

# Basic Geochemical Data of Zn, Pb and Cu and Hydrothermal Ore Genesis

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## *Abstract*

An efficient transport and a local accumulation of the ore metals is controlled by: 1. availability of water, 2. availability of metals and sulfur, 3. availability of compounds forming complexes with ore metals (chloride, bisulfide), 4. existence of channels and driving forces, 5. existence of steep geothermal gradients or solutions which cause ore precipitation. A concentration of metals at and above 1 ppm must be achieved in ore solutions (information from recent ore brines, fluid inclusions and solubility data of ore and gangue minerals). The availability of complexing chloride has been estimated from data on metamorphic and granitic rocks. Certain ore deposits can be correlated with magmatic, sedimentary or both sources by their lead isotope data.

## *Zusammenfassung*

### *„Geochemische Grunddaten von Zn, Pb und Cu und hydrothermale Erzentstehung“*

Transport und lokale Anreicherung von Erzmatalen werden durch folgende Faktoren kontrolliert: 1. das Vorhandensein von Wasser, 2. das Vorhandensein von Metallen und Schwefel, 3. das Vorhandensein von Verbindungen, die mit den Erzmatalen Komplexe eingehen (Chloride, Bisulfide), 4. das Vorhandensein von Kanälen für die Lösungen und von treibenden Kräften, 5. die Existenz von steilen geothermischen Gradienten oder Lösungen, die eine Erzausfällung bewirken. In Erzlösungen muß eine Metallkonzentration von etwa 1 ppm oder dar-

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über erreicht werden (Ergebnisse von rezenten, metallreichen Solen, Flüssigkeitseinschlüssen und Löslichkeitsdaten von Erz- und Gangmineralen). Auf das Vorhandensein komplexierender Chloride wurde aus Daten von metamorphen und granitischen Gesteinen geschlossen. Bestimmte Erzlagerstätten können auf Grund ihrer Blei-Isotopen magmatischer oder/und sedimentärer Herkunft sein.

As in modern petrology concepts about the formation of ore deposits should rely on field observation, experiment and theory. Observations on geologic setting, on mineral composition and intergrowth as well as computations and measurements of mineral solubilities contribute to the knowledge of ore metal solutions. Recent sampling of ore brines in the Salton Sea area (California) and the Red Sea holes, progress in sophisticated analytical methods and experiments in sulfide systems have substantially influenced our views.

In this report I will consider the temperature range above early diagenesis of sediments and below the melting minimum of granitic rocks ( $\sim 700^{\circ}\text{C}$ ) as that of "hydrothermal solutions".

Several properties of a natural system are required for an effective transport and deposition of ore metals:

- a) Availability of hot water or steam
  - b) Availability of metals and their sulfide anions
  - c) Availability of complexing compounds which change the very low solubility of metal sulfides drastically
  - d) Occurrence of channels and driving forces for water circulation
  - e) Occurrence of steep gradients of temperature, water and/or rock composition to dissolve and precipitate metals within short distances
- a) *Availability of water* is often no problem in the middle and upper continental earth's crust.
- b) *Availability of metals (I) and sulfides (II)*

I. The abundant rock types and magmatic melts occurring in the continental crust contain Zn, Cu and Pb in concentrations mainly in the range of 10 to 100 ppm. The average abundance of these metals in granitic rocks, greywackes and shales (and their metamorphic equivalents) decreases in the sequence: Zn, Cu and Pb as visible in several frequency diagrams of Figure 1 plotted from data of a worldwide sampling compiled by *Wedepohl* (1972, 1973). One can observe that Zn, Cu and Pb occur almost everywhere in the continental crust in reasonable quantities to support solutions. The problem is to get these metals extracted into hydrothermal solutions. According to leaching experiments of andesite and shale by *Ellis* (1968) the proportion of extracted Cu and Pb (no data on Zn) increases with temperature and salinity of the solution and decreases with sulfur content of the rock. The almost complete extraction of Zn and Cu from Icelandic tholeiitic basalts by acid hydrothermal waters (pH 1.5) and the partial extraction of these metals by alkalic hot waters (pH 9.5) has been investigated by *Wedepohl* (1972; Fig. 30-G-1).

