

Canadian Mineralogist
Vol. 23, pp. 333-352 (1985)

CHEMICAL CONTROLS ON SOLUBILITY OF ORE-FORMING MINERALS IN HYDROTHERMAL SOLUTIONS

DAVID CRERAR, SCOTT WOOD* AND SUSAN BRANTLEY

*Department of Geological and Geophysical Sciences,
Princeton University, Princeton, New Jersey 08544, U.S.A.*

ANDREW BOCARSLY

Department of Chemistry, Princeton University, Princeton, New Jersey 08544, U.S.A.

ABSTRACT

The transport, deposition and zoning of hydrothermal ores are controlled by three main factors: the crystal chemistry and stability of the mineral phase, the physicochemical properties of aqueous electrolyte solutions at high T and P, and the thermodynamic and molecular properties of aqueous species of metals. Recent solubility and spectroscopic data permit the following generalizations on the chemistry of transition-metal complexes at elevated temperatures. Bonding changes from primarily ionic to covalent from left to right across each transition row. The d^{10} transition-metals behave more as Pearson soft acids, preferentially complexing with soft bases (electron donors) such as HS^- , whereas metals to the left show increasing "hardness", bonding to moderately soft electron-donors such as Cl^- . The Pearson rule successfully describes speciation to about 250°C, but breaks down at higher T as all metals become harder, and electrostatic interaction increases. Recently recognized relativistic effects predict increased tendency toward covalent bonding down each vertical group of elements; this in part explains the preference of Au and Hg for HS^- complexes and may also explain the apparent differences in speciation between Sb and Bi. Ligand numbers decrease with temperature, and neutral complexes like FeCl_2 predominate above roughly 300°C. This can be attributed to some or all of the following changes at higher temperatures: decreasing dielectric constant of water, descent from octahedral to tetrahedral complex coordination, pronounced decrease in activity coefficients of

anionic ligands, and increasing importance of hydrolysis. Increased solubility of ore minerals at higher temperatures can be attributed to some of the above effects; an equally important explanation is the temperature dependence of oxygen and sulfur fugacities and of pH buffering capacity. The buffer capacity also depends on solute composition and may help explain the rapid precipitation of minerals in porphyry-type ores and the more gradual precipitation in Mississippi-Valley-type deposits.

Keywords: ore deposits, ore zoning, metal-ion complexes, transition metal chemistry, hydrothermal solutions, buffer, mineral solubility.

SOMMAIRE

Le transfert, la déposition et la zonation des minerais hydrothermaux dépendent de trois facteurs principaux: la cristalochimie et la stabilité de la phase minérale, les propriétés physicochimiques de la solution aqueuse de l'électrolyte à température et pression élevées, et les propriétés thermodynamiques et moléculaires des espèces cationiques en solution. Des données récentes sur la solubilité et la spectroscopie permettent les généralisations suivantes au sujet du chimisme des complexes des métaux de transition à température élevée. Les liaisons passent de principalement ioniques à covalentes de gauche à droite dans chaque rangée de transition. Les métaux de transition d^{10} se comportent davantage en acides mous de Pearson; ils sont préférentiellement complexés par les bases molles (donneurs d'électrons) comme HS^- , tandis que les métaux à gauche démontrent une "dureté" de plus en plus grande, et forment des liaisons avec des donneurs d'électrons plutôt mous, comme

*Present address: Department of Geological Sciences, McGill University, 3450 University Street, Montreal, Quebec H3A 2A7.

le Cl⁻. La règle de Pearson réussit à décrire la spéciation jusqu'à environ 250°C, mais non à température plus élevée, où tous les métaux deviennent plus durs, et où les interactions électrostatiques augmentent. Des effets relativistes récemment étudiés prédisent une tendance aux liaisons covalentes dans chaque rangée d'éléments, ce qui explique en partie la préférence de l'or et du mercure pour les complexes HS⁻ et ce qui pourrait aussi expliquer les différences apparentes de spéciation entre Sb et Bi. Le nombre de ligands diminue avec la température, et des complexes neutres comme le FeCl₂ sont les plus importants à une température supérieure à environ 300°C. On attribue ce changement à certains des facteurs suivants (ou à tous ceux-ci) aux températures élevées: diminution de la constante diélectrique de l'eau, transition de la coordinance des complexes d'octaédrique à tétraédrique, diminution prononcée des coefficients d'activité des ligands anioniques, et importance accrue de l'hydrolyse. L'augmentation de la solubilité des minéraux des minerais à températures élevées découle de certains des effets cités; une explication tout aussi importante serait la dépendance des fugacités de l'oxygène et du soufre ainsi que de la capacité du tampon du pH sur la température. La capacité du tampon dépend aussi de la composition du soluté et pourrait expliquer la précipitation rapide des minéraux dans le minerai de type porphyre et leur précipitation plus graduelle dans les gîtes dits de type Mississippi Valley.

(Traduit par la Rédaction)

Mots-clés: gîtes minéraux, zonation du minerai, complexes ioniques de métaux, chimisme de métaux de transition, solutions hydrothermales, tampon, solubilité des minéraux.

INTRODUCTION

This paper focuses on some of the chemical factors that control the transport and deposition of hydrothermal metallic ores. We are concerned primarily with the general properties of aqueous transition-metal complexes, since it is now recognized that complex ions are responsible for most ore transport. Whereas the temperature range of primary concern in this paper is roughly 25° to 400°C, many of the principles discussed are valid to much higher temperatures.

It is helpful to reduce the overall problem of genesis of hydrothermal ores to a series of simpler questions. Some of these questions can be partly answered at present, and others await future research; together they represent pieces of a puzzle that is slowly being assembled, with much yet to come: (1) What are the specific reactions and equilibrium constants for the dissolution and precipitation of ore minerals? (2) Why do some of the transition metals form common hydrothermal ores, whereas many others form only rare deposits? For example, of the first-transition row, from Sc to Zn, only four metals typically form large hydrothermal deposits (Mn, Fe, Cu, Zn); some of the remaining six metals in this series are so

unreactive that experimentalists often use them to construct or line corrosion-resistant autoclaves (Ti, Cr, Ni). (3) What causes ore zoning, which is here represented by the highly simplified sequence Mo → Fe → Ni → Sn → Au → Cu → Zn → Pb → Sb → Hg from source to periphery of many deposits (*e.g.*, Barnes 1975). This is recognized as more than a simple effect of temperature: Susak & Crerar (1982) have recently emphasized that ore zoning depends on many variables, such as degree of saturation, temperature, pH, sulfur and oxygen fugacities, mineral stoichiometries, crystal structures, and the molecular and thermodynamic properties of the aqueous metal-complexes. (4) What are the major controls of ore deposition? Again, these factors include increased pH and total concentration of reduced sulfur, and decreased temperature and chloride activity (see reviews by Barnes 1979 and Crerar *et al.* 1978), but other variables such as sulfur and oxygen fugacities and even co-ordination changes in the aqueous complexes might play a role (Susak & Crerar 1984). (5) What are the molecular and thermodynamic properties of the complex ions responsible for ore transport? Consider the simplified process: source minerals → aqueous species → ore minerals. We know much about the properties of the ore and source minerals, and somewhat less about the leaching and ion-exchange processes responsible for initial dissolution of metals. However, surprisingly little is known about aqueous metallic species at high temperatures, and this is the most serious current barrier to an understanding of the chemistry of ore formation.

SOLUBILITY OF ORE MINERALS

Despite several decades of experimental research, much remains to be learned about the solvation reactions and solubilities of common ore-forming minerals. Solubility experiments are beset by experimental difficulties, such as the corrosive nature of the solutions and the need to control or determine multiple variables, including pH and oxygen and sulfur fugacities. Despite these problems, there does exist a useful body of information on the solubilities of many ore minerals under geologically pertinent conditions. In addition, there are now sufficient data on fundamental properties such as the valence, ligation number and stability of aqueous metal-complexes to permit some preliminary generalizations about transition-metal behavior in such systems. Excellent reviews on mineral solubilities and properties of observed transition-metal complexes are given by Khodakovskiy *et al.* (1975), Giordano (1978), Barnes (1979), Baes & Mesmer (1976, 1981), Frantz *et al.* (1981), Barrett & Anderson (1982), Seward (1981, 1984) and Bourcier (1983).

In addition, our group has recently completed

solubility measurements on the multiphase assemblage galena + sphalerite + gold + bismuthinite + argentite + molybdenite + stibnite + pyrite + pyrrhotite + magnetite in hydrothermal NaCl solutions from 200° to 350°C. These experiments provide an internally consistent data-set, particularly helpful in comparing the relative chemical behavior of the eight metals Pb, Zn, Au, Bi, Ag, Mo, Sb and Fe. We have listed what we believe to be the most important aqueous species over the range of these experiments in Table 1. Our thermodynamic data will be presented in a future publication (Wood, Crerar & Borcsik, in prep.; preliminary data are tabulated by Wood 1985). Table 1 illustrates many of the properties discussed below.

TABLE 1. SPECIATION OF EIGHT ORE METALS IN HYDROTHERMAL SOLUTIONS*

Metal	Low Chloride		High Chloride
	Low pH	High pH	
Fe	Fe ²⁺	FeOH ⁺ , Fe(OH) ₂ [°]	FeCl _n ²⁻ⁿ (n=0-3)
Zn	Zn ²⁺	ZnOH ⁺ , Zn(OH) ₂ [°]	ZnCl _n ²⁻ⁿ (n=0-3)
Pb	Pb ²⁺	PbOH ⁺ , Pb(OH) ₂ [°]	PbCl _n ²⁻ⁿ (n=0-3)
Bi	Bi ³⁺	Bi(OH) ₂ ⁺ , Bi(OH) ₃ [°]	BiCl _n ²⁻ⁿ (n=0-2)
Au	AuHS [°] or HAu(HS) ₂ [°]	Au(HS) ₂ ⁻	AuCl [°]
Ag	AgHS [°] or HAg(HS) ₂ [°]	Ag(HS) ₂ ⁻	AgCl [°]
Mo	H ₂ MoO ₄	HMoO ₄ ⁻	MoO ₄ ²⁻
	or		
	Mo-bicarbonate or -carbonate complexes		
Sb	Sb [°] (aq), HSbS ₂ , H ₂ SbS ₄	Sb(OH) ₂ ⁺ , Sb(OH) ₃ [°]	Unchanged

* as deduced from the multiphase sulfide-solubility experiments of Wood *et al.* (1983).

