of recent volcanic activity. meteoric waters play an important role in the differentiation of gaso-thermal exhalations from deep-seated magmas. Apart from exhalations of volcanic origin these regions coutain pure hydrothermal exhalations formed due to vapourization of ground waters which cause intensive wall-rock alteration. He has also shown that in the presence of high temperature regime, deep infiltration of atmospheric waters along zones of tectonic faulting, may result in four kinds of geochemical conditions, which give rise to different kinds of thermal waters in regions of recent volcanic activity. The saturation of waters with volcanic gases in the upper oxidising zones of active volcanoes leads to the formation of highly acid H_2S-CO_2 (fumarole) thermal waters, and sulphate or chloride-sulphate waters, which show a complex cationic composition, due to a probable participation of waters of magmatic origin in the deep seated varieties. The thermal waters formed in the deep reducing high temperature conditions in regions of active volcanoes are nitrogenous-carbon dioxide waters which are weakly acid at greater depths, alkaline at the surface, and Cl_2-Na waters which are highly siliceous, strongly superheated and characterized by a very uniform composition. Carbonate thermal waters of different ionic compositions are formed in a reducing environment at depth in the sphere of influence of thermal affect of magma chambers, from infiltrational waters and possibly also some marine residual waters. Finally there are the nitrogenous waters, which are formed under telethermal conditions away from the influence of the thermal effect of magmatic chambers. These waters are the least reactive of all. On their way towards the surface these waters of different kinds undergo many changes or reactions with the country rock but their essential natures are not much modified.

Fluid inclusion studies are thought to reveal the best representative sample of a mineralizing solution. The data concerning fluid inclusion chemistry and its possible implications as to the nature of the ore forming fluids are reviewed by Roedder (1960, 1967). There are many works on the fluid inclusion studies of individual mineral deposits, and some of the most important are by Roedder (1967, 1972), Groves et al (1970), Groves and Solomon (1969), Sawkins (1966), Hall and Friedman (1963), Pidckney and Haffty (1970) and Billings et al (1969).

In general the chemical composition of fluid inclusions is somewhat similar to hot thermal waters. They are usually rich in CO_2 and occasionally in H_2S. They are usually low in sulphur content. Other gases reported in minor amounts are N_2^+, NH_3, H_2 and Ar. The chief dissolved ions are Na^+, Ca^{2+} and Cl^- and the other minor constituents are K^+, F^-, HCO_3^-, SO_4^{2-}, Fe^{2+} and Fe^{3+}. The solutions are usually neutral and there is generally a certain uniformity of composition in fluid inclusions from various deposits.

Recently Pinckney and Haffty (1970) from a study of fluid inclusion in fluorite, barite and quartz from the Cave-in-rock district, Southern Illinois, reported high concentrations of zinc and copper. They found that in these inclusions zinc, varied from 10ppm to 1040ppm, and copper varied from undetectable amounts to 350ppm. The chlorine concentration in these inclusion fluids varied from 2500ppm to 152000ppm. They also showed that variations in base metal content and chlorine were closely correlated with the different periods of deposition of sphalerite. There was also a very good correlation between the zine and chlorine contents of these inclusions.

The recent discovery of deep subsurface geothermal brines, some of which are actually depositing metal sulphides in great quantities has added a lot to our knowledge of the nature of mineralizing solutions. Toom (1970) has reviewed the existing knowledge about these brines. A vast amount of data has accumulated in recent years about the chemistry and other aspects of these geothermal brines, Busch (1970), Bugelskiy et al. (1969), Dunham (1970), White (1965, 1968), Pavlow (1969), Downing (1970), Downing and Howitt (1969), Lebedev and Nikitina (1969).

The Salton Sea brines of California occur at depths of 4700 feet to 8100 feet and the temperature is said to be around 300°C at 3000 feet, and 360°C at 7000 feet. These brines are predominantly K-Na-Ca-Cl types with many dissolved cations. On an average they contain 2000ppm iron, 1400ppm manganese, 500ppm zinc, 90ppm lead, 12ppm arsenic, 6ppm copper, 2ppm cadmium and 1ppm silver. Sulphur ranges from 15-30ppm which is less than 5% of the sulphide required to precipitate metals as sulphides. In this respect they are very similar to the fluid inclusions which are usually sulphur deficient, Roedder (1967). All the dissolved sulphides are present in form H_2S and HS^-.