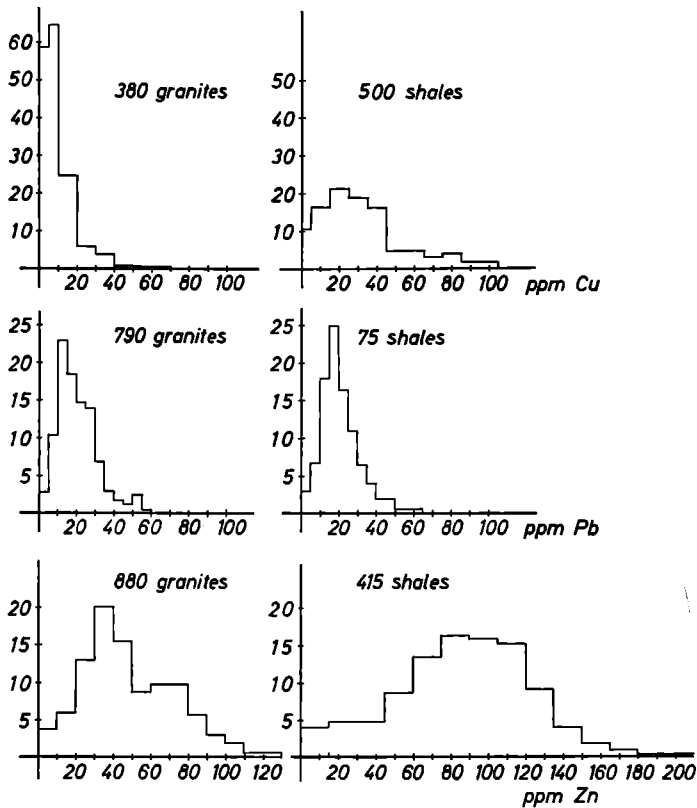


Fig. 1. Frequency distribution of Cu, Pb and Zn in granites and shales according to the compilation by Wedepohl (1972, 1973).

In magmatic rocks, zinc mainly occurs in the  $\text{Fe}^{2+}\text{Mg}$  structural positions of biotite, amphibole and magnetite; copper is abundant as chalcopyrite and in the structure of rock forming  $\text{Fe}^{2+}\text{Mg}$  minerals; lead has a strong tendency for the potassium position in feldspars and mica. In sedimentary rocks, Zn, Cu and Pb are incorporated in clay minerals; Zn and Cu partly occur in ferric iron oxides. Copper sulfides are more common in sediments than sphalerite and galena. Support of ore metals in hydrothermal solutions has to be expected from the consolidation of magmatic melts and from the extraction of wall rocks at fissures, voids etc. The different stability of the Zn, Cu and Pb host minerals against decomposition or dissolution in hydrothermal solutions partly controls the availability of these metals in ore depositing fluids. Chalcopyrite will be the least soluble of the mentioned host minerals of common rocks. All the three metals can be readily extracted from biotite, hematite etc. by reducing solutions. This fact can partly explain the predominance of sphalerite and galena over copper sulfides in numerous hydrothermal deposits.

II. Sulfide sulfur is abundant in granitic rocks in a concentration range of 100 ppm to 400 ppm S. Geosynclinal sediments contain on average 1000 ppm S (Ronov & Yaroshevskiy, 1967). The sulfur content of metamorphic rocks is expected to be closer to that of granitic than of argillaceous rocks. Reduced sulfur mainly occurs in the form of iron sulfides in common rocks. Because of the very low solubility of these sulfides hydrothermal waters need higher ionic strength, complexing compounds etc. to extract some sulfide from rocks and melts. Sulfide sulfur can be accumulated in a high temperature environment from a condensation of magmatic gas and at the low temperature level from bacterial sulfate reduction. Hydrothermal solutions with modest sulfide concentrations ( $< 0,1 \text{ m } \Sigma \text{HS-S}^{2-}$ ) and low in chloride cannot extract Cu, Pb and Zn from rocks and melts because of the very low solubility of the respective sulfides.