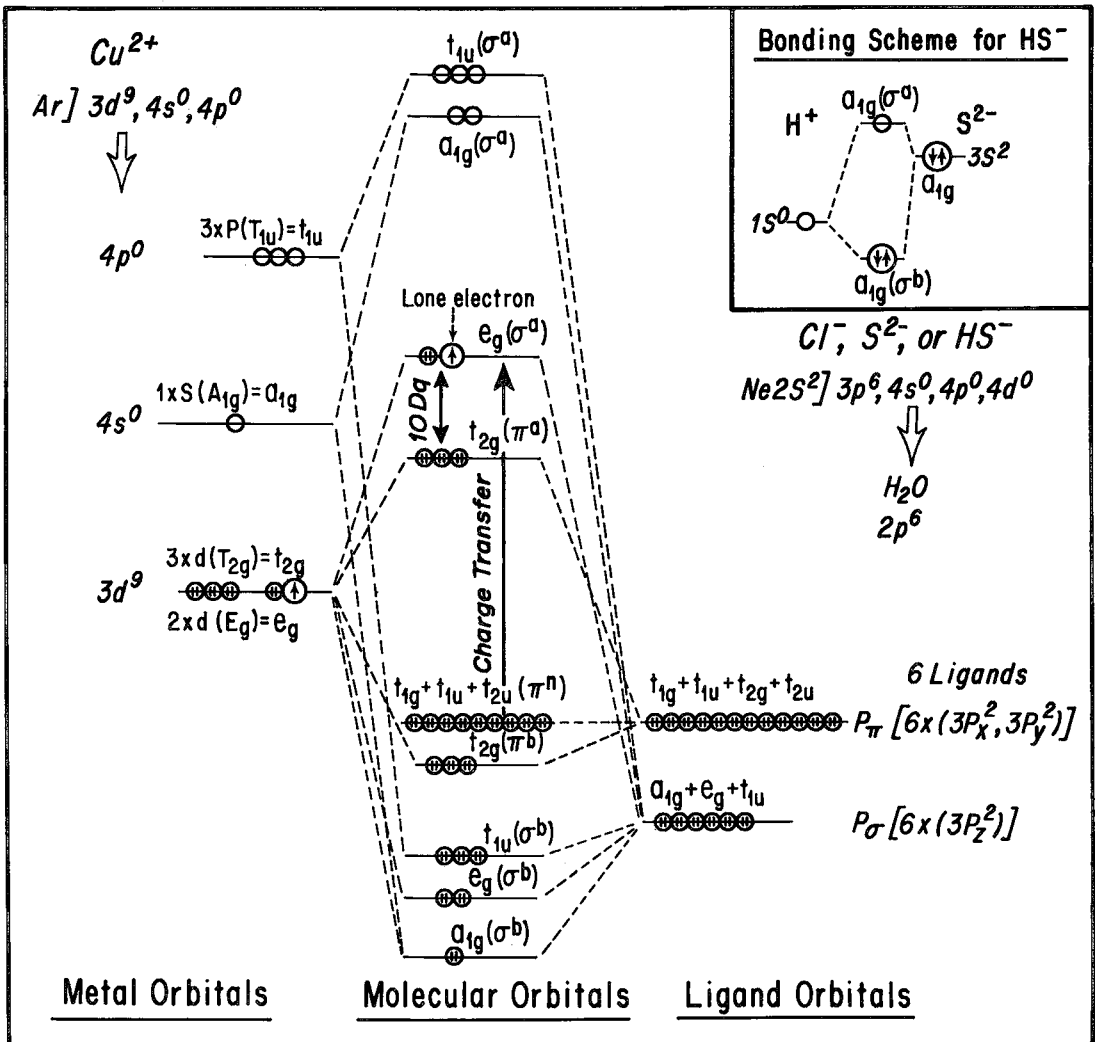
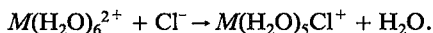


FIG. 1. Molecular orbital diagram depicting hypothetical energy-levels for an octahedral copper (II) complex with ligands such as Cl⁻, HS⁻ and H₂O. The electron transition marked 10 Dq results from the splitting of metal d-orbitals in a ligand field as illustrated further in Figure 5.

CHEMISTRY OF
AQUEOUS TRANSITION-METAL COMPLEXES

The nature of complex ions

For present purposes we treat aqueous transition-metal complex ions as well-defined molecular entities having a specific geometry and co-ordination number and co-ordinate bonding well described by ligand-field molecular-orbital theory (Huheey 1978, Figgis 1966). Over much of the range of hydrothermal ore-forming conditions, most transition-metal complexes appear to be either octahedrally or tetrahedrally co-ordinated (Susak 1981, Susak & Crerar 1984). The geologically most important ligands include Cl^- , OH^- and HS^- , in addition, of course, to H_2O . Other potential ligands, such as organic acids, NH_3 , F^- , S_x^{2-} , $\text{S}_2\text{O}_3^{2-}$, HCO_3^- and so on, are discussed by Barnes (1979). There is always competition between H_2O and other available ligands; thus formation of a one-chloro octahedral complex actually involves the displacement reaction



Complex ions may be contrasted with ion pairs such as NaCl^\ominus , which are held together primarily by coulombic attraction (for a detailed discussion, see Pytkowicz 1983). Since transition-metal complexes are true molecules, they can be described by molecular-orbital (MO) theory: their bonding framework can be represented, at least qualitatively, by MO diagrams such as Figure 1. Details on the construction of MO diagrams for transition-metal complexes are given by Figgis (1966) and Ballhausen (1962). The electron contribution from the *s* and *p* orbitals of six ligands (such as Cl^- , H_2O , HS^-) are shown on the right-hand side, and the contribution from the higher metal (Cu^{2+}) orbitals on the left. The diagram can be easily restructured for other metals and ligands by adding or removing the appropriate number of electrons from the e_g and t_{2g} molecular orbitals. Of particular interest are the electron transitions labeled "charge transfer" and "10 Dq." The former typically occurs in the near-UV and is very intense; the latter occurs in the visible region of the spectrum, is weak (parity-forbidden $g \rightarrow g$), varies with the field imposed by the co-ordinating ligands, and is responsible for the color of transition-metal compounds. Much information can be derived about the structure and thermodynamic properties of metal complexes from spectroscopic measurements of these transitions; we will return to this subject below.

Comparative complexing behavior of the transition metals

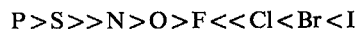
The first-transition series has the electron config-

urations $[\text{Ar}]3d^14s^2$ (for Sc) through $[\text{Ar}]3d^{10}4s^2$ (for Zn), except for Cu (which is $[\text{Ar}]3d^{10}4s^1$). The 4*s* electrons are lost before the 3 *dⁿs*, so that the divalent cations have the configurations $[\text{Ar}]d^1$ through $[\text{Ar}]d^{10}$. A similar rule applies to the two lower-transition rows; therefore, the ionic behavior of the entire series is governed by *d* orbital chemistry.

The aqueous behavior of this part of the periodic table and its nearest neighbors can be subdivided into three main groups, following the general argument of Giaquinta *et al.* (1983): (1) cations with the d^0 rare-gas configuration, (2) "noble-metal" cations with the complete d^{10} configuration, and (3) transition-metal cations with partly filled d^n orbitals.

For the d^0 cations (*e.g.*, Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Sc^{3+} , Ti^{4+}), interactions with ligands (anions or neutral dipoles) are predominantly coulombic or ionic. The stability of a complex increases with the ratio of charge to radius (ionic potential, *Z/r*) of the cation, and smaller anions are generally preferred. At room temperature, d^0 cations form fluoride species, but do not combine appreciably with the heavier halogens, including chlorine. The halogens compete unfavorably with the water dipole in the first co-ordination shell. At higher temperatures, association increases, but one should not expect particularly strong chloride complexes of Sc^{3+} or Ti^{4+} , for example.

In contrast, the d^{10} cations (*e.g.*, Zn^{2+} , Cd^{2+} , Hg^{2+} , Cu^+ , Ag^+ , Au^+ , Sn^{2+} , Pb^{2+}) form more covalent complexes and bond preferentially with the less electronegative ligands. Chloride complexes are therefore more stable than fluoride, and HS^- is particularly preferred. Since the d^{10} cations more readily accept transferred negative charge, they form their most stable complexes with the most polarizable ligands in the general order (Graddon 1968):



In natural hydrothermal systems, the valence of the Group-IB metals (Cu, Ag, Au) is 1 and that of the IIB metals (Zn, Cd, Hg) is 2. Hence all six of these metals fall in the special d^{10} category, and each should form highly stable, predominantly covalent chloride and bisulfide complexes, a prediction borne out by many experiments (summarized by Barnes 1979).

All other transition metals fall between the two extremes of the ionic d^0 and more covalent d^{10} cations. The relative chemical behavior of these intermediate metals is dictated by four main properties: (1) A change from predominantly ionic to more covalent bonding from d^0 to d^{10} apparent in the increasing electronegativities across each transition row. (2) A parallel increase in the electrostatic interaction with anions or dipoles, as indicated by the general increase

in ionic potential or Z/r across each row (*i.e.*, radii decrease from Ti^{2+} to Cu^{2+} somewhat as in the lanthanide contraction). This increases the stability of complexes formed with a common ligand from left to right in each row. (3) The effect of d -orbital splitting and ligand-field stabilization considered below. This increases the stability of complexes formed by cations with configurations other than d^0 , d^5 and d^{10} . (4) A relativistic property, considered below, which dramatically increases covalency down each vertical column of the heavier transition-metals.

The general effects of these four principal controls are outlined in the following sections.

The hard-soft classification

In the broadest sense, metal-ligand interactions may be regarded as acid-base reactions, with the metal and ligand acting as electron acceptor and donor, respectively. Pearson (1963), among others, has divided metals and ligands into two fundamental classes (see also Huheey 1978). Class-A (or hard) metals and ligands are generally small, highly charged, and are only slightly polarizable. Class-B (or soft) metals and ligands are large, relatively low in charge and are highly polarizable. A classification of some geologically important metals and ligands according to their hard-soft behavior is given in

TABLE 2. CLASSIFICATION OF GEOLOGICAL METALS AND LIGANDS*

Hard Acids	Borderline Acids
$H^+, Li^+, Na^+, K^+, Rb^+, Cs^+$	$Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$
$Ca^{2+}, Mg^{2+}, Ba^{2+}, Ti^{4+}, Sn^{4+}$	$Sn^{2+}, Pb^{2+}, Sb^{3+}, Bi^{3+}, SO_2$
$MoO_3^{3+}, WO_4^{4+}, Fe^{3+}, Al^{3+}, As^{3+}, CO_2$	
Soft Acids	
$Cu^+, Ag^+, Au^+, Cd^{2+}, Hg^+, Hg^{2+}, H^0$ (metal atoms and bulk metals)	
Hard Bases	
$NH_3, H_2O, OH^-, CO_3^{2-}, NO_3^-, PO_4^{3-}, SO_4^{2-}, F^-, Cl^-$	
Borderline Bases	Soft Bases
Br^-	$CN^-, CO, H_2S, HS^-, I^-$

* According to Relative Hardness. Condensed from Huheey (1978).

TABLE 3. RELATIVE HARDNESS OF COMMON METAL IONS AND LIGANDS*

$F^- > Cl^- > Br^- > I^-$	$Zn^{2+} > Pb^{2+}$
$Cu^+ > Ag^+ > Au^+$	$H^+ > Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$
$Zn^{2+} > Cd^{2+} > Hg^{2+}$	$As^{3+} > Sb^{3+} = Bi^{3+}$

* Hardness decreases toward the right.

Table 2; relative hardnesses within each grouping are listed in Table 3.

Hardness and softness correlate roughly with electrostatic and covalent interactions, respectively.

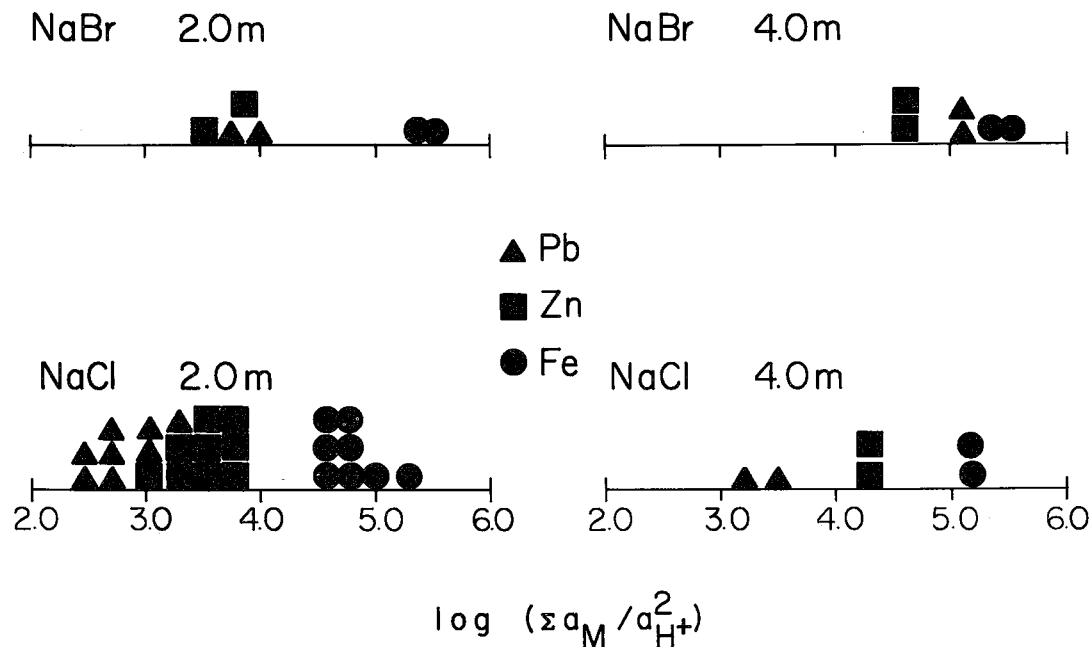


FIG. 2. Solubilities of the assemblage pyrite - pyrrhotite - magnetite - galena - sphalerite in 2.0 and 4.0 molal NaCl and NaBr solutions at 200°C. The metal concentrations are divided by $(a_{H^+})^2$ to normalize the effect of pH on solubility. Note the reversal in order of solubility from $Fe > Zn > Pb$ in chloride solutions to $Fe > Pb > Zn$ in bromide solutions, which verifies the prediction of Pearson's hard-soft rule.

