THE HALLIMOND LECTURE 1984

Granites and hydrothermal ore deposits: a geochemical framework

HANS P. EUGSTER

Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland 21218 USA

ABSTRACT. The geochemical evolution of tin–tungsten deposits and their associated sulphides can be discussed in terms of four sequential processes: acquisition of the ore-forming elements (OFEs) by the granitic magma, emplacement of these elements in minerals and residual melt of the crystallizing granite, release of the OFEs to the circulating hydrothermal fluids and transport to the depositional sites, and finally, deposition of ore minerals through interaction of these fluids with the wall rock. Based on their crystallographic behaviour, it is useful to distinguish three principal classes of OFEs, here identified as BOC, LHC, and ALC elements. BOC (bivalent octahedral cation) elements are similar to ferrous iron and here are represented mainly by Zn, Mn, and perhaps Cu. Li also belongs to this class, although it is monovalent. LHC (large highly charged cations) elements encompass As, Nb, Mo, Sn, Sb, Ta, and W and they are similar to ferric iron or titanium in their crystallographic role. ALC (alkali-like cations) are capable of occupying alkali positions and are represented mainly by Pb, Ag, and Hg.

LHCs are rejected from the polymerized silicate liquid network and become enriched in the roof of the acid magma chamber, where more non-bridging oxygens are available. Transport to the roof may be enhanced by the formation of hydrous complexes, as is the pronounced enrichment of Na and Li. BOCs, along with Cl, F, and B, fractionate strongly into the vapour phase during vesiculation. HCl in the ore fluid is crucial for the alteration process and can be produced during boiling by a hydrolysis reaction of the NaCl dissolved or immiscibly present in the silicate magma.

Considerable laboratory information is available concerning release mechanisms of the OFEs to hydrothermal fluids. We can distinguish congruent and incongruent dissolution, both in response to acid buildup, as well as congruent and incongruent exchange not involving HCl. Melt-fluid fractionation is also thought to be important, though the physical mechanisms are not well understood. Any of these release mechanisms may be coupled with reduction or oxidation reactions. LHC, BOC, and ALC elements respond differently to each of these mechanisms, and these differences may in part be responsible for the observed separation of ore minerals in space and time. It is suggested that LHC elements are released preferentially during acid, non-oxidizing conditions typical of early stages, while BOC elements respond more readily to later acid–oxidizing environments, as well as exchange reactions with or without oxidation.

Depositional reactions have been formulated with respect to two contrasting types of country rocks: carbonates and schists. Differences are related to the process of neutralization of the HCl produced by ore deposition: carbonate dissolution on one hand and feldspar-muscovite or biotite–muscovite conversion on the other. In carbonate rocks, evaporite-related sulphates may provide the H_2S necessary for sulphide precipitation, while in schists disseminated sulphides and organic matter may be important sulphur reservoirs in addition to the sulphur liberated from the granite. A variety of situations can be envisaged with respect to the sources of the OFEs and the sulphur species required for ore deposition, including granite and wall rocks. Chloride is recognized as the crucial anion for OFE release, transport, and deposition, although F and B play a role yet to be evaluated. Final HCl neutralization is an essential step in the reactions responsible for the deposition of ore minerals.

The ultimate sources of the OFEs must be related to the continental material involved in the process of melt production by partial melting. Oxidized sediments provide sources for LHC and ALC elements in the form of heavy minerals and clastic feldspars and micas. Organic-rich reduced sediments are hosts to BOC and LHC elements as sulphides and ALC elements in organic matter. Remelting of igneous and metamorphic rocks can enrich LHC, BOC, and ALC elements in the melt by extraction from opaques, Fe–Mg silicates, feldspars, and micas.

KEYWORDS: granites, hydrothermal deposits, tin-tungsten deposits, ore-forming elements.

THE Hallimond Lecture presents me with the welcome opportunity to speak on a topic in which I am not considered to be an expert: hydrothermal ore deposits. For many years I have endeavoured to educate metamorphic petrologists to the importance of treating metamorphic fluids as aqueous solutions and not just as mixtures of gases. This

lesson never needed to be emphasized to economic geologists interested in hydrothermal ore deposits: they were already applied solution chemists. The bridge from ore fluids to metamorphic fluids was provided by Julian Hemley 25 years ago (Hemley, 1959) when he developed a quantitative model for the alteration of silicate wall rocks by ore fluids involving proton metasomatism.