The Red Sea brines occur at depths of about 2000 meters below sea level and have temperatures from 34°C to 56°C. The salinity of these brines varies from 74000ppm Cl to 255,000ppm Cl. They are high in iron and manganese, the later usually predominant in amount. Other dissolved metals include zinc, copper, lead and barium.

Compared to the average sea water composition these brines have a high Ca/Na ratio. The ratio of K/Na is slightly lower than the sea water while the ratios of Mg/Ca, HCO_3/Cl, SO_4/Cl, Br/Cl, and B/Ci are very low compared to sea water.

The brines of the Chelekin peninula are another example. According to Lebedev and Nikitina (1969) these brines are annually depositing 100 tons lithium, 10 tons rubidium, 300-350 tons lead, 48-50 tons zinc, 24-35 tons copper, 18-24 tons cadmium, 6-8 tons arsenic, 1200 tons boron and 7200 tons strontium.

The characteristics of these brines show that they are active mineralizers. A general comparison of these various kinds of waters discussed above shows that they have one character in common. They are all rich in volatiles, usually CO_2, with mean amounts of other gases. The dissolved ions are predominantly K-Na-Ca—Cl^- with minor amounts of other cations. Amongst the many anionic species are CO_2, HCO_3, Cl, SO_4, etc.

This brief survey indicated that it is possible to put broad limits on the composition of the mineralizing solutions. There may be variation in the composition of these mineralizing fluids from place to place. For example, Kraynov (1967) has reported unusually high fluorine contents in subsurface waters in the Lovozero massif which is said to contain a vey high silica content as well in the form of silicon hexafluoride complex.

SOLUBILITY OF METALS IN HYDROTHERMAL SOLUTIONS

Solubilities of many ore forming metals, ore minerals and gangue minerals have been discussed and reviewed in great detail by Smith (1963), Barnes and Czamanske (1967) and Holland (1967). A brief summary is given here.

Krauskopf (1957) has shown that the lower concentration limit significant for ore-formation is 10^{-6} g/I, which is considerably below even the minimum solubilities recorded. Thus the experimentally determined Zn, Ag, Pb, and Cu - sulphide concentrations at high temperatures can be regarded as fully acceptable geologically. However, Barton (1958) has shown that simple solubility is completely inadequate to account for most heavy metal transport in ore forming fluids.

The solubility of sphalerite has been determined in various kinds of solutions. Sphalerite solubility seems to be generally susceptible to a rise in temperature, The comparatively smaller solubilities in alkali chloride solutions and greater solubilities in NH_4Cl are supposed to suggest the general evidence against chloride complexing and the possibility of hydroxide or amine complexing, which is thought to be a consequence of high temperature. Melentyev et al (1968) have shown that is contrast to the unidirectional effect of the temperature, a decrease in the acidity of the solution first promotes a decrease in the solubility and then an increase. The solubility of sphalerite is very greatly affected within a pH range of 1-7.

In a solution of pH_2 the solubility of sphalerite decreases 60 times with a change of temperature from 200°C to 100°C, and sphalerite is deposited. In solution of pH_4 the effect of temperature decreases, while at pH_7 the solubility of sphalerite in this temperature interval does not vary more than $1\frac{1}{2}$ fold. These solubilities are measured in dilute alkali chloride solutions. On change in acidity of the solution from pH_2 to pH_4 at a constant temperature (200°C), the solubility decreases 100 times. On further decrease in the acidity to pH_7 the solubility can increase about 10 fold.

Argentite and chlcocite were found by Melentyev et al (1968) to have the same solubility pattern as sphalerite. In this case however, at higher temperatures, the solubility minima of argentite shift in the direction of lower pH values. This is particularly evident above 180°C. In the case of sphalerite, the minima shift towards the region of more alkaline solutions.