Pearson (1963) proposed that in a competitive situation, soft acids bind preferentially with soft bases, and hard acids with hard bases. From available data we see that the soft ligands HS^- and H_2S form relatively strong complexes with Hg, Au, Ag, Cu and Sb, weaker complexes with Pb and Zn, extremely weak complexes with Fe and Sn, and probably do not form complexes at all with W and Mo. On the other hand, the borderline base Cl^- forms relatively strong complexes with Fe, Sn, Pb and Zn and most other transition metals, except for the d^0 ions, which tend to form weak chloride-ion pairs as opposed to molecular complexes (Giaquinta *et al.* 1983).

Pearson's rule is consistent with the results of recent experiments by S. Wood, in which the solubility of the assemblage pyrite – pyrrhotite – magnetite – galena – sphalerite was measured in both NaCl and NaBr aqueous solutions, as summarized in Figure 2. Relative solubilities follow the orders: sphalerite > galena in chloride solutions, galena > sphalerite in bromide solutions. At higher Cl^- and Br^- concentrations this solubility reversal is enhanced. This implies a reversal in the relative stability of the lead and zinc complexes (assuming no change in stoichiometry), an expected effect since

Pb^{2+} (a soft acid) prefers to complex with the softer Br^- , and Zn^{2+} (the harder acid) prefers the harder Cl^- . This trend implies that Pearson's rule is valid to at least 200°C, although Seward (1981) has pointed out that at higher temperatures, all metal-ligand interactions become harder.

We should offer one *caveat* concerning the use of Pearson's rule: it works well for determining relative preferences between ligands and metals only if there are fairly large differences in hardness or softness. The rule fails when comparing very similar species. For instance, we cannot use the rule to predict the preference of Sb and Bi for bisulfide and chloride complexes, respectively, because these metals are too similar in softness. In such cases, some of the other effects discussed in this paper must be considered.

One implication of the hard-soft rule is that we should not expect mixed-ligand complexes to be very important if the various ligands are quite different in hardness. This is due to a phenomenon first described by Jørgenson (1964) called symbiosis. The hardness or softness of a given acid is not only a property of the acid itself, but also depends on the properties of the complexed ligands. A soft, polarizable ligand will cause the metal itself to become softer, and a hard, highly electronegative ligand will cause the metal to be harder. Thus a borderline metal, once complexed with a soft ligand, becomes softer and is more disposed toward acceptance of another ligand of similar softness. The HS^- ligand is much softer than OH^- and Cl^- ; hence, we do not expect mixed $\text{HS}^- - \text{Cl}^-$ and $\text{HS}^- - \text{OH}^-$ complexes to be important.

Relativistic effects

An additional effect, only recently recognized, is that the velocity of the inner *s* and *p* electrons of the heavier metals such as Pt, Au, Pb, Bi and Hg approaches the speed of light. These electrons are, therefore, drawn closer to the nucleus of the atom and are more difficult to remove. The contraction of the *s* and *p* orbitals causes increased shielding of the *d* and *f* orbitals. Quantum-mechanical calculations show that the heavier metals should display a greater tendency toward covalent bonding because *d* and *f* orbitals are better shielded (Fig. 3). This has a pronounced impact on the properties of all elements heavier than Xe. Excellent reviews of this subject are given by Pitzer (1979) and Pyykkö & Desclaux (1979).

For example, in Sn the *s* and *p* electrons are held about equally tightly, and Sn can readily attain either a +2 or a +4 valence state. The next element down, Pb, occurs only in the +2 state. This is because the relativistic contraction of the *s* electrons is greater than that for the *p* electrons; the *s* electrons are, in

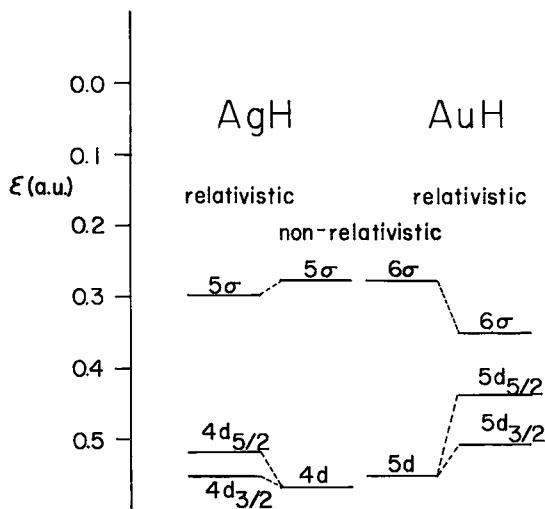


FIG. 3. Calculated energy-levels for the molecules AgH and AuH redrawn from a diagram in Pyykkö & Desclaux (1979). Note that the nonrelativistic levels for both Au and Ag are similar, but that the relativistic levels are quite different. The primary relativistic effect (manifested to a higher degree in gold) is the contraction of the *s* and *p* orbitals and hence a decrease in their energy. The contraction of the *s* and *p* orbitals causes increased shielding of the *d* and *f* orbitals, which expand and increase in energy. The energy levels for complexes such as AgHS° , AuHS° , AgCl° and AuCl° should be qualitatively similar to those shown, with implications for the relative stabilities of Ag and Au complexes.

effect, inert. This is the so-called inert-pair effect (Sidgwick 1933). Similarly, the contraction of the *s* electrons in gold raises its ionization potential far above that of Cu or Ag. The color of gold relative to silver is attributable to a relativistic decrease in the band gap analogous to the convergence of 6*s*,*p* and 5*d* orbitals in going from AgH to AuH in Figure 3. Relativity might also explain why mercury is a liquid and cadmium is not, at room temperature.

In hydrothermal solutions, complex ions of the heavier transition-metals should therefore become increasingly covalent. Thus, gold bisulfide complexes should be stronger than silver bisulfide complexes; our experimental data seem to support this, since our preliminary stability-constants for gold bisulfide complexes are larger than those for silver bisulfide (Wood 1985). The Cl⁻ complexes of these heavier metals will also be more covalent and possibly stronger. Relativistic effects probably explain the apparent preference of bismuth for chloride and of antimony for bisulfide ligands, in spite of similar *Z/r* ratios and electronegativities of the Bi and Sb ions (Table 1). Spin-orbit coupling, also a relativistic effect, may cause additional differences in behavior between the second- and third-row transition elements. Spin-orbit coupling increases as the fourth power of the atomic number, and so will increase greatly for the heavier elements. Although spin-orbit coupling does significantly affect the spectra of the complexes (Figgis 1966), its influence on their stability has not yet been measured.

Summary: electronegativity versus ionic potential

It is instructive to plot important ore-metal ions on an ionic potential (*Z/r*) versus electronegativity diagram. Figure 4 is an adaptation of such a figure by Whitfield & Turner (1983). On diagrams of this type, the metals separate into four overlapping fields corresponding to the predominant mode of complexation in natural hydrothermal solutions. At low to intermediate ionic-potential and high electronegativity, the more covalent complexes, such as the bisulfides, are important along with chloride species; this fits the experimentally observed bisulfide complexing of As, Sb, Cu, Zn, Ag, Cd, Au and Hg. Complexing in this region is essentially determined by relative concentrations of Cl⁻ and HS⁻ in solution (except for As and Sb, which do not appear to form strong chloride complexes). At intermediate ionic potentials and low electronegativities, chloride and hydroxy complexes predominate, depending upon pH and Cl⁻ activity. For the hydroxy complexes, the metal-oxygen bond strength approximates that of the H-O bond in H₂O (e.g., Mason & Moore 1982). For metals such as Fe, Mn, Ni, Co and Sn, bisulfide complexes are extremely weak; this helps explain why experimental geochemists looked in vain for many years for bisulfide complexes of *d*¹ to *d*⁹ ions such as Fe²⁺, whereas all of the *d*¹⁰ ions form quite stable bisulfide complexes. At very high ionic potentials and intermediate to high covalency, strong oxyanions such as molybdic and tungstic acids

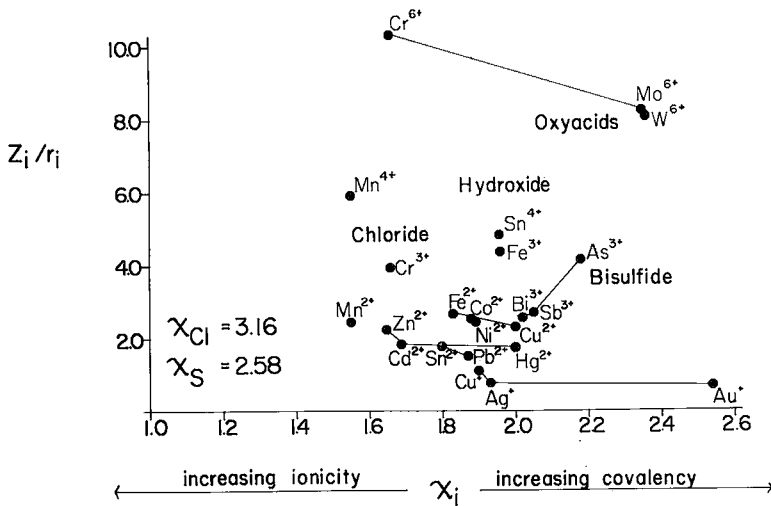


FIG. 4. Plot of ionic potential (*Z/r*) versus Pauling electronegativity. Crystal radii and electronegativities are taken from Huheey (1978). Ions in selected columns of the periodic table are connected by solid lines, as are ions of the first-transition series. Note that the ions separate into broadly general, overlapping fields of complexing behavior. The fields of the most common hydrothermal speciation are labeled.

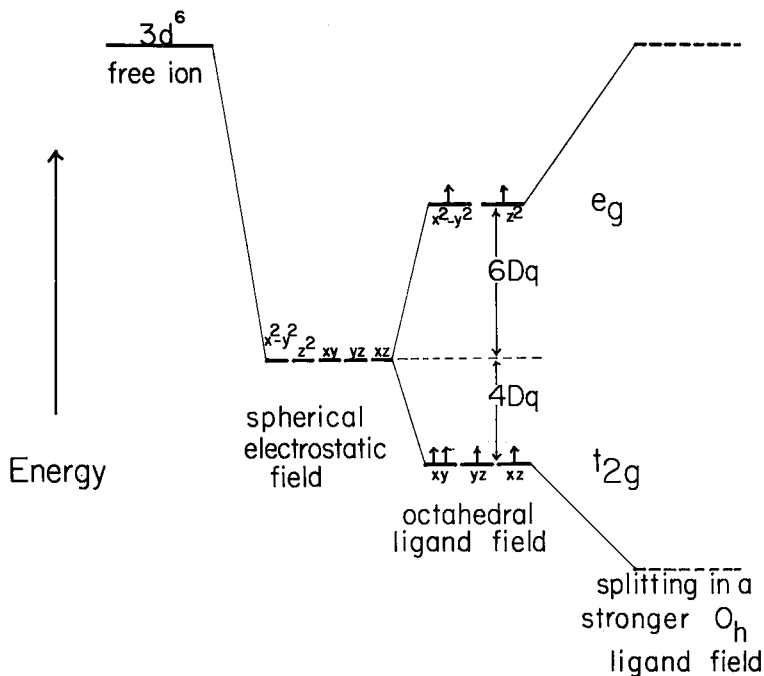


FIG. 5. Effect of an applied octahedral ligand-field on the total energies of $3d$ complex ions using high-spin Fe^{2+} ($3d^6$) as an example. The energy levels of the free ion $3d$ orbitals considered by themselves would plot below the t_{2g} level as shown here. Note that $10Dq$ depends strongly on the strength of the ligand field (*i.e.*, on ligand type and metal–ligand bond length).

predominate (*e.g.*, H_2MoO_4 , H_2WO_4); for such species, the metal–oxygen bond strengths exceed the H–O bond strength of water.