A key contribution to our ability to study such reactions experimentally was provided by John Frantz with the development of the acid–base buffers (Frantz and Eugster, 1973) and we used these buffers in solubility studies on minerals such as muscovite–K-spar (Gunter and Eugster, 1980), wollastonite (Gunter and Eugster, 1978), and magnetite (Chou and Eugster, 1977). It was the latter investigation which led me to the study of ore deposits (Eugster and Chou, 1979). Work on tin-tungsten deposits was initiated after visits to the Sn–W mines of SE China and NE Portugal and the realization that the techniques used for magnetite could be adapted to cassiterite and wolframite solubility determinations. Cassiterite solubility measurements are nearly completed (Wilson and Eugster, 1984) and wolframite data will be presented soon, but in this contribution I would like to take a more qualitative approach to the problem of ore deposits associated with granites and present a general geochemical framework which helps to illuminate the gaps in our knowledge and the needs for future research.

Since the article of Holland (1972) on this subject the tin literature has been summarized by Taylor (1979) and a large number of detailed geochemical studies on individual deposits have appeared, many of which are concerned with fluid inclusions and isotopic measurements. They include the studies of Patterson et al. (1981) and of Collins (1981) in Tasmania, of Kelly and Rye (1979) in Portugal, of Kelly and Turneaure (1970) and Sillitoe et al. (1975) in Bolivia, of Clark et al. (1983) in Peru, of So et al. (1983) and Shelton and So (1983) in Korea, of Zaw and Thet (1983) in Burma, and of Simmons and Sawkins (1983) in Mexico. Many shorter communications, including abstracts, have been published during the last few years, signalling a rapidly expanding interest in hydrothermal deposits associated with granites. Recent books on acid magmatism by Ishihara (1980) and Evans (1982) also contain relevant chapters, while Burnham and Ohmoto (1980) and Burnham (1979, 1981) have elucidated details of late-stage acid magmatic processes and associated hydrothermal systems. I propose to use Burnham's physical model for crystallizing plutons and their circulating fluids as a framework for my geochemical model.

It is generally agreed that Sn–W deposits are associated with granites or rhyolites derived by partial melting of continental crust and that the tectonic setting is either convergent plate margins or intracontinental rift zones (Taylor, 1979). Ishihara (1981) has identified the associated granites in Japan as belonging to the S type.

Tin and tungsten nearly always occur as cassiterite, wolframite represented by the ferberite-huebnerite solid-solution series, and scheelite, whereas there is great variability in the nature of the associated sulphide assemblages. Pyrite-pyrrhotite are common, as are chalcopyrite, arsenopyrite, sphalerite, and galena. In addition, an almost bewildering variety of minerals may be encountered in these deposits, including molybdenite, stibnite, jamesonite, boulangerite, realgar, orpiment, stannite, and many others. Each deposit has its own set of mineral assemblages and within a particular deposit, assemblages may be distributed in a regular fashion. A commonly observed sequence with increasing distance from the batholith contact is represented by cassiterite-wolframite-sulphides. The nature of the host rock varies. The most frequent examples are greisens, schists, and limestones and each is characterized by different depositional processes. Finally, a wide range of tectonic styles is encountered, underscoring the fact that each deposit is unique and not duplicated elsewhere. Nevertheless, it should be possible to identify those geochemical relationships which are valid for all deposits and hence useful for predictive purposes.

The physical model and the four stages of the ore-forming process. The solidification model developed by Burnham (1979) for hydrous granodiorite bodies associated with porphyry Cu–Mo deposits has been extended and modified to apply to granites of the Sn–W type in an elegant contribution by Jackson et al. (1982). After emplacement in the shallow crust of the silicate liquid undersaturated with respect to water, cooling and crystallization proceeds from the wall-rock contact inward towards the centre. Crystallization of anhydrous phases, largely feldspars, leads to the formation of an H_2O-saturated carapace and, through vesiculation and boiling, separation of an aqueous fluid. When the pressure of the fluid exceeds the strength of the wall rock, hydrofracturing occurs and an extensive fracture system develops, permitting escape of the fluid and marking the onset of hydrothermal circulation. It is important to realize that circulating fluids cannot penetrate the still-liquid centre of the batholith which is impervious to the addition of water.