Analysis of the conditions characterizing the sequence of deposition of the sulphide is possible. On increase in the pH from 1 to 2 at 350°C, only sphalerite and argentite are deposited, while at lower temperatures both sphalerite and argentite are deposited. On cooling the solutions from 350°C to 200°C they can both separate simultaneously, but on further cooling only sphalerite is deposited.

Decrease in the acidity from pH_3 to pH_4 lead to deposition of sphalerite only if the the temperature of the solution is not less than 200°C. Decrease in temperature from 350°C to 160°C leads to the simultaneous deposition of sphalerite and argentite. Decrease in the acidity from pH_5 to pH_7 can result in the deposition of sphalerite only at high temperatures (350°C). Cooling the solution from 350°C to 160°C (between pH_5 and pH_7) results in the simultaneous deposition of sphalerite, argentite and chalcocite.

In view of the combined influences of temperature and acidity of solutions in the solubility of sphalerite, argentite and chalcocite, it appears that the higher the original temperature the smaller is the effect of temperature factors.

Smith (1963) has tabulated the data on pH values of solutions and their solubilities from various sources for As_2S_3, HgS, pbS, H_2S, SiO_2 and Ag_2S. Interpolation of the data quoted above with this shows that, in very general terms, All these minerals solubilities are similarly effected by the acidity of solutions. He (1958) has also shown that along any normal geothermobar, the solubility of quartz and probably most of the other non-volatile solutes, increases continuously with temperature, pressure and depth.

The data on the solubility of quartz and calcite have been reviewed by Holland (1967). Sharp (1965) has shown that both quartz and calcite can be deposited by mixing of solutions at constant pressure. The deposition of quartz is predominant above 300°C and that of calcite below 150°C when thermobaric changes in solutions cause precipitation. Replacement of quartz by calcite or vice versa, can be caused by transport of $CaCO_3$ and SiO_2 along geothermal gradients.

The solubility of quartz in water increases with temperature except at critical temperatures where the density of the solution is small. The solubility of the various polymorphs of silica is higher than that of quartz. It is also independant of the salt concentrations of the solutions with temperatures geologically feasible. The solubility of quartz is also independant of pH of the solution within the narrow range of commonly occurring acidity, though it increases at very high pH values. The solubility of quartz is slightly decreased by the addition of chloride at 600°C and 3Kbars and 700°C and 4Kbars. It is increased by the addition of NaOH to the solution and is proportional to the amount of NaOH added. Quartz reacts with Na_2S solution between 100°C and 250°C, and produces a solution containing Na^+, HS^- and $SiO_2.nH_2O.OH^-$.

In solutions silica usually occurs as one or more $SiO_2.nH_2O$ monomers, which are not charged, which is why there is not much effect of pH on the solutions. However, Shcherban(1967) suggests that consideration of variation in ortho- and meta- silicic acids, as influenced by pH and by Si-content of the solution, indicates precipitation of silica on the acid side of pH 10.26 at 0.009% to 0.0015% H_4SiO_4. He also suggests that under standard conditions from thermodynamic considerations SiO_2 will be precipitated from SiF_6^{2-} complexes at pH4-8.

Under hydrothermal conditions with a normal gradient of 35°C/Km, (though this gradient sometimes increases to as much as 100°C/Km), at temperatures from 100°C to 200°C, 1000 grams of solution can precipitate up to about 200 mg quartz. Unfortunately no data is available as to the amount of quartz mined along with sulphide minerals and therefore no estimate can be given as to the total amounts of solution.

The solubility of calcite in water is known to increase with an increase in CO_2 pressure and decreases with increasing temperature. CO_2 and H_2O are perfectly miscible above 450°C, At low CO_2 pressure (almost pure water) the solubility of calcite in water is very low and remains practically constant up to 150°C, and then falls towards critical temperature. Salts depress the solubility of CO_2 in H_2O which in turn would affect the solubility of calcite. However, the solubility of CO_2 in NaCl solution is higher by 40% as compared to water, Calcite is precipited by the release of CO_2 which is affected by a decrease in pressure. Therefore calcite would be deposited in near surface conditions. Conversely a simple cooling off may not deposit calcite.