Figure 4 emphasizes the pronounced difference in covalency between the Au^+ and Hg^{2+} ions and the other ions in their respective columns. This is most likely attributable to the relativistic effect discussed above.

Diagrams of this type can be used to predict complexing behavior of metals for which no experimental data are available. For example, we predict that the Cu^+ ion may prefer bisulfide complexing, whereas the Cu^{2+} ion may prefer chloride complexing. Similarly, Cr^{3+} may form Cl^- complexes, whereas Cr^{6+} should form an oxyacid in hydrothermal solutions.

Despite the obvious utility of such diagrams, an important additional dimension, ligand-field stabilization, must be included to completely characterize transition-metal speciation.

Ligand-field stabilization

A further control on the relative stabilities of metal complexes is ligand-field stabilization, a quantum-mechanical effect in which the degenerate d^n metal

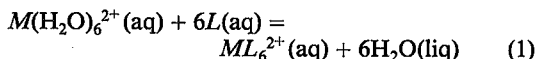
orbitals split to different energy-levels in the field produced by the ligands of a complex ion (*e.g.*, Burns 1970, Huheey 1978). The result is illustrated schematically in Figure 5 for a d^6 ion such as Fe^{2+} , which is octahedrally co-ordinated by 6 ligands such as Cl^- or H_2O . Relative to the unsplit orbitals, the energy of this $t_{2g}^4 e_g^2$ configuration is $4 \times (-4Dq_{\text{oct}}) + 2 \times (6Dq_{\text{oct}}) = -4Dq_{\text{oct}}$. This is termed the ligand-field stabilization energy, LFSE. For tetrahedral co-ordination, the energy levels are exactly reversed. The LFSE for octahedral complexes is always greater than that for tetrahedral complexes of the same metal and ligands ($Dq_{\text{tet}} = 4/9 Dq_{\text{oct}}$). The magnitude of the $10Dq$ splitting parameter varies with the ligand and geometry of the complex.

This simplified description of d -orbital splitting is adequate for present purposes, but ignores multi-electron interactions. More rigorous treatments use ligand-field theory and Tanabe–Sugano energy diagrams to characterize the splitting of electronic terms (*e.g.*, McClure 1959, Ballhausen 1962, Figgis 1966). Also note that ligand-field theory works well for the first-transition series, but decreasingly less so for the $4d^n$ and $5d^n$ series.

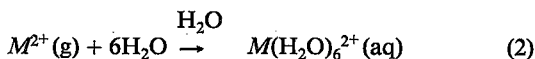
Values of LFSE for the divalent first-row ions are summarized in Table 4. Note that LFSE is zero for

d^0 , d^5 and d^{10} cations, and rises to a maximum for the d^3 and d^8 cations. This effect is reflected in the greater stability of molecules with a high value of LFSE, and is illustrated in Figure 6. The importance of LFSE on lattice and hydration energies is readily apparent; however, the relationship between LFSE and complex stabilities is of more interest to geochemists and is considerably more difficult to understand.

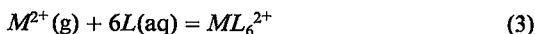
We are particularly interested in trends of complex-ion stability constants across the first-transition row. The stability constant for the complexation reaction



is given by $K = \exp(-\Delta G^\circ/RT)$, where $\Delta G = \Delta H - T\Delta S$. Since ΔS for complex formation is relatively constant across the first series (George & McClure 1959), then the stability constants vary directly with ΔH . To understand the variation of ΔH , we can separate reaction (1) into a hydration step:



and a ligation step:



Because reaction (1) is simply reaction (3) minus (2), then

$$\Delta H_{\text{complexation}} = \Delta H_{\text{ligation}} - \Delta H_{\text{hydration}} \quad (4)$$

Although $\Delta H_{\text{ligation}}$ and $H_{\text{hydration}}$ vary in a similar manner across the first-transition series (following the double-hump trend of Fig. 6), they are usually slightly out of phase, so that their difference ($\Delta H_{\text{complexation}}$) does not display as smooth a pattern. In general, there is an effect of LFSE on complex stabilities as shown by the examples in Figure 6. This additional effect is significant; values of Dq for lattice and hydration energies given by George & McClure (1959, p.398), for example, are approximately 5 kcal/mole for octahedral co-ordination; this means that co-ordination compounds of Ni^{2+} or V^{2+} with a LFSE of $12Dq$ acquire roughly 50–70 kcal/mole additional stability by d -orbital splitting. Further details on the effect of LFSE on stability constants of a complex are given by George & McClure (1959), Figgis (1966, p. 93) and Dasent (1982, p. 172).

TABLE 4. LIGAND-FIELD STABILIZATION ENERGIES OF OCTAHEDRAL AND TETRAHEDRAL COMPLEXES IN WEAK FIELDS

First transition series	Number of d electrons	Ligand field stabilization energy (LFSE) Octahedral complex	Tetrahedral complex
$\text{Sc}^{2+}, \text{Fe}^{2+}$	1, 6	$-4 Dq_{\text{oct}}$	$-6 Dq_{\text{tet}} (-1.78 Dq_{\text{oct}})^*$
$\text{Ti}^{2+}, \text{Co}^{2+}$	2, 7	$-8 "$	$-12 " (-3.56 ")$
$\text{V}^{2+}, \text{Ni}^{2+}$	3, 8	$-12 "$	$-8 " (-5.33 ")$
$\text{Cr}^{2+}, \text{Cu}^{2+}$	4, 9	$-6 "$	$-4 " (-2.67 ")$
$(\text{Ca}^{2+}), \text{Mn}^{2+}, \text{Zn}^{2+}$	0, 5, 10	0 "	0 " (0 ")

*Note that $Dq_{\text{tet}} = 4/9 Dq_{\text{oct}}$

Actually, the effect of LFSE is also obscured by experimental error for the complexes shown in Figure 6. This is particularly true for geologically impor-

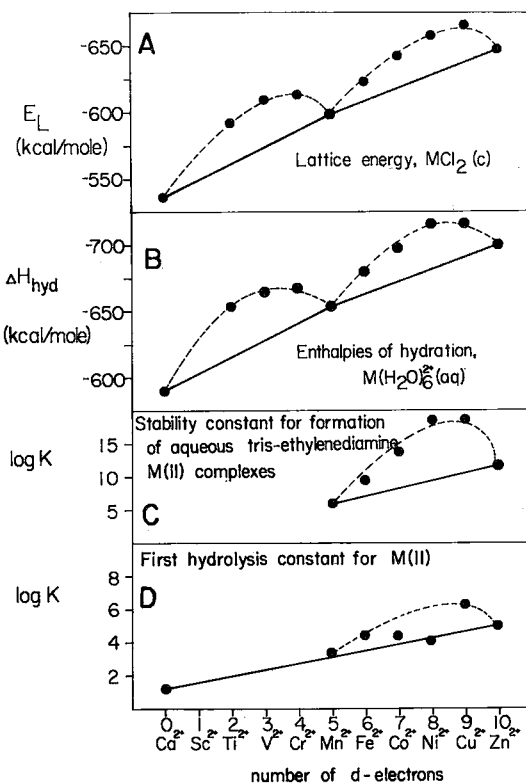


FIG. 6. Plot of various energy-parameters versus number of d electrons for the first-transition row. A) Lattice energy, or the heat of the reaction: $M^{2+}(\text{g}) + 2\text{Cl}(\text{g}) \rightarrow M\text{Cl}_2(\text{s})$. B) Enthalpy for the H_2O reaction: $M^{2+}(\text{g}) + 6\text{H}_2\text{O} \rightarrow M(\text{H}_2\text{O})_6^{2+}(\text{aq})$. C) Log equilibrium constant for the reaction: $M(\text{H}_2\text{O})_6^{2+}(\text{aq}) + \text{tren} \rightarrow M(\text{tren})(\text{H}_2\text{O})_5^{2+}(\text{aq}) + \text{H}_2\text{O}$ (tren is trisethylenediamine). D) Log equilibrium constant for the reaction: $M(\text{H}_2\text{O})_6^{2+}(\text{aq}) + \text{OH}^- \rightarrow M(\text{H}_2\text{O})_5(\text{OH})^+(\text{aq}) + \text{H}_2\text{O}$. The dashed lines are a qualitative representation of an "ideal" double-humped pattern. Data for A, B and C are from George & McClure (1959). Data for D are from Pytkowicz (1983).

tant inorganic complexes such as the hydroxy species illustrated. The stability constants of organic complexes and chelates (such as tris-ethylenediamine) are typically orders of magnitude higher as shown; hence, relative errors are smaller, and the ligand-field effects more apparent. Such organic chelates are geologically important in surface waters and groundwaters and may be significant in lower-temperature hydrothermal systems such as gave rise to the Mississippi-Valley-type Pb-Zn deposits (Barnes 1979, Giordano & Barnes 1981).

The general rise on all plots in Figure 6 from Ca through Zn is attributable to the proportionality between bonding energy and Z^2/r_{cation} (Figgis 1966, p.78) and the decrease in ionic radius across this series. This is a direct expression of the ionic potential term discussed above. Thus, a general increase in stability of transition-metal compounds and complexes is expected from Sc to Zn.

In summary, complex ions with high LFSE (as indicated in Table 4) generally have higher stability-constants. Although experimental data on stability constants of a complex at higher temperatures are insufficient to test this prediction, we can use the overall concept to make some useful generalizations about mineral solubilities and ore-forming processes.

Some geological implications of ligand-field effects

Since ligand-field theory works best for the first-

transition series, we take as our example the elements Sc through Zn. Of these 10 metals, only four, Mn, Fe, Cu and Zn, form major hydrothermal deposits. The metals from Sc to Cr are commonly inert in hydrothermal systems; because of their high LFSE, Co, Ni, Sc, V, Ti and Cr are typically sequestered into first-formed mafic minerals (olivine, pyroxene, ilmenite, magnetite, spinel, etc.) within a crystallizing magma (Burns 1970, p.156), and are not normally concentrated in late-stage ore-forming fluids. However, V can be released during later weathering or alteration processes, hence its presence in uranium roll-front and related sedimentary deposits (Maynard 1983). Ti is occasionally observed as rutile in high-temperature veins; this is somewhat of a mystery at present because of the great insolubility of rutile. Ti may be mobile as the divalent ion under extremely reducing or acidic conditions. In the group from Mn to Zn, the elements Co and Ni also form rare hydrothermal deposits in association with other metals, which must again require unusual geological conditions. Rather surprisingly, the tendency of a metal to form hydrothermal deposits bears little relation to its average crustal abundance: V, Cr, Co, Ni, Cu and Zn all have roughly the same abundance (25–135 ppm), whereas average concentrations of Ti, Mn and Fe are 0.44%, 950 ppm and 5%, respectively (Mason & Moore 1982).