Diffusion into the silicate liquid is too slow to be effective and fracturing is not possible until after complete solidification. Jackson et al. (1982) clearly

show the main ore-forming event to be associated with fracturing of the already crystallized granite and the wall rock as well as the 'release of magmatic fluids as a possible result of a vapour phase separating from an H_2O-saturated melt' (p. 171). The fracture systems may be rejuvenated later by weak meteoric-hydrothermal events which are responsible for redistribution of the ore. For the St Just Mining District, Cornwall, Jackson *et al.* (1982) have documented a complex hydrothermal history spanning at least 100 Ma.

The physical model detailed here allows for three principal sources of ore-forming elements (OFEs): (*a*) Magmatic fluids contributed to the circulating hydrothermal fluid in discrete events related to boiling of the silicate liquid. These events are sensitively coupled to cooling, crystallization, pressure changes and permeability. (*b*) Reactions of the hydrothermal fluids (magmatic or meteoric) with the solidified mantle of the granite. (*c*) Interaction of the hydrothermal fluids with wall-rock minerals. The temperatures associated with hydrothermal events (*b*) and (*c*) are usually estimated to be no higher than 500 °C.

Although the ore-forming processes represent a complex continuum with local variations from deposit to deposit, it is convenient to separate the processes responsible for the ultimate enrichment of the ore-forming elements into four stages: 1. Acquisition of OFEs by the granitic magma during partial melting in the lower crust. 2. Positioning of OFEs in crystals, residual melts and fluids after emplacement of the host granite in the upper crust. 3. Release of OFEs to circulating aqueous fluids during the hydrothermal stage. 4. Transport to and deposition of OFEs in the country rock. Most of the information we have available relates to stages 3 and 4, whereas processes for stages 1 and 2 will have to be based largely on conjecture, formulated in part from simple considerations of crystal chemistry.

For Sn–W deposits we must include in our discussion the following elements: Sn, W, Mo, As, Cu, Fe, Zn, Pb, Sb, Bi, S, and Cl. Additional related elements, such as Ag, Nb, Ta, Hg, Li, B, and F can be added as necessary. Primary hosts for these elements are the granite with its differentiates and the country rock.

Granites associated with Sn–W deposits are usually considered to be highly differentiated, biotite-rich varieties of the S-type (Taylor, 1979; Ishihara, 1981). Most of the OFEs must be stored in the melt or in silicate, carbonate, oxide, and sulphide structures. While we do have information on the abundance of some elements such as tin in individual minerals (Neiva, 1982; Taylor, 1979), these minerals are usually collected near ore bodies

and hence show the effects of the depositional processes. Data rarely are obtained sufficiently removed from the ore deposits to provide adequate background values. Consequently we must be satisfied at this time with qualitative assessments.

After solidification, OFEs will be placed principally in biotite, ilmenite, and feldspars. Muscovite is present in some granites, as well as in the altered phases (greisens) and pegmatites. Such muscovites can contain high concentrations of OFEs. Data on OFE concentrations in individual minerals are scarce, but general trends can be established from the data contained in the Handbook of Geochemistry (Wedepohl, 1969). Biotite and chlorite will be the principal hosts for bivalent OFEs such as Zn and Cu, with values of up to 5000 ppm (see also Graybeal, 1973; Banks, 1974). Magnetite can be an excellent host for Zn and Cu, as in basic and ultrabasic rocks. Granitic magnetites normally are poor in Zn and Cu. Pb is stored primarily in alkali positions, with K-feldspars containing up to 200 ppm and biotites up to 70 ppm. Lead is probably removed early from the granite melt as crystallization proceeds.

Maximum values for highly charged OFEs in biotite are Sn 1000, W 10, Mo 60, Nb 100, Ta 30, and As 2 ppm. Muscovite also is an excellent host for such elements and in muscovite–biotite associations shows the higher concentrations. Maximum values are Sn 1000, W 500, Nb 300, Ta 15 ppm. As pointed out by Durasova (1967), a good correlation exists between Sn and Li in micas. The large, highly charged cations (LHCs) appear to be incorporated most readily into micas with octahedral vacancies by coupled substitutions such as $Sn + 2Li = 2Al$ or $Sn + Li = Al + Mg$. A correlation of Sn with $2Fe^{3+}/(Mg + Fe^{2+})$ has been proposed by Durasova (1967) and similar behaviour is to be expected for the other elements. Ilmenite is another important host for LHCs. Maximum reported values are Sn 1000, Mo 100, W 60, Nb 1000, Ta 300 ppm and sphene could probably contain similar concentrations. It is interesting to note that corresponding values for magnetite are generally lower, Sn 50, Mo 100, W 20 ppm, underscoring the similarity between Ti and LHCs.