According to Krauskopf (1961) the solubility of  $\text{Cu}_2\text{S}$ ,  $\text{PbS}$  and  $\text{ZnS}$  in pure water increases by several orders of magnitude at an increase of temperature from  $25^\circ \text{C}$  to  $300^\circ \text{C}$ . But even at  $300^\circ \text{C}$  dissolved metals in equilibrium with sulfides are still as low as  $10^{-7}$  to  $10^{-9}$  mole per liter ( $\text{Cu}_2\text{S}$ :  $10^{-9}$  mole/liter;  $\text{ZnS}$   $10^{-8}$  mole/liter;  $\text{PbS}$   $10^{-7}$  mole/liter). Water vapor of this temperature low in sulfide and chloride can dissolve metal concentrations of less than about 10 ppb Zn, Pb or Cu from rocks and melts. These concentrations are in the range of normal sea and river water; they are too low for ore metal accumulation in economic deposits.

Several estimates can demonstrate the inefficiency of solutions containing metals in the X to X0 ppb range to form deposits. In this case an ore body containing  $10^6$  to  $10^7$  tons Zn, Pb and/or Cu will need about  $10^{15}$  tons of water as transporting agent. Twice the amount of water presently contained in all the rivers of the world has to pass through the fissures of a rock volume in the size of cubic kilometers ( $n \cdot 10^9$  tons) within a reasonable time. The time is controlled by the tectonic activity which has to keep the fissures open.

Hot water and water vapor passing through rock fissures will dissolve several rock constituents as Si, Ba etc. from compounds which have usually a higher solubility than the minerals containing Zn, Pb and Cu. If one compares the abundance of common gangue and ore minerals of hydrothermal deposits and knows the solubility of quartz, barite etc. the range of ore metal concentrations can be estimated. The solubility of barite depends on temperature, sodium chloride and sulfate concentration (Figure 2a, according to Templeton, 1960 and Strübel, 1967), that of quartz on temperature and pressure (Figure 2b, according to Kennedy, 1950). The solubility of calcite has not been used because it is related to four parameters (temperature,  $P_{\text{CO}_2}$ ,  $P_{\text{total}}$  and NaCl concentration) and decreases drastically from  $100^\circ$  towards  $300^\circ \text{C}$  (Ellis, 1959, 1963).

The solubility of quartz and barite in hydrothermal solutions is of special importance in the temperature range of  $200^\circ$  to  $400^\circ \text{C}$  and at a salinity of sea water and higher. These conditions have been recorded in numerous investigations of paleotemperature and fluid inclusions of vein type deposits. It can be

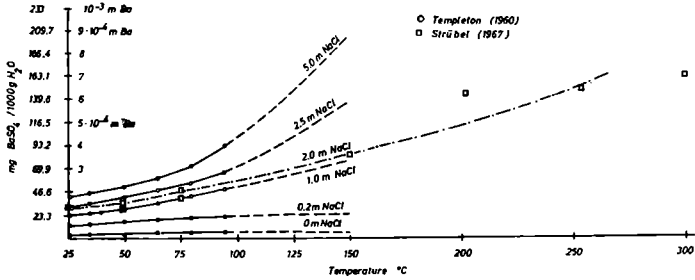


Fig. 2a: Solubility of barite as a function of temperature and NaCl concentration according to Templeton (1960) and Strübel (1967).