The observations that only four of the ten metals in the first-transition row form major hydrothermal

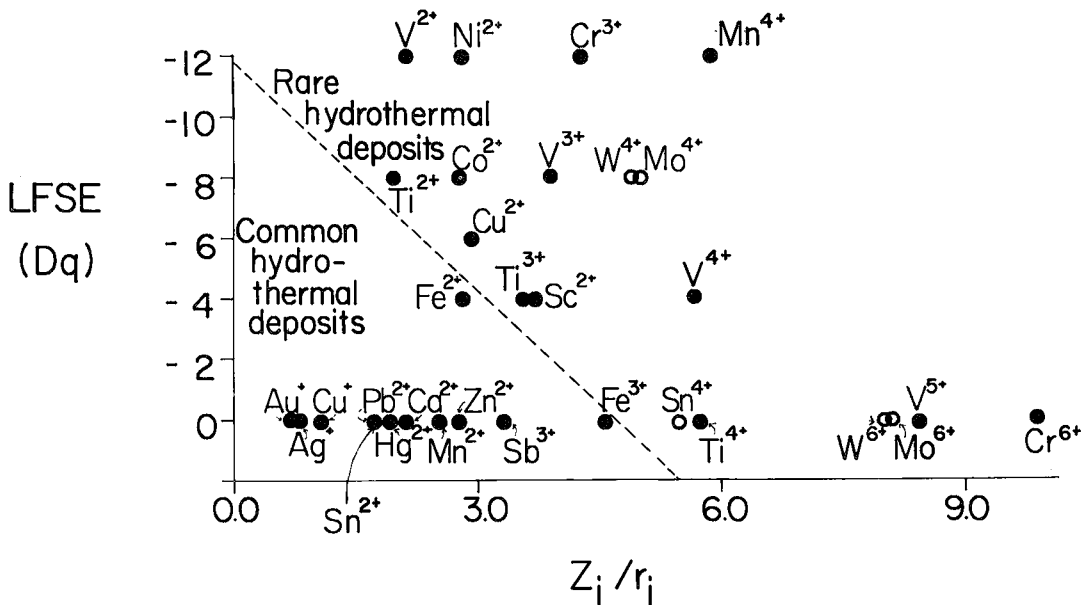
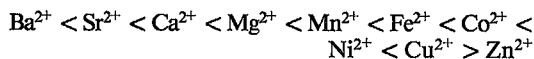


FIG. 7. Plot of LFSE versus Z/r for selected ions. Values of LFSE are taken from Table 4. The valences plotted are the oxidation states of the metals common in geological systems. Note that the metals divide into two general fields of hydrothermal activity. The ions Sn^{4+} , Mo^{6+} and W^{6+} do not conform to the delineated fields since they are quite heavy and more electronegative; on a three-dimensional plot, including electronegativity along with Z/r and LFSE, these metals fall in the hydrothermal field.

deposits can now be at least qualitatively explained. It has long been recognized, for example, that the relative stability of divalent-metal complexes with the same ligand follows the Irving-Williams series (Irving & Williams 1953):



This order arises both from the general increase in Z/r across the group and from ligand-field effects. If complex stabilities were the only control, then mineral solubilities would follow this general order. Of course, additional factors affect mineral solubilities, the chief of these being the thermodynamic properties of the least soluble mineral under the specific chemical conditions; fortunately, these properties are fairly well known.

As mentioned above, a related factor is the stability of metal ions within source minerals and magmas and the relative ease with which they can be partitioned into hydrothermal solutions. This controls the initial supply of metals, hence the ore-forming potential of a hydrothermal fluid. The crystal field about a metal ion in a mineral (or a silicate melt) will typically be the same or greater than that in an aqueous-complex ion, where bond lengths are longer (see Fig. 5). Therefore, those metals with a high LFSE will not be as readily leached from source minerals or magmas in the first place.

Considering the aqueous phase first, complex ions of Ca and Sc should be relatively unstable, as discussed above. At the other extreme, complex stabilities should increase from Mn to Zn, owing both to Z/r and ligand-field effects. Complexes of the d^{10} ions Cu^+ and Zn^{2+} will be particularly stable, since these metals form predominantly covalent bonds with Cl^- , HS^- , OH^- and other common ligands. These and the other d^{10} metals therefore commonly form hydrothermal deposits.

Ti, Cr, V, Co and Ni are not as readily explained, since all have either a high LFSE or high Z/r (or both). Note that the valence of Ti, Cr and V in crystals is commonly 4, 3 and 5, respectively, and their Z/r is very high. Divalent Co and Ni have the highest LFSE (Table 4) and an intermediate Z/r , and plot at the top of the double humps in Figure 6. These properties are illustrated in Figure 7. Significantly, none of these five metals forms common hydrothermal deposits, whereas the divalent metals Mn, Fe, Cu and Zn (which have minimal or zero LFSE) do. Ti, V, Co and Ni should form stable aqueous complexes. However, the high LFSE or Z/r (or both) of these four metals will also tend to stabilize them in crystal sites and magmas; this will reduce their leachability and decrease their net supply to hydrothermal solutions. In addition, it is known that metals

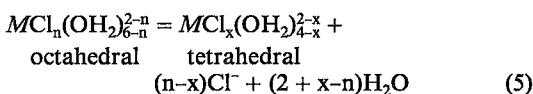
having a high LFSE tend to retain octahedral co-ordination where other metal complexes become tetrahedrally co-ordinated. A transformation from tetrahedral to octahedral co-ordination may favor ore deposition, as discussed in the next section.

There is also evidence that transition metals preferentially accumulate throughout the differentiation of felsic magmas that have a higher proportion of octahedral to tetrahedral sites. Recalling that $D_{\text{tet}} = -4/9 D_{\text{oct}}$, there is a higher LFSE within the octahedral sites. Feiss (1978) has shown, for example, that granodiorites with a high ratio of octahedral to tetrahedral sites [as measured by $\text{Al}_2\text{O}_3/(\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO})$], tend to be the most heavily mineralized.

Complex co-ordination and ore deposition

It is now recognized from spectroscopic studies that most transition-metal complexes are either tetrahedrally or octahedrally co-ordinated over much of the physical and chemical range of ore-forming conditions (Susak 1981, Susak & Crerar 1984). That is, the complex itself consists of a (typically distorted) tetrahedron or octahedron with 4 or 6 ligands at the corners and the metal ion at the centre. The transformation from one co-ordination to the other is broadly analogous to phase transitions in the solid state, and the form with the lower free-energy will predominate for a given set of conditions.

The transition from octahedral to tetrahedral co-ordination may be written:



Note that for the allowed values of n and x ($0 \leq n \leq 6$; $0 \leq x \leq 4$) there is always an increase by two in the number of molecules for the forward reaction. Hence S is positive for the octahedral \rightarrow tetrahedral transition, suggesting that entropy by itself favors the tetrahedral co-ordination.

However, the free energy of reaction (5) sums both entropy and enthalpy contributions, since $\Delta G_r = \Delta H_r - T\Delta S_r$. Following Susak & Crerar (1984), the enthalpy term includes the contribution of LFSE (equation 4), so that at high field-strengths ($10Dq$), octahedral complexes are favored, whereas at low field-strengths other factors may favor tetrahedral or lower co-ordination. As an extreme example, the heaviest d^{10} ions, such as Au^+ and Hg^{2+} with zero LFSE, have a strong tendency to form linear two-co-ordinated complexes, which is also favored by their strongly covalent character (Cotton & Wilkinson 1962, Puddephatt 1978). Increased temperature tips the balance from octahedral toward

tetrahedral co-ordination for four main reasons: (1) The $T \Delta S_T$ term simply becomes greater at T . (2) The magnitude of Dq , hence LFSE, is proportional to $1/r^5$ (Dunn *et al.* 1965, p.12); hence LFSE decreases at higher T with increasing interatomic distance r . (3) At higher T , the dielectric constant of water falls, supporting species of lower charge and ligation number (see below). (4) There is more steric congestion about the metal at higher T since H_2O is vibrationally larger.

The ligand(s) also directly influences co-ordination of the complex since the magnitude of Dq (and LFSE) varies with ligand in the general order: $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < ox^{2-} < H_2O < NCS^- < CH_3CN < NH_3 < en <$

$dipy < phen < NO_2^- < phosph < CN^- < CO$. This list of ligands in order of increasing field-strength (Dq) is termed the "spectrochemical series" (Huheey 1978). Note that the geologically most common ligands such as sulfide, Cl^- and OH^- are weaker than water and will contribute lower LFSE to complexes containing them. Since tetrahedral complexes are favored at lower field-strengths, high concentrations of ligands such as Cl^- promote the octahedral \rightarrow tetrahedral transition.

Finally, the co-ordination of complex ions is also controlled by the electronic configuration of the metal ion itself, as listed in Table 4. Thus, d^5 and d^{10} ions (Fe^{3+} , Mn^{2+} , Zn^{2+} , Cu^+) form tetrahedral complexes at lower T and Cl^- concentration since

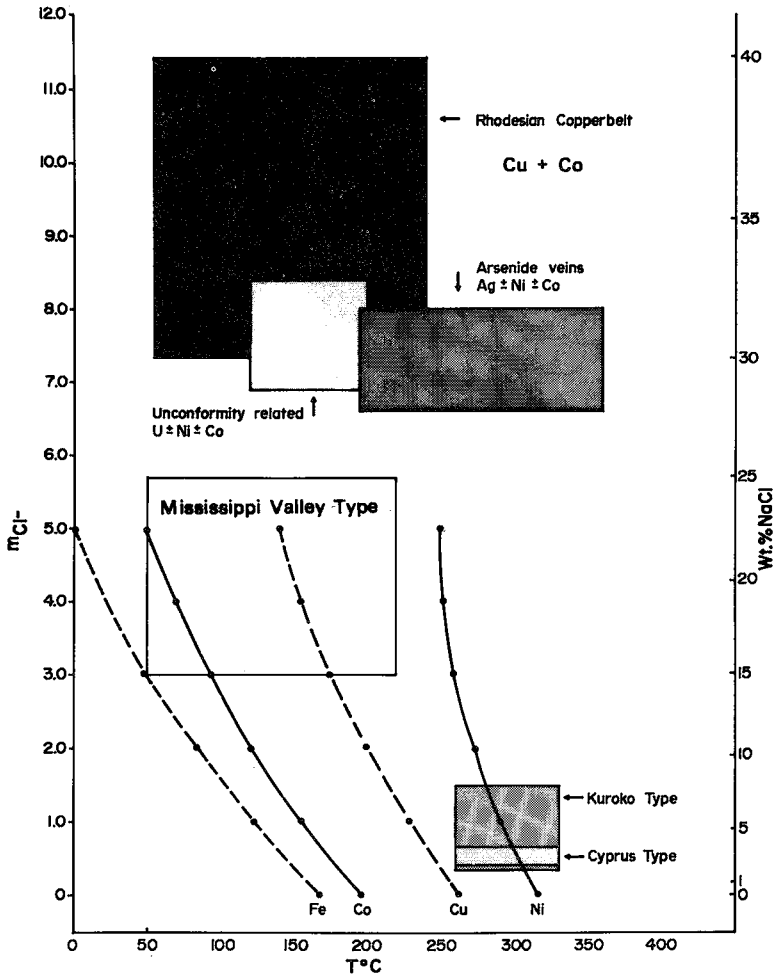


FIG. 8. Conditions of deposition (T , m_{NaCl}) of various types of ore deposits superimposed upon fields of octahedral and tetrahedral co-ordination for chloride complexes of Fe, Cu, Co and Ni. To the left of each line, octahedral complexes predominate and to the right, tetrahedral. Note that the deposits for each metal appear to form in the tetrahedral-dominant region. After Susak & Crerar (1984).

they have zero LFSE. Even at room temperature, the most common co-ordination for the d^{10} ions Zn^{2+} and Cd^{2+} is tetrahedral (Quicksall & Spiro 1966, Giaquinta *et al.* 1983). In these complexes, the tetrahedral geometry simply minimizes the mutual electrostatic repulsion of the ligands.