Though scarce in most granites, sulphides can be significant hosts for some OFEs, particularly Cu.

Next, we must consider what possible anions will make up the ore-forming solutions, the fluids responsible for the acquisition, transport, and deposition of the OFEs. Judging from many fluid inclusion studies, chloride is the dominant species, but fluoride, bisulphide, sulphate, and hydroxide have also been proposed as metal carriers. Skarns associated with Sn–W deposits often are rich in fluorite (Kwak and Askins, 1981*a, b*) and many

greisens are rich in fluorine with lepidolite and topaz the main hosts. Because of the low solubility of fluorite (Richardson and Holland, 1979; Strubel and Schaefer, 1975), metal transport as fluorides should occur only in nearly Ca-free environments. Furthermore, the strength of the cation-F bond in silicates assures the enrichment of fluorine in hydrous minerals such as micas and ampiboles. This is documented by the OH–F exchange data for micas (Munoz and Eugster, 1969; Munoz and Ludington, 1974; Gunow et al., 1980). However, until solubility data on Sn–W minerals in fluorine-bearing solutions become available, we cannot assess the effectiveness of fluorides as metal carriers. At the f_{O_2}-T conditions of the Sn–W transport and deposition, sulphate should not be an abundant anion, nor should HS^- be important. The ranges of temperatures and ligand concentrations to be expected in granitic hydrothermal systems are similar to those of porphyry copper deposits. Based on the experimental work of Crerar and Barnes (1976), Barnes (1979) concluded that:

CuCl, $FeCl^+$, and Fe^{2+} make a significant contribution, but the sulfide complexes do not. At 350 °C, concentrations of thousands of parts per million of both iron and copper are present, . . .

At the neutral to acid pH range to be expected in Sn–W deposits we can also eliminate (OH) complexes and restrict our discussion to mononuclear chloride complexes. Except for AgCl, all metal chlorides are highly soluble in subcritical and supercritical aqueous fluids and the main unresolved question centres on speciation. Wilson and Eugster (1984) have measured cassiterite solubility in super-critical chloride fluids between 400 and 600 °C, at 1.5 kbar pressure. Under geologically reasonable f_{O_2} conditions, Sn is stannous and the dominant species is $SnCl^+$; Sn concentrations as high as 1000 ppm can be obtained at the pH of muscovite-K-feldspar-quartz (see fig. 1). Finally, fluid inclusion studies on Sn–W deposits by Kelly and Rye (1979), Patterson et al. (1981), Collins (1981), Haapala and Kinnunen (1979), So et al. (1983), and others document that chloride is the chief anion in the ore-forming fluids, with molalities ranging from 0.5 to 5.0 and ore deposition temperatures from 500 to about 200 °C.

Sources of OFEs and release to hydrothermal fluids. The processes of ore deposition are not initiated until boiling has begun to separate an aqueous hydrothermal fluid from the crystallizing melt and after hydrofracturing has been sufficiently extensive to permit circulation of such fluids, driven by the thermal gradient associated with the intrusion. Meteoric waters may also become involved in the circulation systems and mixing of fluids
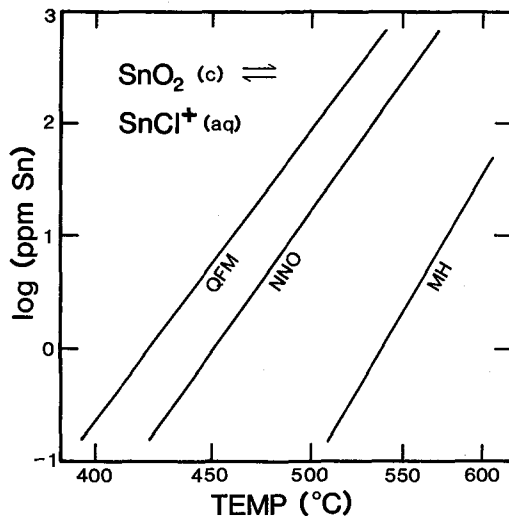

FIG. 1. Cassiterite solubility at 1.5 kbar as a function of T and f_{O_2} (QFM, NNO, and HM) for a 2 m total chloride solution in equilibrium with albite + K-spar + muscovite + quartz. $SnCl^+$ is the dominant tin species. From Wilson and Eugster (1984).

represents an important depositional mechanism to be discussed later.