Apart from their susceptibility to temperature pressure conditions the solubility of minerals in hydrothermal solutions is subject many other factors. Smith (1963) has attempted a general cassification, reproduced below.

1. Concentrates sensitive to hydrogen ion concentration.
    - A. Simple ions.
        - I anions
        - II cations
    - B. Complex ions.
        - I oxy-ions
        - II thio-ions
2. Concentrations sensitive to oxidation potential.
3. Concentrations sensitive to CO_2 concentration.
4. Concentrations sensitive to H_2S concentration.
5. Concentrations sensitive to H_2O concentration.

The influence of pH on the solubility of certain metallic sulphides was pointed out. Generally changes in the hydrogen ion concentration control the amounts of silicic acid and CO_2 in solutions. Also in metallic sulphides, polysulphides and oxy- and sulphide-complexes, the pH of the solutions determines their approach to conditions of saturation.

Hydrothermal solutions are usually considered to be reducing in nature because of the sulphide ion present. The ratio of sulphide/sulphate therefore is a good index of the oxidation of the solution. Oxidation tends to decrease the concentration of sulphide and poly - sulphide ions. Trivalent iron, which is a strong oxidant, is usually present in the form of hematite, magnetite or ferric hydroxides in rocks and can easily release its oxygen and is itself either dissolved or reprecipitated as pyrite or pyrrhotite near veins.

The concentration of CO_2 is highly variable in different hydrothermal types of solutions. In high temperature hydrothermal solutions up to 30% CO_2 in fluid inclusions of minerals has been noted while low temperature hydrothermal solutions the amount of CO_2 is usually very low. CO_2 content in such solutions would decrease due to carbonatization during wall-rock alteration and in high temperature areas this may result in the formation of new hydrothermal minerals in the wall-rock. The precipitation of calcite and/or dolomite in vein rocks is also a function of CO_2 concentrations.

The concentration of H_2S similarly is also very variable in hydrothermal solutions. Reaction of H_2S with wall-rock decreases its concentration further and usually results in the precipitation of pyrite and (or) pyrrhotite.

Water is the most important constituent of hydrothermal solutions and its content should also be variable at different points in space and time, a factor which in its turn would determine the concentrations of different solutes. The variation in the content of water shall also directly affect the solubility of various cations and anions and thus fluctuations in its water content can cause precipitation of various minerals, Smith (1963).

Water freely reacts with the country rocks and usually results in the formation of hydrous minerals like chlorite, sericite, etc., in the wall rock.

THE TRANSPORT OF BASE METALS

The problem of the transport of base metals has two main aspects, namely, the essential nature of the transporting fluids themselves and the main mode of occurrence of various metals in these fluids. Both these questions have been debated for a long time and there is still a lot of controversy in various schools.

Korzhinskii (1958) first formulated the hypothesis of 'Acid Transport'. He postulates a three stage mechanism of the acid wave. The first is the zone of increasing acidity of the advancing wave. At this stage leaching of the rocks increases with ascending waves and there is usually little precipitation. The second is the zone of maximum leaching which is accompanied by the precipitation of weak bases like Al, Fe, Ti, etc. In this zone, however, leaching sharply predominates over precipitation. The third and last is the zone of fading acidity of the advancing wave. Leaching is on its minimum here while the precipitation of bases increases. In telethermal ore-veins (carbonates, fluorite, barite) the precipitation sharply predominates over the preceeding leaching. The latter may even be absent.