The combined effect of T and Cl^- activity on complex co-ordination is illustrated in Figure 8, from Susak & Crerar (1984). This shows the estimated beginning of the octahedral \rightarrow tetrahedral transition for divalent Fe, Co, Cu and Ni. To the left of each line, aqueous chloro complexes of the indicated metal are octahedral; to the right of each line, tetrahedral complexes appear then rapidly predominate. As expected, tetrahedral complexes occur at higher T and Cl^- for each metal.

This diagram also appears to indicate that most ore-forming environments occur either in the tetrahedral field or near the octahedral \rightarrow tetrahedral transition. Susak & Crerar (1984) suggested that tetrahedral complexes correspond to higher solubilities of minerals and are primarily responsible for ore transport. This would be the predominant co-ordination of the metals Mn, Fe, Cu and Zn, which all have zero to minimal LFSE and all form hydrothermal ores. Alternatively, as noted above, these four metals are more readily leached from source minerals in the first place, and we should therefore expect to find them concentrated as hydrothermal deposits.

This explanation is attractive, but is still quite speculative. The importance of co-ordination changes in the aqueous phase to ore zoning and deposition should be tested with further experimental data.

Effects of temperature and pressure on complex stability

The general effects of T and P on aqueous metal complexing have been discussed in some detail by Seward (1981) and will be only briefly summarized here. We should also note that McKenzie & Helgeson (1984) have recently estimated the thermodynamic properties of selected metal ions up to 900°C and 2 kbar based on the dielectric constant of water and predictive models described by Helgeson & Kirkham (1976).

Except at temperatures above roughly 400°C, pressure has only a small effect on the dielectric constant of water, particularly over the 0–1 kbar range characteristic of near-surface ore-forming fluids. However, pressure does increase the dissociation of complexes to ionic species because of the general decrease in partial molal volume accompanying ion formation. For a similar reason, pressure changes on the order of kilobars can also induce the change in tetrahedral \rightarrow octahedral co-ordination since the ΔV_r for reactions such as (5) is typically positive in

the forward direction (Rodriguez & Offen 1971; references in Seward 1981).

The most dramatic effect of temperature is its influence on the dielectric constant of water. This constant falls from 78.47 at 25°C to 12.87 at 350°C and vapor-saturated pressure (Helgeson & Kirkham 1974) and always decreases with an isobaric rise in temperature. Since the coulombic force is inversely proportional to the dielectric constant, all electrostatic interactions increase at elevated temperatures. Ion association increases markedly for many salts and other electrolytes. Strong acids become weak, and ionic salts form ion pairs at higher temperatures. The implications for transition-metal behavior are numerous. Firstly, there will be an increased tendency toward type-A or hard-metal behavior at higher T, even for the d^{10} ions. Available enthalpy and entropy data suggest increasing formation of inner-sphere complexes and "structure-breaking" behavior (Seward 1981). This means that complexes with intermediate or hard ligands, such as OH^- and Cl^- , will become more stable at elevated T, a prediction borne out by the observed increase in hydrolysis or hydroxy complexing (Khodakovskiy & Yelkin 1975, Baes & Mesmer 1981) and the increased stability of chloro complexes with temperature (Crerar *et al.* 1978, Barnes 1979, Seward 1981, 1984). This, coupled with the expected increase in solubility products, helps explain the higher solubilities of transition-metal minerals in higher-temperature hydrothermal solutions.

In addition, it has become increasingly apparent from recent experimental data that ligation numbers decrease with temperature, so that complexes of low to neutral charge, such as $FeCl_2^0$, predominate over wide ranges of concentration at temperatures above roughly 300°C (see references above and Chou & Eugster 1977, Frantz *et al.* 1981). In fact there is now some evidence for purely molecular aqueous species of feldspar stoichiometry such as $NaAlSi_3O_8^0$ at very high T (Anderson & Burnham 1983). This is to be expected, since the low dielectric constant of water at these temperatures will not support highly charged species. Lower ligation numbers are also favored by the change from octahedral to tetrahedral co-ordination at higher T noted above. The co-ordination change itself reflects the increasing electrostatic contribution to bonding energies, as well as the general decrease in Dq and LFSE at higher temperatures.

Temperature also exhibits an effect on the activity coefficients of common hydrothermal electrolytes (Fig. 9). The activity coefficient decreases markedly with temperature to values on the order of 0.05 for 1:1 salts at 350°C (Wood *et al.* 1984). The overall effect on ore-mineral solubilities is complicated; however, a decrease in ligand activity generally is correlated with a decrease in ligation number.

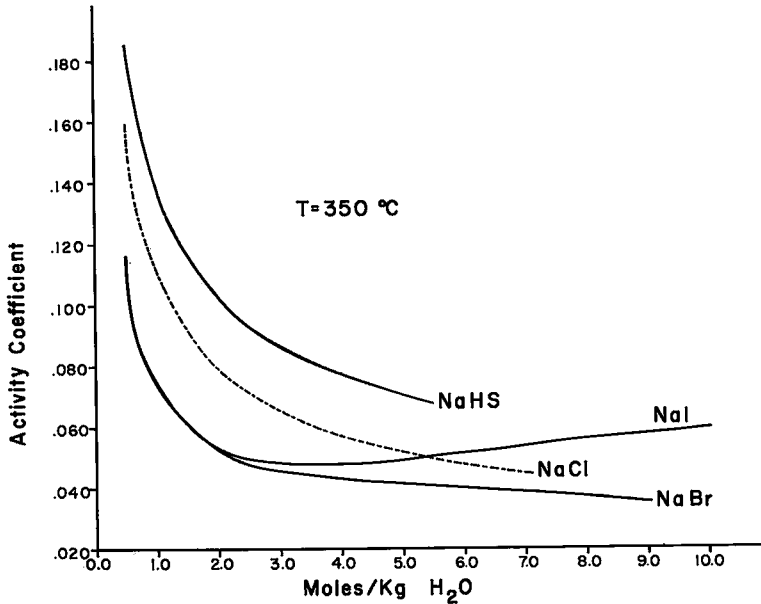


FIG. 9. Plot of the mean molal stoichiometric activity-coefficient for some sodium salts at 350°C. Data from Wood *et al.* (1984). Note that the activity coefficients for all salts at this temperature are similar and quite low.

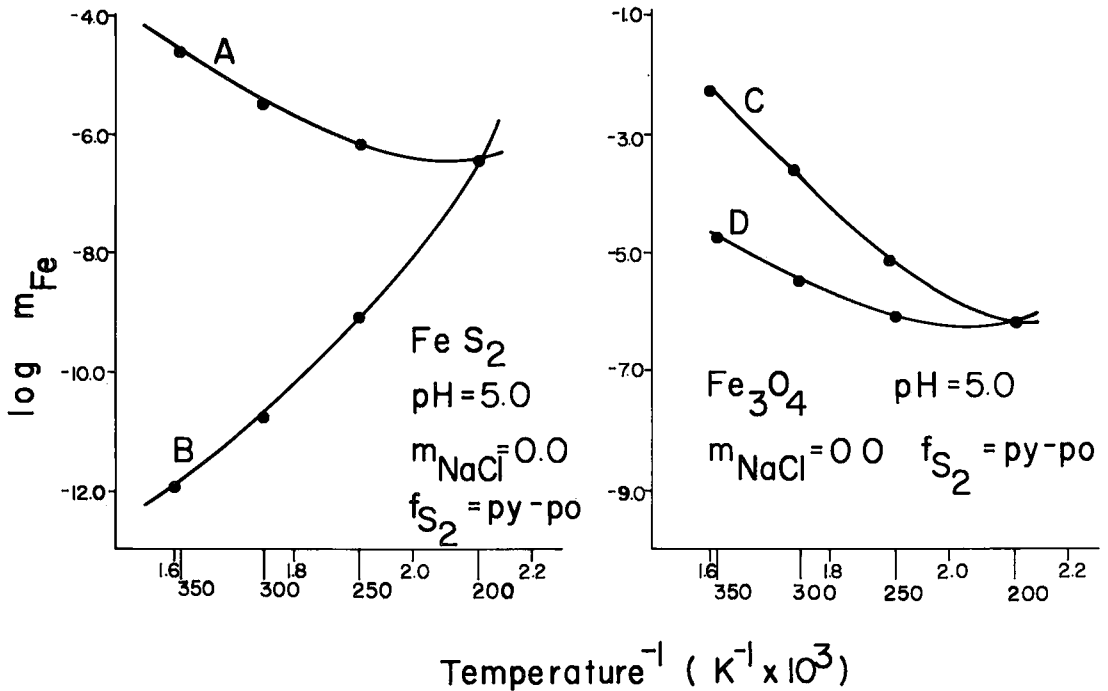


FIG. 10. Plot of the log of the solubility of FeS_2 and Fe_3O_4 versus $1/T$ for different fugacities of oxygen. A) Solubility of FeS_2 as Fe^{2+} when oxygen fugacity is buffered by py-po-mt. B) Solubility of FeS_2 as Fe^{2+} at constant oxygen fugacity, $\log f(\text{O}_2) = -43.9$. C) Fe_3O_4 solubility at constant $\log f(\text{O}_2) = -43.9$. D) Fe_3O_4 solubility when oxygen is buffered by py-po-mt. All solubilities are calculated in pure water for the hydrated Fe^{2+} ion; the introduction of chloride complexing merely increases the total solubility at each point without changing trends depicted. Solubility data taken from Crerar *et al.* (1978).

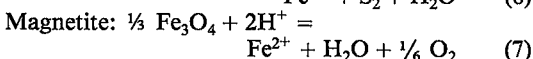
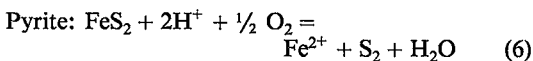
To summarize, higher T results in low- to neutral-charge complexes, lower ligation numbers, tetrahedral co-ordination and higher solubility. Although pressure reverses some of these trends, solubility still generally increases with P because of increased density of solvent. Pressure effects are generally not as significant as changes due to temperature over the limited range in pressure of near-surface ore-forming environments. The net result is a major increase in both mobility and the potential for ore deposition as high- Γ metal-rich solutions circulate and cool.

Effects of oxygen and sulfur fugacity and pH

An important and yet often overlooked control on solubility is the effect of temperature on buffers of oxygen and sulfur fugacities. In an ore-forming environment, oxygen and sulfur fugacities are most likely buffered either by solid assemblages such as hematite-magnetite and pyrite-pyrrhotite or aqueous buffers such as sulfate-sulfide. The oxygen and sulfur fugacities of these buffering systems generally increase dramatically with temperature. The effect of a temperature change on mineral solubilities will therefore be more complicated than the intrinsic temperature-dependence of the solubility alone.

Though we restrict further comment to the oxygen fugacity, similar arguments can be made for any other buffered intensive variable such as sulfur fugacity or pH.

The effects of changes in gas fugacities on ore-mineral solubilities are illustrated by solubility reactions such as:



Note that an increase in oxygen fugacity causes an increase in solubility of pyrite but a decrease in that of magnetite. Thus, different minerals are affected differently depending upon the dissolution reaction.

Figure 10 differentiates the intrinsic effect of temperature on ore-mineral solubility from the indirect effect of temperature on the oxygen fugacity buffer. Curve A represents the expected solubility of pyrite in equilibrium with the pyrite-pyrrhotite-magnetite buffer. Curve B represents the expected FeS_2 solubility if the oxygen fugacity were held at a single value independent of temperature (data to calculate all solubilities were taken from Crerar *et al.* 1978). Obviously, the solubility increases substantially when the buffered fugacity changes with temperature; in contrast, the solubility at constant oxygen fugacity decreases slightly with increasing temperature. Curve C in Figure 10 represents magnetite solubility at

constant oxygen fugacity, whereas curve D gives the solubility of magnetite when the buffer equilibrates at temperature. The effect is opposite to that for pyrite since magnetite solubility is inversely related to oxygen fugacity.