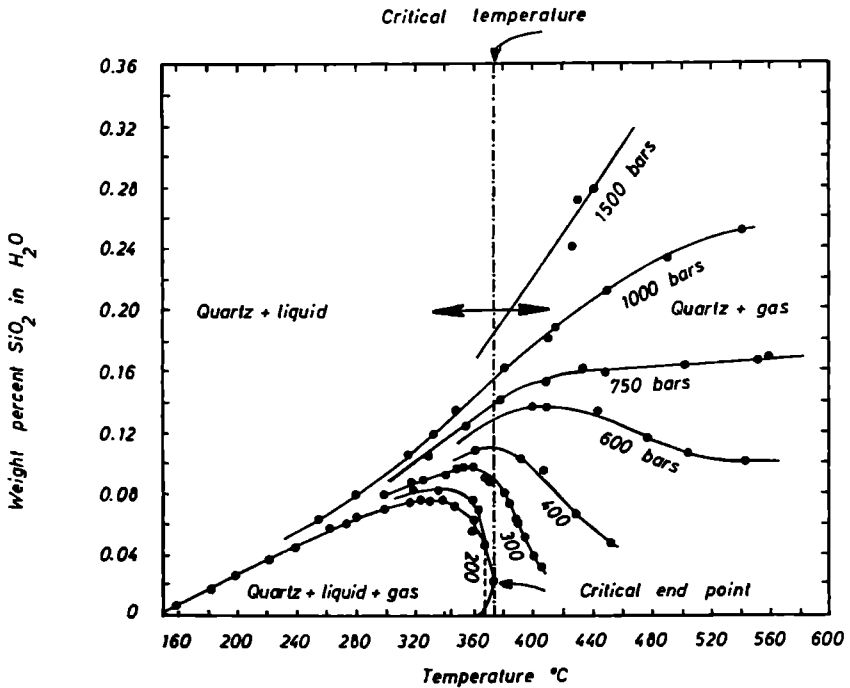


Fig. 2b: Solubility of quartz as a function of temperature according to Kennedy (1950). The influence of NaCl on the solubility can be neglected.

assumed that hydrothermal solutions are often saturated with respect to quartz and baryte because of the abundance of these minerals in common country rocks.

From Figures 2a+b it can be derived that at a temperature of 300° C, a pressure according to that of 3 km depth, a sodium chloride concentration of sea water and a sulfate concentration of about 100 ppm: 1000 ppm quartz and 100

ppm baryte will be in solution. Only the concentration of dissolved  $\text{BaSO}_4$  changes with salinity. An equal increase of the NaCl and the sulfate concentration has opposite effects which can almost compensate each other. If a ratio of quartz to ore minerals of 1000 and of baryte to metal sulfides of 100 (to 10) can be observed in hydrothermal deposits these are probably formed from solutions containing about 1 ppm of ore metals. These conditions and even lower gangue to ore mineral ratios (related to higher than 1 ppm metal concentrations in solution) are expected to have occurred abundantly in nature. A much lower metal concentration in the ppb range would be connected with a tremendous quartz mobilization. In our example of a relatively small ore deposit of  $10^8$  to  $10^7$  tons formed at  $300^\circ$  in 3 km depth a correlated mobilization of  $10^{12}$  tons ( $300 \text{ km}^3$ !) of quartz is to be expected, an unreasonable mass transport.

Metal concentrations at and above 1 ppm have been observed in nature (Table 1) as for instance: 2—3 ppm Cu, 80 ppm Pb and about 500 ppm Zn in a brine of about  $320^\circ \text{C}$  at the Salton Sea (California) (Helgeson, 1968); 0.3 ppm Cu, 0.6 ppm Pb and 5 ppm Zn in a submarine brine at Atlantis II Deep in the Red Sea (Emery, Hunt & Hays, 1969); 10 ppm Pb in a highly saline brine in the Cheleken district (Lebedev, 1967) etc. up to 9000 ppm Cu and 1% Zn in fluid inclusions of gangue minerals from North American deposits (Czamanske, Roedder & Burns, 1963).

In these solutions Zn is generally more abundant than Pb and Pb more than Cu. The sequence in abundance can be controlled by differences in solubility of the respective sulfides (see Table 2) or by the different abundance of the metals in common rocks and magmatic melts (Figure 1:  $\text{Zn} > \text{Pb} \geq \text{Cu}$ ).