This theory has recently been criticised in various schools. It can, however, be valid for the more soluble sulphides, such as Zn, Fe, Mn, Co, and Ni, but invalid for insoluble metallic sulphides like Hg, Sb, As, and Ag. It, however, seems that the concept of advancing wave of 'acid' solution is misunderstood. It is probable that the original solutions were slightly acidic in the begining which by their very reactivity would be quickly neutralized or even may become slightly alkaline. The alkaline solution in turn would react with the country rock and be saturated in silica, probably in the form of silicicacid, which is redeposited in the location of the leached out bases, Smith (1963). Basing his arguement on Korzhinskii's hypothesis, Shoherban (1967) has suggested a pH range of 4-8 for the precipitation of silica from silicon hexafluoride complexes. Helgeson (1964) has, however, pointed out that at the prevailing temperatures of mineralization, pH is not a very dependable parameter and it may be varying between 3 and 9, while it is also susceptible to the total dissolved NaCl.

Recent data on the mineralizing solutions, however, indicates that they are usually slightly alkaline to neutral. White (1965, 1968), Busch (1970), Dunham (1970), Dowing (1967), Downing and Howitt (1967), Pavlov (1969) and Bugelskiy (1969) etc.

The mode of transport of different ions in hydrothermal solutions has been reviewed by Barnes and Czamanske 1967) in detail. The dilemma of the mode of transport of metals in solutions is generally accentuated by the lack of experimental data. Various aspects of the questions in regard to transport problem have been discussed by Smith (1963), Roedder (1967), Hall and Friedman (1963) and Helgeson (1964).

Krauskopf (1964) has shown that the transport of metals in the form of vapours is of no consequence, except possible for the transport of silver at temperatures below 400°C. Most of the ore-deposits are usually formed around or below 400°C and, therefore, the transport of these metals in a vapour phase could not have played any significant role. However, at higher temperatures gaseous transport may be the predominant mode. Walton (1960) has shown that the transport of silica under supercritical conditions by diffusion can be a very efficient and rapid process. Sourirajan and Kennedy (1961) have shown that NaCl can be transported by hot water vapour near magmatic chambers. Thus it seems probable that gaseous transport may be a very important mode under hypothermal conditions, while in epi- and meso-thermal environments, most of the metals would be transported predominantly in a liquid phase, Helgeson (1967).

The transport of metals in colloidal form was once a favoured hypothesis. It has been rejected on the basis of the instability of colloids within the geologically feasible range of temperatures and pH conditions. Moreover, the reversal from colloidal to a non-colloidal state is an irreversible change and can not explain the reversals in zoning.

Transport of metals as simple non-ionized molecules is also incompatible with the zoning sequence usually observed. Moreover, the simple solubility of ls is negligibly low and is not sufficient to account for the deposition of the mounts of ore-minerals.

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limits. However, there is a lot of controversy

concerning the relative importance of the different complexes that may be existing at any one time in the hydrothermal solutions. It is usually agreed, however, that these complexes can be limited to two predominant types, namely, the halides in the form of chlorides or polysulphides. Other types of complexes like carbonates, hydroxides and sulphates etc., may be locally important, but in general they are negligible as compared to chlorides and sulphides.

Helgeson (1964) has reviewed the theoretical aspect of chloride complexing in the system PbS-NaCl-HCl-H_2O. He has shown from theoretical considerations that lead can form many chloride complexes of different orders under various temperatures and chloride ion concentrations. However, the most important complexes are $PbCl^+$ and $PbCl_4^{2-}$. At elevated temperatures above 300°C, $PbCl^+$ is the most stable complex in dilute and concentrated NaCl solutions, while at lower temperatures it is stable only in dilute NaCl solutions, and $PbCl_4^{++}$ is stable in concentrated solutions. The solubility of lead increases from 20ppm to 100ppm at 125°C to as much as 600ppm at temperatures up to 350°C. This range of solubility of galena in NaCl-HCl-H_2O solutions is enough to account for hydrothermal ore-deposits.

Helgeson has also shown that the solubility and stability of other ore-forming metals in chloride solutions is sufficient to account for hydrothermal deposits. The order of stability of chloride complexes at 25°C is :

Cu^{2+} Zn^{2+} Pb^{2+} Ag^+ Hg^{2+}

and their respective log K_{298} values at this temperature are :

0, —2, —1.57, —3.3, —7.3.

This order coincides perfectly well with zonal sequences and hence it is probable that these metals are transported as chloride complexes under hydrothermal conditions.