For the pyrite - pyrrhotite - magnetite buffer, the oxygen fugacity varies by roughly 13 orders of magnitude between 200° and 350°C; this enormous change is typical of all common mineral-based gas buffers (*e.g.*, Eugster & Wones 1962, Huebner 1971, Barton & Skinner 1979) and can effect corresponding major changes in mineral solubilities with temperatures. This helps to explain the sharp rise in solubility of minerals such as Au at higher temperatures (*e.g.*, Fyfe & Henley 1973, Seward 1983) and the observation that some metals such as Au, Mo and Cu occur primarily in higher-T deposits.

We conclude that in a buffered system, the solubility of minerals such as gold, pyrite, galena and sphalerite (for which solubility increases with oxygen fugacity) will increase dramatically with temperature. If instead the system were held at a constant fugacity of oxygen while the temperature increased, then the solubility of such minerals would increase less dramatically and could perhaps even decrease; this could occur in natural environments, for example, by osmotic equilibration (see Greenwood 1961 for a definition) of oxygen with a large-capacity constant-temperature reservoir. The effect of temperature on mineral pH buffers is similar. For example, the pH of the sericite - K-feldspar buffer increases by 2 units from 350°C to 25°C (Montoya & Hemley 1975, Barnes 1979) at constant activity of potassium ion. Therefore a temperature decrease of 300°C in systems buffered by silicate minerals could effect a drop of four orders of magnitude in the solubility of a divalent metal sulfide due to pH alone [as calculated, for example, from the stoichiometry of reactions such as (6) above, or (9) below].

Buffer capacity and solubility

Another important control on the potential for corrosion or metal precipitation of an ore-forming solution is the pH-buffer capacity of the hydrothermal fluid itself. This is defined as the increment of acid or base that causes unit change in pH. The buffer capacity of a hydrothermal solution is a direct measure of its ability to resist pH change during wall-rock alteration, ore dissolution, and ore precipitation.

Dissolution reactions such as (6) and (7) for common ore-minerals consume H^+ : the actual quantity of a mineral that can dissolve or precipitate in a specific solution is therefore controlled by the capacity of the buffer. Weakly buffered systems dissolve relatively little metal before the pH increases; a slight addition of base will quantitatively precipitate dis-

solved metals from the same solution. Conversely, strongly buffered systems display high corrosion and low potential for precipitation.

A simple pH-buffer consists of a weak acid and the salt of its conjugate base (or, conversely, a weak base and the salt of its conjugate acid). Geologically common conjugate pairs include $H_2S + HS^-$, $H_2SO_4 + HSO_4^-$, $HSO_4^- + SO_4^{2-}$, $H_2CO_3 + HCO_3^-$, $HCO_3^- + CO_3^{2-}$, $NH_3 + NH_4^+$, $HCl + Cl^-$, etc. The buffer capacity of a mixture of conjugate acid-base systems ($HA-A^-$, $HB-B^-$, $HC-C^-$, etc.) is given by

$$\beta = dC_b/dpH = -dC_a/dpH = 2.303 \left([OH^-] + [H^+] + \frac{[HA][A^-]_t/[HA]_t + [A^-]_t}{[HB][B^-]_t/[HB]_t + [B^-]_t + \dots} \right) \quad (8)$$

where C_b and C_a are, respectively, the number of moles/litre of strong base or strong acid required to produce a change in pH of magnitude dpH (see Stumm & Morgan 1981, Butler 1964). Bracketed quantities in expression (8) denote concentrations.

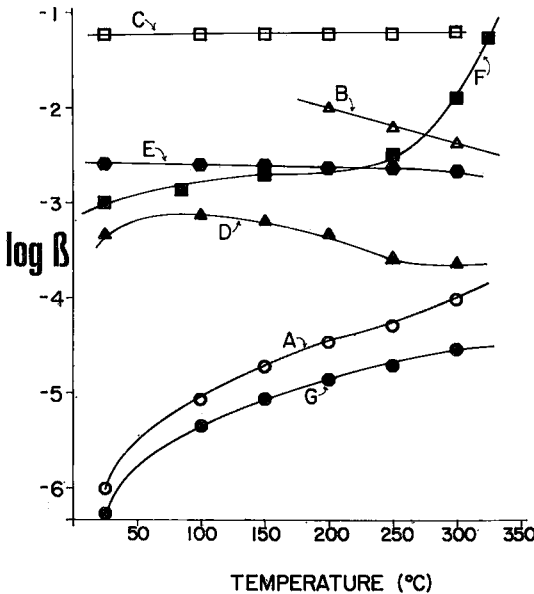


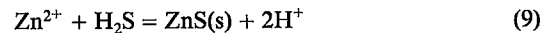
FIG. 11. Calculated buffer-capacities (β) for six different types of hydrothermal solutions, plotted as a function of temperature. Equilibrium data from Seward (1973), Busey & Mesmer (1977), Baes & Mesmer (1981), Drummond (1981), Cobble *et al.* (1982) and Bourcier (1983). Data for seawater were estimated by Bischoff & Seyfried (1978). The letters refer to the discussion in the text and to the compositions given below: A) 0.5 m NaCl, quartz-saturated. B) 0.5 m NaCl, 0.1 m total carbon, 0.001 m NaOH, calcite-saturated. C) 0.5 m NaCl, 0.1 m total sulfur, 0.05 m NaOH. D) 0.5 m NaCl, 0.1 m total sulfur. E) 0.5 m NaCl, 0.1 m total carbon, 0.001 m NaOH. F) Seawater system (Bischoff & Seyfried 1978). G) 0.5 m NaCl.

The first two terms of the expression account for the contribution of water to the buffer capacity. These terms are important in extremely acid or extremely basic conditions, and partly explain the large buffering capacity of high- and low-pH solutions. The final terms are the buffering contributions of the individual acid-base pairs. Note that polyprotic acids of interest in hydrothermal solutions can also be approximated as a mixture of monoprotic acids (see Butler 1964, p.245; Ricci 1952, p.196). For a simple mixture of one acid-base pair, $d\beta/dpH$ equals 0 when $[HA]$ equals $[A^-]$; maximum buffer-capacity thus occurs at a pH equal to the pK_a of the acid.

Because the degree of association of most acids and bases increases with temperature, equation (8) predicts that the buffering capacity of a solution will also change with temperature. We have plotted calculated buffer-capacities *versus* temperature for six solutions in Figure 11. Except for seawater, all buffer capacities were calculated by determining equilibrium speciation for a given solution using a modified version of the program described by Crerar (1975) and equation (8). The efficacy of equation (8) for higher-temperature, partly associated systems was verified by finite-difference methods (adding small increments of base and numerically differentiating).

Calculations for the solutions used were run at geologically reasonable values of pH. Only one solution (0.5 m NaCl, 0.1 m total S, 0.05 m NaOH) was found to be sufficiently basic that $[HA]$ is approximately equal to $[A^-]$, thus showing maximum buffer-capacity. Most acid-base pairs of geological importance have maximum buffer-capacity at a basic pH for ore-forming temperatures (Barnes 1979, p.409). If ore-forming solutions are usually neutral to slightly acid, as suggested by Barnes (1979), Crerar *et al.* (1978) and many others, maximum buffer-capacity must rarely be attained.

For a given increase in pH, a specific quantity of metal will precipitate. For example, for the simple precipitation-reaction



one mole of ZnS precipitates for every two moles of H^+ consumed. The importance of pH buffering to ore transport and deposition is illustrated by considering three limiting cases such as systems A, B and C, in Figure 11. Systems C and B are 600 and 40 times better buffered than A, respectively. Since wall-rocks act as proton sinks, the passage of ore fluid through unaltered rock is equivalent to a basic titration. Hence solutions C and B could travel 600 and 40 times further than A through the same rock material (assuming the same extent of reaction between wallrock and fluid per unit distance) before undergoing the same change in pH or depositing as much sulfide.

Solution A is a NaCl-rich hydrothermal solution saturated in quartz, such as might be associated with a granodiorite pluton (addition of 0.1 m H₂S(aq) would shift the buffer capacity slightly to curve D on Fig. 11). The low buffer-capacity of such solutions should contribute to the rapid precipitation of copper, molybdenum and other sulfide ores in country rocks about large intrusive bodies.

In contrast, metal precipitation due to a pH increase in solution B would occur gradually. Solutions similar to B, strongly buffered by the H₂CO₃-HCO₃⁻ conjugate pair, are representative of ore fluids in carbonate terranes, for example, the Mississippi-Valley-type (MVT) Pb-Zn deposits. Such deposits formed from solutions that traveled considerable distances through carbonate rocks (Beales 1975, Anderson 1975). Sverjensky (1984) has recently suggested that hydrothermal fluids associated with MVT deposits could maintain a mildly acidic pH over distances on the order of 100 km. We calculate the buffer capacity for this ore-forming solution at 125°C to be 2.3×10^3 eq/pH, which falls exactly on curve E of Figure 11. This high buffer-capacity could help explain how MVT ore-forming solutions can travel great distances and only gradually precipitate metals.

An important effect of temperature is also apparent on the buffer curves of Figure 11. Note that the buffer capacity of systems A and D decreases significantly at lower temperatures; therefore, hydrothermal solutions associated with silica-rich systems such as felsic plutons should precipitate metals more rapidly than those in carbonate systems as the solutions cool and react with basic country-rocks. In contrast, the buffer capacity of system B (which is saturated in calcite) actually increases at lower temperatures; again, this could explain the retention of dissolved metals by ore solutions in carbonate terranes such as those hosting the MVT deposits.

Finally, the relatively high buffer-capacity of heated seawater shown in Figure 11, coupled with its observed acidity at higher T (Bischoff & Seyfried 1978), implies that seawater must be quite corrosive under hydrothermal conditions. The hot springs and "black smokers" that occur along oceanic spreading centres do in fact discharge vast quantities of leached Fe, Mn and other metals. Such processes are now believed responsible for many of the voluminous massive-sulfide ores.

CONCLUSIONS AND RECOMMENDATIONS

The conclusions and generalizations presented throughout this paper combine existing experimental data on high-temperature aqueous systems with current theories on transition-metal chemistry. These

conclusions are preliminary at best because of severe limitations in the experimental data.

Much remains to be learned about the chemistry of hydrothermal systems. Further studies are required on the thermodynamics and molecular chemistry of transition-metal complexes for the full range of natural ligands. These studies should include both the common ore-forming metals as well as those that form only rare deposits or are relatively inert in hydrothermal solutions. It would be as instructive to understand why some metals do not form common natural deposits as to understand why many others do.

There is also a real need for further data on the electrolytic components of natural ore-forming solutions. The thermodynamic properties of multicomponent salt solutions should be measured over the full range of submagmatic temperatures. Of particular concern are the association constants and activity coefficients of geologically common salts. Such data are actually a prerequisite to understanding all natural hydrothermal systems, whether metal-bearing or not.

The limiting factor in understanding hydrothermal deposits and processes is ultimately the experimental difficulty of working with high-P-T corrosive aqueous solutions. The many problems left unanswered in this paper will be resolved primarily by the ingenuity of future experimentalists.

ACKNOWLEDGEMENTS

This work was supported by NSF grants number EAR-7514929A01, -7925931 and -8206147 and by a generous award from the Shell Companies Foundation to D.A.C. We thank Julian Hemley and Hans Eugster for constructive, thoughtful reviews, and Robert F. Martin for his painstaking editorial assistance.

REFERENCES

- ANDERSON, G.M. (1975): Precipitation of Mississippi Valley-type ores. *Econ. Geol.* **70**, 937-942.
- & BURNHAM, C.W. (1983): Feldspar solubility and the transport of aluminum under metamorphic conditions. *Amer. J. Sci.* **283-A**, 283-297.
- BAES, C.F., JR. & MESMER, R.E. (1976): *The Hydrolysis of Cations*. Wiley-Interscience, New York.
- & ——— (1981): The thermodynamics of cation hydrolysis. *Amer. J. Sci.* **281**, 935-962.
- BALLHAUSEN, C.J. (1962): *Introduction to Ligand-Field Theory*. McGraw-Hill, New York.