As mentioned earlier, three sources for OFEs can be envisaged: the silicate melt, the already crystallized granite mantle surrounding that melt, and the minerals of the wallrock into which the granite has intruded. I will discuss these in turn.

During the past decade a large number of papers have been published on the major and trace element fractionation patterns in silicic magma chambers, including the classic study by Hildreth (1979) of the Bishop Tuff (see also Bacon et al., 1981; Bailey and Macdonald, 1975; Christiansen et al., 1984; Crecraft et al., 1981; Fryer and Edgar, 1977; Mahood, 1981; Mahood and Hildreth, 1983; Taylor et al., 1981). As pointed out by Hildreth (1979), the roof of the magma chamber may become enriched in silica, alkalis, Sn, W, Mo, U, B, Be, F, and other elements by convection-driven thermo-gravimetric diffusion. Watson (1976) and Ryerson and Hess (1978) have pointed out that trace element behaviour in the liquid is largely controlled by melt polarization and Mahood and Hildreth (1983) state flatly that

Liquid structure appears to be the overriding control on trace-element partitioning in these strongly polymerized magmas, . . . (p. 28).

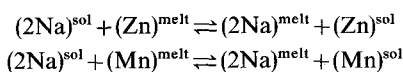Polymerization is most extensive in silica-rich magmas and in magmas where Al + (Na,K) proxy

for Si. However, the roof of the chamber is also the place where dissolved H_2O and hence the concentration of non-bridging OH groups is highest, enhancing cation mobility and depolymerization. The larger, highly charged cations (LHCs) such as Nb, Ta, Sb, Mo, Sn, W, U cannot enter the polymerized framework as easily as do Al and Ti and hence are enriched in the roof along with Na, Li, Be, F, and Cl. Mahood and Hildreth (1983) suggest that

. . . differentiation within high-silica systems can be controlled by two . . . liquid-state processes: (1) diffusive emigration of trace components from the most polymerized parts of the magma . . . ; (2) transport of trace metals as volatile complexes within a thermal and gravitational gradient in a volatile-rich 'wet' system. (p. 27.)

Christiansen et al. (1984), in a study of topaz rhyolites, while not ruling out thermogravitational diffusion, relegate it to a minor role compared to fractional crystallization. They ascribe the high Na/K ratios to the effect of fluorine on residual melt compositions and the fractional crystallization of quartz and sanidine. They also define the differences between F-dominated and Cl-dominated systems, the latter usually of peralkaline character and enriched in LREE, Na, Fe, Zn, Nb, and other elements. Their explanations, however, do not fit the large Na, Li, and LHC enrichments so common in highly siliceous systems in which fluorine does not play an important part. Clearly a further hitherto unnoticed mechanism must be involved here. Hildreth (1979) acknowledges R. L. Smith as having pointed out that strong LHC enrichment commences with a roofward increase in the Na/K ratio and that this is opposite to the normal differentiation trend. Extreme enrichment of Na and Li over the other alkali ions is also typical of aqueous solutions down to room temperature and is usually accounted for by the larger hydration shells of the smaller ions with the higher surface charge. Good examples are seawater and the Na-Li brines of Great Salt Lake, Utah (Handy and Hahl, 1966) and the Salar of Uyuni (Rettig et al., 1980). Consequently, K is strongly fractionated into the solids, mainly, but not necessarily, clay minerals (see Eugster and Jones, 1979). By analogy, we can postulate that large, polymerized, 3-dimensional islands exist in the melt which are separated by channels of hydrated, partially depolymerized melt enriched in LHCs and alkalis. These channels represent high diffusivity paths leading to the roof of the magma chamber. Hydrated Na^+ ions are enriched in these channels, due to their lower surface charge, with K^+ fractionated preferentially into the Si-Al-K islands. Thus the Na enrichment need not be linked

to crystallization of sanidine at depth. Experiments to check this model could readily be devised. Note that the behaviour of Rb and Cs does not conform to this model: both are enriched towards the top (Hildreth, 1979, p. 57). Christiansen et al. (1984) pointed out the extreme Rb and Cs enrichment in the less silicic, but fluorine-rich Spor Mountain rhyolite and it is quite possible that the distribution of these large trace alkali metals is dominated by F and Cl complexing rather than by hydration.