Kuz'mina (1961, in Helgeson) has determined the solubility of galena and sphalerite in NH_4Cl, NaCl and LiCl solutions in the temperature range 300°C to 450°C. The solubility of galena within this range and also at 25°C is greater than sphalerite in chloride solutions. Moreover PbS and ZnS respond differentially to varying chloride concentration. However, it seems probable that the order of stabilities of galena and sphalerite at 25°C persists at elevated temperatures.

Both monovalent copper and zinc at 25°C show a very high degree of complex formation in concentrated NaCl solutions while divalent copper does not.

The stability of AgCl and $AgCl_2^-$ complexes shows little net change in temperature range of 25°C to 300°C. The polychloride complexes of silver ($AgCl_3^{--}$, $AgCl_4^{3-}$) form to a very high degree in concentrated NaCl solutions at 25°C. The equilibrium constant of silver chloride (AgCl) seems to increase with temperature up to 200°C with a gentle maximum and then decreases slightly. The equilibrium constant of $AgCl_2$ at 25°C is (—1.9) and gradually increases to a gentle maximum and then decreases to (—2.5 to (—3.5) at 300°C to 400°C.

Mercury has a roughly similar pattern of complex formation to that of silver. $HgCl^+$ complex shows a very high degree of stability to up to 300°C to 400°C. High order polycomplexes ($HgCl_4^{2-}$) are extremely stable at 25°C.

This short review of the stability and solubilities of various metal chloride complexes suggests that there is a strong argument in favour of the hypothesis of metal transport as chloride complexes. The data on the composition of various types of hydrothermal waters strongly suggest that they usually contain from 3-30% NaCl and from a geological point of view it is one of the most feasible modes of transport.

An alternative hypothesis to explain the transport of metals is that most of these metals are carried as sulphide or bisulphide complexes. These postulated complexes are assumed to be stable at high temperatures and usually break down with decreasing temperatures whereby they are deposited as sulphides. Sulphide complexes of As, Sb and Hg are highly soluble at high pH's and high concentrations of total sulphide. The bisulphide complexes of copper, zinc, cadmium, lead, silver, mercury, antimony and arsenic are adequately stable at reasonable pH values, but the total sulphide must exceed the sulphophile metals by two orders of magnitude.

In highly alkaline conditions sulphure usually exists as the S^{2-} ion. With increasing H^+ however, it will combine with the hydrogen ion to form HS^- and finally H_2S, but at any one instant there is always some S^{2-} ion left, Barton (1958).

Arnston, Dickson and Tunell (1960) have shown that alkaline aqueous solutions in contact with free sulphur produce sodium polysulphide and thiosulphates, which form soluble complex ions with ore forming metals.

Barnes and Czamanske (1967) have produced a lot of evidence on the basis of sulphide/bisulphide solubility of metal ions in solutions, that in sulphur-rich conditions most of the metals can be carried in the form of sulphide or polysulphide complexes. Barnes and Kullerud (1961) have shown from a thermodynamic argument that it is possible to postulate limiting conditions in terms of pH, pS_2, pO_2 and temperature. According to them it is a common experience to find sphalerite, pyrite, digenite, covellite and baríte association, but never with free sulphur. This association will be formed around 250°C, in neutral to weakly alkaline conditions whereby HS^- is the predominant sulphur ion. pS_2 under such conditions will very between $10^{-8.5}$ and $10^{-14.7}$ atm and pO_2 is 10^{-35} to 10^{-50}atm. They have shown that the solubility of sphalerite under these conditions would be enough to form hydrothermal ore deposits, The total sulphur content would be around 1.0 molal.

Barnes and Romberger (1962, in Helgeson) have determined the solubility of sphalerite in NaCl solutions containing high sulphur up to 200°C. They have shown that the amount of zinc chloride is usually negligible within these experimental conditions. At total sulphur content (0.5m) under neutral to alkaline solutions up to 200°C the predominant species is ZnH_2S^-, while under low total sulphur conditions and temperatures above 200°C $ZnCl^-$ complexes are most important.