- BARNES, H.L. (1975): Zoning of ore deposits, types and causes. *Trans. Roy. Soc. Edinburgh* **69**, 295-311.
- (1979): Solubilities of ore minerals. In *Geochemistry of Hydrothermal Ore Deposits* (2nd edition; H.L. Barnes, ed.). Wiley-Interscience, New York.
- BARRETT, T.J. & ANDERSON, G.M. (1982): The solubility of sphalerite and galena in NaCl brines. *Econ. Geol.* **77**, 1923-1933.
- BARTON, P.B. & SKINNER, B.J. (1979): Sulfide mineral stabilities. In *Geochemistry of Hydrothermal Ore Deposits* (2nd edition, H.L. Barnes, ed.). Wiley-Interscience, New York.
- BEALES, F.W. (1975): Precipitation mechanisms for Mississippi Valley-type ore deposits. *Econ. Geol.* **70**, 943-948.
- BISCHOFF, J.L. & SEYFRIED, W.E. (1978): Hydrothermal chemistry of seawater from 25° to 350°C. *Amer. J. Sci.* **278**, 838-860.
- BOURCIER, W.L. (1983): *Stabilities of Chloride and Bisulfide Complexes of Zinc in Hydrothermal Solutions*. Ph.D. thesis, Penn. State Univ., University Park, Pennsylvania.
- BURNS, R.G. (1970): *Mineralogical Applications of Crystals Field Theory*. Cambridge University Press, Cambridge, England.
- BUSEY, R.H. & MESMER, R.E. (1977): Ionization equilibria of silicic acid and polysilicate formation in aqueous sodium chloride solutions to 300°C. *Inorg. Chem.* **16**, 2444-2450.
- BUTLER, J.N. (1964): *Ionic Equilibrium, a Mathematical Approach*. Addison-Wesley, Reading, Mass.
- CHOU, I-MING & EUGSTER, H.P. (1977): Solubility of magnetite in supercritical chloride solutions. *Amer. J. Sci.* **277**, 1296-1314.
- COBBLE, J.W., MURRAY, R.C., JR., TURNER, P.J. & CHEN, K. (1982): High temperature thermodynamic data for species in aqueous solution. *EPRI Rep. NP-2400 Research Project 1167-1*, San Diego State University Foundation, San Diego.
- COTTON, F.A. & WILKINSON, G. (1962): *Advanced Inorganic Chemistry - A Comprehensive Text*. Interscience, New York.
- CRERAR, D.A. (1975): A method for computing multicomponent chemical equilibria based on equilibrium constants. *Geochim. Cosmochim. Acta* **39**, 1375-1384.
- , SUSAK, N.J., BORCSIK, M. & SCHWARTZ, S. (1978): Solubility of the buffer assemblage pyrite + pyrrhotite + magnetite in NaCl solutions from 200 to 350°C. *Geochim. Cosmochim. Acta* **42**, 1427-1437.
- DASENT, W.E. (1982): *Inorganic Energetics: An Introduction*. Cambridge University Press, Cambridge, England.
- DRUMMOND, S.E., JR. (1981): *Boiling and Mixing of Hydrothermal Fluids: Chemical Effects on Mineral Precipitation*. Ph.D. thesis, Penn. State Univ., University Park, Pennsylvania.
- DUNN, T.M., McCLURE, D.S. & PEARSON, R.G. (1965): *Some Aspects of Crystal Field Theory*. Harper and Row, New York.
- EUGSTER, H.P. & WONES, D.R. (1962): Stability relations of the ferruginous biotite, annite. *J. Petrology* **3**, 82-125.
- FEISS, P.G. (1978): Magmatic sources of copper in porphyry copper deposits. *Econ. Geol.* **73**, 397-404.
- FIGGIS, B.N. (1966): *Introduction to Ligand Fields*. Wiley-Interscience, New York.
- FRANTZ, J.D., POPP, R.K. & BOCTOR, N.Z. (1981): Mineral-solution equilibria. V. Solubilities of rock-forming minerals in supercritical fluids. *Geochim. Cosmochim. Acta* **45**, 69-77.
- FYFE, W.S. & HENLEY, R.W. (1973): Some thoughts on chemical transport processes, with particular reference to gold. *Minerals Sci. Engng.* **5**, 295-298.
- GEORGE, P. & McCLURE, D.S. (1959): The effect of inner orbital splitting on the thermodynamic properties of transition metal compounds and coordination complexes. *Progress Inorg. Chem.* **1**, 381-463.
- GIAQUINTA, P.V., TOSI, M.P. & MARCH, N.H. (1983): Coordination chemistry and ionic solvation in divalent metal halide aqueous solutions. *Phys. Chem. Liq.* **13**, 1-24.
- GIORDANO, T.H. (1978): *Dissolution and Precipitation of Lead Sulfide in Hydrothermal Solutions, and the Point Defect Chemistry of Galena*. Ph.D. thesis, Penn. State Univ., University Park, Pennsylvania.
- & BARNES, H.L. (1981): Lead transport in Mississippi Valley-type ore solutions. *Econ. Geol.* **76**, 2200-2211.
- GRADDON, D.P. (1968): *An Introduction to Coordination Chemistry* (2nd edition). Pergamon, Oxford.
- GREENWOOD, H.J. (1961): The system NaAlSi₂O₆-H₂O-argon: total pressure and water pressure in metamorphism. *J. Geophys. Res.* **66**, 3923-3946.
- HELGESON, H.C. & KIRKHAM, D.H. (1974): Theoretical prediction of the thermodynamic behavior of aque-

- ous electrolytes at high pressures and temperatures. I. Summary of the thermodynamic/electrostatic properties of the solvent. *Amer. J. Sci* **274**, 1089-1198.
- _____ & _____ (1976): Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. III. Equation of state for aqueous species at infinite dilution. *Amer. J. Sci.* **276**, 97-240.
- HUEBNER, J.S. (1971): Buffering techniques for hydrostatic systems at elevated pressures. In *Research Techniques for High Pressure and High Temperature* (G.C. Ulmer, ed.). Springer-Verlag, Berlin.
- HUHEEY, J.E. (1978): *Inorganic Chemistry* (2nd edition). Harper and Row, New York.
- IRVING, H. & WILLIAMS, R. (1953): The stability of transition metal complexes. *J. Chem. Soc.*, 3192-3210.
- JØRGENSEN, C.K. (1964): "Symbiotic" ligands, hard and soft central atoms. *Inorg. Chem.* **3**, 1201-1202.
- KHODAKOVSKIY, I.L., POPOVA, M.YA. & OZEROVA, N.A. (1975): On the role of sulfide complexes in the transport of mercury by hydrothermal solutions. *Geochem. Int.* **12**, 37-47.
- _____ & YELKIN, A. YE. (1975): Measurement of the solubility of zincite in aqueous NaOH at 100, 150 and 200°C. *Geochem. Int.* **12**, 127-133.
- MASON, B. & MOORE, C.B. (1982): *Principles of Geochemistry* (2nd edition). J. Wiley & Sons, New York.
- MAYNARD, J.B. (1983): *Geochemistry of Sedimentary Ore Deposits*. Springer-Verlag, New York.
- MCCLURE, D.S. (1959): *Electronic Spectra of Molecules and Ions in Crystals*. Academic Press, New York.
- McKENZIE, W.F. & HELGESON, H.C. (1984): Estimation of the dielectric constant of H₂O from experimental solubilities of quartz, and calculation of the thermodynamic properties of aqueous species to 900°C at 2 kb. *Geochim. Cosmochim. Acta* **48**, 2167-2177.
- MONTOYA, J.W. & HEMLEY, J.J. (1975): Activity relations and stabilities in alkali feldspar and mica alteration reactions. *Econ. Geol.* **70**, 577-594.
- PEARSON, R.G. (1963): Hard and soft acids and bases. *J. Amer. Chem. Soc.* **85**, 3533-3539.
- PITZER, K.S. (1979): Relativistic effects on chemical properties. *Acc. Chem. Res.* **12**, 271-276.
- PUDDEPHATT, R.J. (1978): *The Chemistry of Gold*. Elsevier, Amsterdam.
- PYTKOWICZ, R.M. (1983): *Equilibria, Nonequilibria and Natural Waters*. I. Wiley-Interscience, New York.
- PYYKKÖ, P. & DESCLAUX, J.P. (1979): Relativity and the periodic system of elements. *Acc. Chem. Res.* **12**, 276-281.
- QUICKSALL, C.O. & SPIRO, T.G. (1966): Raman spectra of tetrahalozincates and the structure of aqueous ZnCl₄²⁻. *Inorg. Chem.* **5**, 2232-2233.
- RICCI, J.E. (1952): *Hydrogen Ion Concentration*. Princeton University Press, Princeton, N.J.
- RODRIGUEZ, S. & OFFEN, H. (1971): Pressure effects on the absorbance of cobaltous chloride solutions. *Inorg. Chem.* **10**, 2086-2087.
- SEWARD, T.M. (1973): Thio complexes of gold and the transport of gold in hydrothermal ore solutions. *Geochim. Cosmochim. Acta* **37**, 379-399.
- _____ (1981): Metal complex formation in aqueous solutions at elevated temperatures and pressures. In *Nobel Symposium on the Chemistry and Geochemistry of Solutions at High Temperatures and Pressures* (F. Wickman & D. Rickard, eds.). *Phys. Chem. Earth* **13-14**, 113-132.
- _____ (1983): The transport and deposition of gold in hydrothermal systems. In *Gold'82: The Geology, Geochemistry and Genesis of Gold Deposits* (R.P. Foster, ed.). *Geol. Soc. Zimbabwe Spec. Publ.* **1**, 165-181.
- _____ (1984): The formation of lead (II) chloride complexes to 300°C: a spectrophotometric study. *Geochim. Cosmochim. Acta* **48**, 121-134.
- SIDGWICK, N.V. (1933): *The Covalent Link in Chemistry*. Cornell University Press, Ithaca, N.Y.
- STUMM, W. & MORGAN, J.J. (1981): *Aquatic Chemistry* (2nd edition). John Wiley & Sons, New York.
- SUSAK, N.J. (1981): *Spectra, Thermodynamics, and Molecular Chemistry of some Divalent Transition Metal Chloro-Complexes in Hydrothermal Solution to 300°C*. Ph.D. thesis, Princeton University, Princeton, New Jersey.
- _____ & CRERAR, D.A. (1982): Factors controlling mineral zoning in hydrothermal ore deposits. *Econ. Geol.* **77**, 476-482.
- _____ & _____ (1984): Spectra and coordination changes of transition metals in hydrothermal solutions: implications for ore genesis. *Geochim. Cosmochim. Acta* **49**, 555-564.
- SVERJENSKY, D.A. (1984): Oil field brines as ore-forming solutions. *Econ. Geol.* **79**, 23-37.
- WHITFIELD, M. & TURNER, D.R. (1983): Chemical periodicity and cycling of the elements. In *Trace*

Metals in Seawater (C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton & E.D. Goldberg, eds.). Plenum Press, New York.

WOOD, S.A. (1985): *Some Aspects of the Physical Chemistry of Hydrothermal Ore-Forming Solutions*. Ph.D. thesis, Princeton University, Princeton, New Jersey.

_____, CRERAR, D.A. & BORCSIK, M. (1983): Solubility of a multi-phase sulfide system in hydrothermal

chloride solutions. *Geol. Soc. Amer. Abstr. Programs* **15**, 722.

_____, _____, BRANTLEY, S.L. & BORCSIK, M. (1984): Mean molal stoichiometric activity coefficients of alkali halides and related electrolytes in hydrothermal solutions. *Amer. J. Sci.* **284**, 668-705.

Received June 26, 1984, revised manuscript accepted December 19, 1984.