### c) Availability of complexing compounds

The very low solubility of sulfides in pure water and an increase of solubility in complexing experiments make it highly probable that complexing constituents occur in those hydrothermal solutions which form economic metal deposits. Appreciable metal concentrations can be transported as chlorides and/or hydrogen bisulfide complexes to form sulfide bodies (Helgeson, 1969; Hemley & al., 1967; Barnes & Czamanske, 1967). Results of their experiments on sulfide solubility are listed in Table 2 which prove that concentrations at and above 10 ppm Zn, Pb, Cu are attained under conditions which can have existed in nature. Holland (1972) reports that the quench of aqueous NaCl solutions, equilibrated with granitic melts at  $800\text{--}850^\circ \text{C}$ , has a pH between 1.4 and 2.2 and Hemley & al. (1967) have measured in comparable systems (potassium feldspar-muscovite-quartz-saline solution) at  $200^\circ$  to  $300^\circ \text{C}$  a pH of about 4 to 5. The experiments by Barnes (reported in Barnes & Czamanske, 1967) and by Romberger & Barnes (1970) on bisulfide complexing have been performed in a weakly acid to alkaline pH range. For a significant metal transport of Zn, Pb and Cu as bisulfide com-

Table 1  
Metals in hydrothermal waters

Water type, locality	Temperature [pH]	NaCl in g/l	Sulfide in ppm	Zn in ppm	Pb in ppm	Cu in ppm	Reference
Brine Salton Sea, Calif. (USA) Shell 2 Imp. Irr. Distr.	~320° C	208	30	500	80	3	Helgeson (1968)
Brine Red Sea Atlantis II Deep	56° C	249	n.d.	5	0.6	0.3	Emery, Hunt and Hays (1969)
Brine Caspian Sea (USSR) Cheleken	80° C	241	—	5.4	10.7	3.7	Lebedev (1967)
Hydrothermal water Mexico Cerro Prieto Mexicali	340° C	12—18	180—700	0.006	0.005	0.005	Mercado (1966, 1967), for reference: Ellis (1968)
Hydrothermal water Taupo, New Zealand Well 2 Broadlands	275° C	1.9	150	0.007	0.002	0.15	Ellis (1968)
Hydrothermal water Weirakei, New Zealand Well 48	250° C	2.4	12	0.009	0.002	0.06	Ellis (1968)
Hydrothermal water Auckland, New Zealand Well 1 Ngawha	230° C	1.5	2700	n.d.	0.01	0.02	Ellis (1968)
Formation waters Western Canada sedimentary basin	20—120° C [7.2]	91 [1—460]	n.d.	0.8 [0.03—28]	n.d.	0.12 [0.02—0.5]	Billings, Hitchon and Shaw (1969)

Table 2

Solubility of sulfides in complexing solutions in ppm of metal  
(c: calculated; m: measured)

Metal (compound)	Complexing compound	100° C	200° C	300° C	500° C	Reference
Zn (ZnS)	3 mol. NaCl	0.29 c	8.2 c	205 c	n. d.	Helgeson (1969)
Zn (ZnS)	0.5 mol. KCl silicate buffer a)	n. d.	n. d.	65—650 m	2600—6500 m	Hemley et al. (1967)
Zn (ZnS)	2 mol. KCl silicate buffer a)	n. d.	n. d.	260—1800 m	3600—13 000 m	Hemley et al. (1967)
Zn (ZnS)	1 mol. HS- 0.5 mol. H <sub>2</sub> S	n. d.	50 c	n. d.	n. d.	Barnes, Czamanske (1967)
Cu (Cu <sub>2</sub> S)	3 mol. NaCl	0.025 c	4.0 c	950 c	n. d.	Helgeson (1969)
Cu (CuFeS <sub>2</sub> )	3 mol. NaCl	0.034 c	0.64 c	12.7 c	n. d.	Helgeson (1969)
Cu (CuS)	1 mol. HS- 0.5 mol. H <sub>2</sub> S	n. d.	180 c	n. d.	n. d.	Barnes, Czamanske (1967)
Cu (CuS)	0.66 mol. NaHS (+ H <sub>2</sub> S)	25 m	240 m	n. d.	n. d.	Romberger, Barnes (1970)
Pb (PbS)	3 mol. NaCl	0.13	1.0	13	n. d.	Helgeson (1969)
Pb (PbS)	2 mol. KCl silicate buffer a)	n. d.	n. d.	620 m	16 600 m	Hemley et al. (1967)

a: silicate buffer: K-feldspar or pyrophyllite-muscovite-quartz and 1000 bar total pressure



plexes total sulfide concentrations almost as high as one molal are needed in neutral to weakly alkaline solutions.