In the system ZnS-H_2S-$NaCl$-H_2O, Hinners and Holland (1963) have shown that at 80°C and neutral conditions $ZnS \times hH_2S$ complexes usually Predominate. The same conclusion has been drawn by Anderson (1952) for $PbS \times nH_2S$ complexes in the system $PbS \cdot H_2O$. In both the cases the solutions were saturated in H_2S. Thus in chloride solutions saturated with H_2S the chloride complexes will dominate in the acid region, metal - H_2S complexes in the neutral region which will finally give way to bisulphide metal species in the alkaline conditions, Helgeson (1964).

Nriagu and Anderson (1970) have calculated the solubilities of CdS, PbS, CuS, HgS in solutions containing Cl^-, S^{2-}, HS^-, H_2S as the dominant species. They have shown that sulphur rich solutions in equilibrium with metal sulphides in the form of S^{2-}/HS^- complexes, sufficient quantities of metals can be mobilized to form ore deposits. They suggest that brines carry enough sulphur to precipitate metal sulphides from chloride complexes.

It is clear from this discussion that given enough sulphur, most of the metals can be transported as sulphide/polysulphide complexes in hydrothermal solutions. The actual concentration of sulphide ion in this model is its weakest point and has not been supported from the evidence of natural waters, Roedder (1967). An equally strong criticism of this model is the low solubility of pyrite in high sulphide solutions, the most suitable for base metal complexes. Pyrite, however, is moderately soluble in some solutions, moderately high in sulphide and NH_3, but then from the evidence of natural solutions there is never enough NH_3 in these solutions. Waters high in NH_3 only, on the other hand, are usually low in iron. Hall and Friedman (1963) have suggested that ore-fluids transporting base metals and silver are usually very saline brines, high in

Na-Ca-Cl, and are weakly alkaline to acid. The base metal content of these brines is directly related to chlorine content and temperature, and also to the calcium content. Also brines high in iron are generally high in Zn, Pb, Cu, and Ag. Roedder (1967) has shown that brines high in base metal content are usually low in sulphur content. Moreover, brines precipitating sulphides in natural high temperature conditions do contain sulphur, but it is stoichiometrically too small to precipitate all the metals.

This apparent deficiency of brines in sulphur content has always been produced as an evidence against the transport of metals in the form of sulphide or bisulphide complexes. With respect to geothermal brines at Salton Sea, this deficiency in sulphur has been explained on the basis of the differences in mobility of the voltile gases like H_2S, CO_2 etc., and the metals, White (1965), Barnes (1967). Because of the high volatility of the gaseous components they will escape to the top through the shale membranes much more easily and quickly as compared to the salts and metals. Barnes (1967) thinks that most of these solutions are never deficient in sulphur. The apparent deficiency in sulphur of inclusion fluids and other mineralizing fluids is thought to be due to the high mobility which makes it easier for sulphur to escape, and thus the resulting solution shall always be stoichiometrically deficient. He produces the deposition of native sulphur at thermal springs as evidence in support of his hypothesis.

Other workers who assume the apparently sulphur deficient character of the mineralizing solutions as inherent, have forwarded alternative mechanisms for the formation of sulphides.

Lovering (1961) has suggested that during the ascent of mineralizing solutions when they come across some pyritous beds, these solutions react with the pyrite in rocks thus releasing sulphur while the iron goes into solution. The released sulphur in turn causes the precipitation of base-metal sulphides from chloride complexes. This reaction is further accelerated by the decrease in temperature.

Barnes (1967) has criticised this idea on the basis of the total lack of evidence of any reaction between the solutions and pyrite. He claims, that in most pyritous beds where there has been mineralization, the pyrite crystals do not show any reaction rims and all the crystals are usually intact. Moreover, granted the possibility, the first phase of the mineralizing solutions after they have reacted with the pyrite bearing bed will form a protective interface and these solutions would be unable to react further.