Along with LHCs, Na, Li, and SiO_2, the latter probably transported as H_4SiO_4 along the hydrated channels, the roof is also enriched in the volatiles Cl, B, F, and H_2O, a crucial fact for the development of ore fluids. These elements, along with most LHCs, and chloride are partitioned preferentially, into the aqueous fluids forming during the crystallization of silicate liquids. Kilinc and Burnham (1972) documented the very strong enrichment of chloride in the supercritical fluid in equilibrium with the melt, while Holland (1972) reported the results of similar experiments on Zn, Mn, and Fe. Although these experiments were not reversed, there is little doubt that Zn and Mn are fractionated strongly into the fluid. Zn, Mn^{2+}, and Fe^{2+} are bivalent octahedral cations (BOCs) and their behaviour must be distinguished from that of the LHCs. Holland's (1972) experiments were carried out at about 850 °C and 2 kbar with solutions of variable chlorinities (total chloride molality). In all runs, Na was the principal exchangeable constituent and it is convenient to define the melt-fluid distribution in terms of Na-Zn and Na-Mn exchange reactions:

$$(2Na)^{sol} + (Zn)^{melt} \rightleftharpoons (2Na)^{melt} + (Zn)^{sol}$$
$$(2Na)^{sol} + (Mn)^{melt} \rightleftharpoons (2Na)^{melt} + (Mn)^{sol}$$

with the constants

$$(K_D)_{Na,Zn} = \frac{(Na^{melt})^2(Zn^{sol})}{(Na^{sol})^2(Zn^{melt})} = K_{Zn}$$

and

$$(K_D)_{Na,Mn} = \frac{(Na^{melt})^2(Zn^{sol})}{(Na^{sol})^2(Zn^{melt})} = K_{Mn}.$$

The average values for K_{Zn} and K_{Mn} for all twenty-three experiments are 14 and 11 respectively, with extremes ranging from 6 to 30. As fig. 2 illustrates, Zn and Mn are fractionated from the melt into the fluid about as effectively as Fe is fractionated from biotite into the fluid at 600 °C. Consequently, repeated episodes of water saturation and vapour separation during crystallization of the granite are an effective means for removing elements such as Zn, Mn, and probably also Cu and LHC elements such as Sn from the melt and adding them to the
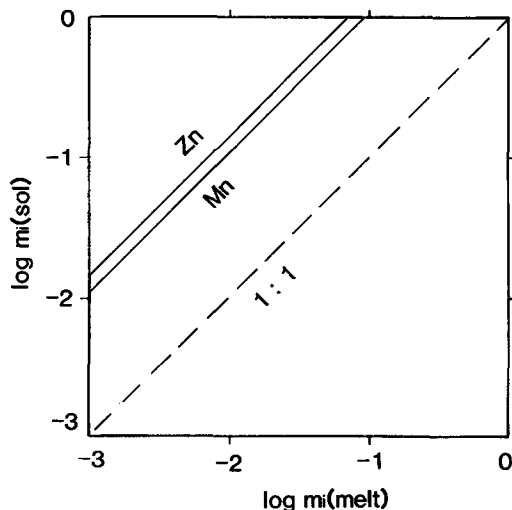
FIG. 2. Distribution of Zn and Mn between melt and an aqueous fluid, with a sodium molality of one in both phases. Based on the average of all experiments reported by Holland (1972).

circulating fluids. For comparison, the distribution constants for chloride between vapour and melt quoted by Kilinc and Burnham (1972) range from 13 to 83 for

$$K_{Cl} = m_{Cl}^{sol}/m_{Cl}^{melt} \text{ at } 750-700 \text{ °C.}$$

According to experiments of Candela and Holland (1984), Manning (1981), and Ryabchikov et al. (1980, 1981) Cu, Mo, and Sn also are fractionated strongly from silicate melts into hydrous fluids.

The strong Cl enrichment in the fluid observed by various investigators, together with the low quench pH values reported by Holland (1972) for such fluids, lead us to postulate that chloride present in the melt, upon vesiculation, undergoes hydrolysis by a reaction such as

$$2NaCl_{(melt)} + H_2O \rightarrow 2HCl_{(vapour)} + Na_2O_{(melt)}$$
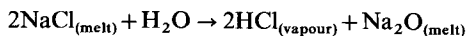
with the HCl strongly enriched in the aqueous fluid.