The extraction of zinc by chloride complexing aqueous solutions from granitic melts has been proved experimentally by *Holland* (1972). The relation between the partition ratio of Zn (between vapor and melt) and the chloride concentration of the aqueous phase has been reproduced as Figure 3 from *Holland's* original diagram. The partition ratio increases from 2 to 60 as the chloride concentration increases from 1 to 5 moles NaCl per kilogram (equal to 5.8 to 29 weight percent). This indicates a strong partition into the aqueous phase. One molal chloride concentrations are common in liquid inclusions of quartz from hydrothermal deposits (*Roedder*, 1967). Granite quartz from SW Germany and E France contains liquid inclusions with concentrations of 3 to more than 4 molal chloride according to *Goguel* (1963).

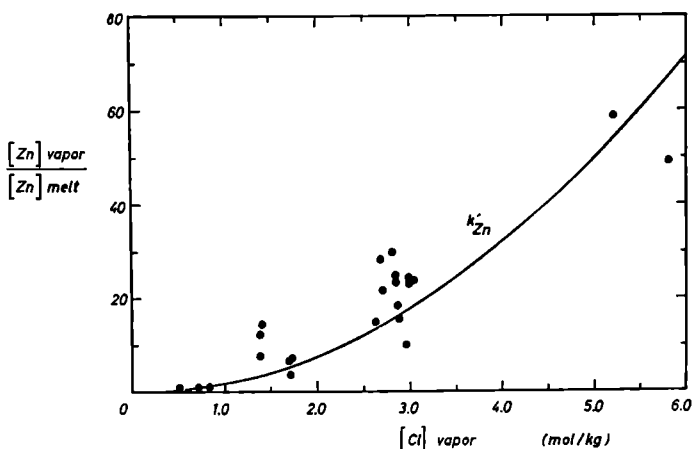


Fig. 3: The ratio of the concentration of zinc in the aqueous vapor to zinc in the granitic melt as a function of the chloride concentration in the aqueous phase according to *Holland* (1972). Plots of 22 experimental runs at 810–855° C temperature and 1.8–2.3 kb pressure. The curve represents a  $K'_{Zn}$  of 9.5.

Because of the above mentioned significance of chloride complexing in hydrothermal metal transport ore formation with some probability is primarily controlled by the availability of chlorine. It can be expected that the maximum quantity of zinc that can be removed from a granite melt or a sedimentary country rock depends on their chloride content. In his model of zinc extraction from granites *Holland* (1972) used melts with 3500 ppm Cl. Average granites contain only 200 ppm Cl. But the largest proportion of their primary chlorine must have been lost during degassing and consolidation because chlorine favours the vapor phase during the partitioning between melt and gas (molal partition coefficient  $K^{Cl} = m_{Cl}$  in melt/ $m_{Cl}$  in aqueous phase: 0.01–0.08 at 700–750° C and

2—8 kbars: *Kilinc and Burnham, 1972*). Therefore a knowledge of the initial chlorine concentration of granitic melts is important for our considerations.

Gneisses and mica schists of greenschist and amphibolite facies contain on average about the same chloride concentration as granites (as estimated from their mica, analyzed by *Haack, 1969*). *Johns & Huang (1967)* report a mean of 354 ppm Cl in 68 schists and 207 ppm Cl in 24 gneisses. During high grade metamorphism granitic melt can be formed in zones of migmatization. The fraction of partial melting of schists and gneisses will be controlled by their water content which is on average close to one percent. If partial melting occurs at 10 km depth (3000 bars pressure), about 8 % of water is soluble in a granitic melt, and a fraction of only 12 % melt will be formed in the metamorphic rock. In case of an extreme partitioning of chlorine into the melt its concentration will be 2000 ppm Cl. As a model melt *Holland (1972)* uses a granite containing 3550 ppm Cl and 1.8 to 5.4 % H<sub>2</sub>O. Compared with the above computed chloride concentration in anatectic melts from gneisses and schists his model contains an appreciably higher chloride content. Deeper origin of partial melts, if saturated with water, is correlated with the formation of smaller fractions of melt and higher water and chloride concentrations in the melt. This consideration explains larger differences in primordial chloride concentrations of granitic melts which support a higher or lower chloride content in the vapor phase. According to the reported partition experiments only those granites, which are abnormally high in chloride, should be considered as potential sources of hydrothermal metal deposits.