White (1968) has suggested several possible mechanisms for the formation of sulphides. In one mechanism he postulates that the saline Na-Ca-Cl brines rich in metals (from a few ppm to thousand ppm) usually exist at a deeper zone. The base metals are largely in the form of chloride complexes. On the other hand, in an upper zone, meteoric waters circulate in rocks actively. There may be mixing in an intermediate zone due to convection or diffusion. This mixing may be very sharp or gradational. The meteoric waters would have dissolved a lot of sulphur from the country rock and the ascending sulphur in the form of H_2S from the deeper zone. The mixing of these waters will consequently result in decreasing the temperature. This would cause a reaction and breakdown of the chloride complexes which may result in the formation of sulphides.

Other models are simple variants of this model. In one such model, a gaseous phase escaping from the brine reservoir is thought to be not necessary. The enrichment of the overlying colder solutions in sulphide species is attributed to a difference in the mobilities of H_2S, SO_2, H_2O. Consequently the "base metal sulphides are precipitated in those parts of a perfect and imperfect membrane system where temperatures and concentrations permit S^{+2} to compete successfully with the Cl-complexes for the available base metals."

In still other models, white argues the possibility of reaction with pyrite, the formation of pyrite followed by base metals and the mixing of the mineralizing solutions with meteoric waters.

DEPOSITION OF METAL SULPHIDES FROM HYDROTHERMAL SOLUTIONS

Deposition of metal sulphides from the ore bearing solutions can occur by a fall in temperature; the reaction of the solutions with wall rock and mixing of the ore-solutions with meteoric ground waters, changes in pH or a decrease of the pressure gradient etc.

The cooling of the hydrothermal solutions can be brought about by various mechanisms. Some heat is generally dissipated into the cooler surroundings. In this respect heat conduction is one of the possible factors, though it is considered to be relatively unimportant, The conduction of heat through the wall rock is usually controlled by factors such as flow rates of solutions and its variation with time, length of time during which the solution flows, and the rate of change of the solution at its source. Lafitte (1958 has shown that if temperature decreases suddenly, a reversed thermal gradient may be set up for a long time.

Reaction between hydrothermal solutions and wall rock may be partially responsible for cooling. In this case if the reactions are endothermic, the heat will be supplied by the solutions which may result in cooling. However, most of the well-known wall-rock alteration reactions are known to be exothermic, for example, as in the case of sericitization and kaolinization, which can actually cause a rise in temperature of the environment by as much as 100°C.

Cooling can be effectively brought about by mixing of hot hydrothermal solutions and the relatively cooler meteoric ground waters. In this case the ascending hot solutions through a geothermobaric gradient, will loose most of their heat content by mixing and thus result in deposition.

Cooling can also be affected by adiabatic expansion. The adiabatic expansion in this case may be reversible or irreversible. When slowly rising fluids expand reversibly without any heat exchange with the environment the entropy remains constant. However in reversible adiabatic expansion large pressure drops are required to effect a relatively small temperature change. In the case of irreversible adiabatic expansion the enthalpy remains constant, and a throttling action can cause a sudden drop from a high pressure to a lower pressure region with an accompanying drop in temperature. At temperatures above 350-400°C a pressure drop from 1500 to 250 bars may result in temperature changes from 600°C to 430°C, pistorius and Sharp (1960).

However, at temperatures below 400°C the isotherms are usually very steep and the irreversible adiabatic expansion can result in heating of the solutions. In irreversible adiabatic expansion the pressure differential set up can cause appreciable brecciation.

During the reaction of the hydrothermal solution with the wall rock, there is usually a vast amount of ion exchange involved. Hydrogen ion and sodium ions are usually fixed in rocks, while ions like Fe^{2+}, Al^{3+}, Mg^{2+} etc. may be released into the solutions, thus causing changes in the pH of the solutions, whereby deposition may ensue, Helgeson (1964).

It has also been suggested that the volatile sulphur and CO_2 of the hydrothermal solutions may escape leaving these solutions behind. During their course, they will react with iron minerals to form pyrite or other iron carbonates. The hydrothermal solutions in their turn may react with these minerals and thus result in the deposition of sulphides, Lovering (1961) White (1965).

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