As a consequence of his partition experiments *Holland (1972)* has computed the metal (Zn) loss from degassing granitic melts before and during consolidation. In case of his relatively high chloride concentration and depending on the primordial water content metal loss ranges from 20 to 100 percent of the original zinc content of the granitic magma. If a metal loss of more than 20 percent is to be expected, systematic differences between intrusive and volcanic rocks in Zn, Pb and Cu should be observed. Recent compilations of data on zinc and copper can be used for a comparison of granites and rhyolites (obsidians etc.) (*Wedepohl, 1972, 1973*). The average zinc concentration in 1106 granitic rocks and in 234 salic volcanic rocks (rhyolites, pitchstones and obsidians) is 50 ppm and 98 ppm Zn, respectively. The average copper concentration in more than thousand granitic rocks and 100 salic volcanics (rhyolites, obsidians, pitchstones) is close to 10 ppm Cu and 6 ppm Cu, respectively. Data on lead are similar for intrusives and extrusives. The zinc balance which should be used with some caution yet supports an assumption of a metal loss during consolidation of granitic melts. But most of this zinc probably will diffuse and not be concentrated in ore deposits.

Another problem is that of an evidence for special metal concentrations in those granites which are associated with ore deposits. *Putman & Burnham (1963)* did not observe any association between certain zinc and lead concentrations in intrusives and the occurrence of mineral deposits in granite areas of Arizona (USA).

But they found abnormally high copper in intrusives correlated with mineralization. *Parry & Nackowski* (1963) claim that abnormally low Zn-, Pb- and high Cu-concentrations in biotites from monzonitic intrusives in the Basin and Range stocks of Utah and Nevada are indicators of economic sphalerite, galena and copper sulfide deposition. The stocks containing copper above but lead and zinc below a certain level show characteristics of deuteric alteration. *Gavrilin & al.* (1967) describe correlations of albitization and sericitization of granitic rocks with hydrothermal mobilization of Pb und Zn.

Subsolidus mobilization of zinc during muscovite formation in granite has been observed by *Haack* (1969). The zinc concentration in biotite is positively correlated with the muscovite/biotite ratio in granites (biotite of biotite granites contains on average 290 ppm Zn; biotite of two mica granite with muscovite > biotite: 520 ppm Zn).

The evidence presented in the above paragraph that lead zinc mineralization is indicated by the metal composition of related intrusives must be called meagre. This can have different reasons: Not at every intrusive from which a reasonable fraction of ore metals has been extracted during cooling, conditions favour a local precipitation to concentrate Zn and Pb into an ore body. Country rocks around an intrusive, penetrated by saline hydrothermal solutions, can contribute high fractions of a metal deposit. In certain mineralized areas magmatic plutons are even completely absent. At some of these places highly saline formation waters containing ore metals at the ppm level occur as in the Western Canada sedimentary basin. *Billings & al.* (1969) report concentrations of 20 ppm Zn and 0.5 ppm Cu in these waters as most probably being leached from shales.

Lead isotope data, as those compiled and partly contributed by *Doe* (1970), can locally solve the problem of the origin of lead in certain deposits. A direct magmatogenic origin must be concluded from the conformity between the isotopic composition of lead from a magmatic rock (or its feldspar) and that of galena from a related deposit. These ores are usually isotopically uniform. As examples, *Doe* (1970) mentions Butte (Montana, USA), Bingham Canyon (Utah, USA) and the Nelson batholith (British Columbia, Canada) etc. This group includes types in which at least a fraction of ore metal is derived from wallrock alteration of the outer zones of a pluton which are already consolidated. This stage can be characterized by sericitization mentioned above.

In lead ore being partly or completely supported by the lead of a country rock the isotopic composition of lead is usually more radiogenic and variable than that of the igneous body. The latter can have supplied complexing solutions, heat and a fraction of the metals. This case seems to be abundant.

For another type of ore formed at elevated temperature, any close association with magmatism can be excluded. It is usually characterized by highly radiogenic isotope ratios which in some cases can be traced back to rocks of the basement. The Mississippi-Valley type ore deposits belong to this association. Radiogenic lead is usually more easily to be extracted during wallrock alteration because of

its occurrence in metamict minerals or in structural positions favourably to uranium and thorium instead of lead etc.

#### *d) Channels and driving forces*

The opening of deep faults, fissures and voids through which hydrothermal solutions can move, are often restricted to major tectonic events and belts. The relation between tectonism and magmatism has probably led to an overestimation of magmatic sources of ore metals in the past. Recent examples of closing of steam pipes in hydrothermal areas demonstrate the high rate of mineral deposition from solutions containing compounds with modest solubility. The closing of fractures by mineral deposition has to be compensated by the tectonic movement to get a deposit of reasonable size. In several vein type deposits tectonic movement during deposition is visible in brecciation of ore. The present author has estimated the time needed for the deposition of the three about 15 km thick Pb-Zn-Cu ore lenses of the Rammelsberg deposit (NW Germany) being a few thousand years only. This is a syngenetic sedimentary bed containing about  $7 \cdot 10^6$  tons of metals most probably formed from submarine hydrothermal brines. The estimate of 0.3 cm per year as rate of deposition is based on the proportion of ore to silicate and the assumption of a reasonable rate of detrital accumulation in shallow seas (0.3 mm per year). The accumulation of the recent metalliferous Red Sea sediment ( $>10^8$  tons ore) has been estimated from  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  growth as being at least 0.4 mm per year (K $\mu$ , 1969). The order of magnitude cm per year has been measured in studies of the movement of the present ocean floor. The time of deposition in single ore veins ( $x \cdot 10^4$  to  $x \cdot 10^5$  years) is shorter than the cooling time of a granitic intrusion of a reasonable size ( $x \cdot 10^6$  years).

Outside areas of tectonic activity dissolution of country rocks can form channels through which hydrothermal solutions move. A chloride content of the solutions increases the solubility of  $\text{CaCO}_3$  appreciably (Ellis, 1963). Mississippi-Valley type deposits often occur in limestones.

The most effective driving forces for the movement of hydrothermal solutions are gradients of temperature and pressure to allow convection. Local pressure gradients can even occur between pore space and fractures. Steep temperature gradients are to be expected within and around contacts of magmatic intrusions and in "heat domes" of regional metamorphism. Notwithstanding a remarkable mobilization of structural water from clay minerals and of NaCl containing formation waters, regional metamorphism is commonly not concentrating ore metals locally. Ore minerals formed during regional metamorphism are often randomly distributed. The zonal distribution of mineral associations (telescoping) in the thermal gradient of magmatic intrusions indicates that at least the driving force for the movement of hydrothermal solutions is of magmatic origin.

### e) Ore precipitation

Ore precipitation needs oversaturation of solutions with respect to Zn, Pb, Cu sulfides. Complexing experiments mentioned in previous paragraphs, demonstrate the important influence of temperature and composition of a solution on the solubility of metal sulfides. Magmatic intrusions at shallow depth cause the steepest possible thermal gradients. A rapid change of the composition of a metal solution is achieved by mixing with waters lower in complexing anions. Magmatic vapors, brines, formation waters, sea water, geothermal waters and fresh water contain different concentrations of chloride as an important complexing anion. Mixing of waters of different origin seems to be an effective mechanism to precipitate different sulfides over short distances. Data on stable isotopes (D/H) indicate the rarity of truly magmatic solutions. Very often the  $^{34}\text{S}/^{32}\text{S}$  composition of gangue minerals (baryte etc.), even of vein deposits with magmatic affinities, is close to that of contemporaneous sea water. This can be explained by the participation of formation waters at least in the process of ore and gangue mineral precipitation.

Another cause of precipitation is the change in  $p_{\text{H}}$  of ore solutions by reaction with country rocks having a reasonable buffering capacity as limestones and clays.

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