Although Holland's (1972) experiments were not specifically designed to determine the equilibrium constant for this reaction

$$(K)_{P,T} = \frac{(a_{HCl}^v)^2 \cdot a_{Na_2O}^m}{(a_{NaCl}^m)^2 \cdot f_{H_2O}}$$

we have estimated K at 850 °C from his data. There is considerable uncertainty with respect to the reliability of the quench pH measurements and consequently K for different experiments varies between 0.1 and 10, with several values close to unity. In other words, HCl molalities can be expected to be roughly equal to NaCl molalities. More precise measurements are in progress.

Acid fluids charged with OFEs will be expelled episodically from the crystallizing magma into the already solidified granite mantle and the adjacent wallrocks, representing the earliest stage of ore-fluid formation. OFE concentrations in such fluids can be further enhanced by reaction with granitic minerals of the mantle, the second OFE source, as well as minerals of the wall rocks, the third source. Interaction of HCl-rich fluid with silicates, oxides, carbonates, and other minerals of the crystallized granite and the wall rocks neutralizes the HCl and produces a fluid rich in NaCl, KCl, $CaCl_2$, $FeCl_2$, and other metal chlorides, especially LHCs. For solid-fluid equilibria, Eugster and Gunter (1981) have estimated metal chloride abundances from solubility data. Clearly, cation concentrations are strongly dependent on total chloride molalities. However, it is not safe to assume that the more saline a solution is, the more effective it will be in transporting OFEs (Wang et al., 1984).

Separation of an aqueous fluid also can lead to enrichment in H_2S and HF. These acids have been suggested as important transport agents for OFEs. Because of the importance of sulphur in the depositional process, we will want to consider the role of magmatically derived H_2S (see later). Information on the role of HF is conflicting. Christiansen et al. (1984) point out that F-rich rhyolites can become extremely enriched in Rb, Cs, Nb, Y, U, Th, Ta, qualitatively consistent with fractional crystallization of observed phenocrysts. In a number of contributions, Gunow et al. (1980), Munoz and Swenson (1981), Chivas (1981), Gilzean and Brimhall (1983) document fluorine as an important metal transport agent in Mo deposits, particularly during early stages, but that in granites associated with Sn-W deposits HF is less important and usually no more than a trace constituent. For the Koloula porphyry copper, Chivas (1981) has estimated f_{HF} levels of 0.003 bars, much lower than expected f_{HCl} levels in the ore fluids. As mentioned earlier, Ca and F are not likely to be transported in the same fluid. However, if Ca levels are low, fluoride concentrations other than those due to HF could be appreciable, accounting for the skarns as reaction products of fluid-wall rock interaction. The metal-carrying ability of such fluids needs to be tested. Candela and Holland (1984) showed that F does not enhance Mo enrichment in fluids in equilibrium with melt.

Because of the enrichment of chloride in crustal materials, hydrothermal fluids associated with granites are likely to be dominated by chloride and I will restrict the discussion to transport of ore metals in chloride-rich fluids. Fluids expelled from

Table I. Release mechanisms for OFEs

I. Congruent dissolution.

$$Fe_3O_4(mt) + 6HCl + H_2 \longrightarrow 3FeCl_2 + 4H_2O \tag{1}$$
$$2FeTiO_3(ilm) + 10HCl + H_2 \longrightarrow 2FeCl_2 + 2TiCl_3 + 6H_2O \tag{2}$$

II. Incongruent dissolution.

$$3KAlSi_3O_8(kf) + 2HCl \longrightarrow KAl_3Si_3O_{10}(OH)_2(ms) + 6SiO_2(q) + 2KCl \tag{3}$$
$$2KAl_3Si_3O_{10}(OH)_2(ms) + 2HCl + 3H_2O \longrightarrow 3Al_2Si_2O_5(OH)_4(ka) + 2KCl \tag{4}$$
$$FeMgSi_2O_6(px) + 2HCl \longrightarrow MgSiO_3(di) + SiO_2(q) + FeCl_2 + H_2O \tag{5}$$
$$3KFe_3AlSi_3O_{10}(OH)_2(bi) + 20HCl \longrightarrow KAl_3Si_3O_{10}(OH)_2(ms) + 6SiO_2(q) + 9FeCl_2 + 2KCl + 12H_2O \tag{6}$$
$$Fe_3O_4(hm) + 2HCl \longrightarrow Fe_2O_3(hm) + FeCl_2 + H_2O \tag{7}$$
$$3KFe_3AlSi_3O_{10}(OH)_2(bi) + 2HCl \longrightarrow KAl_3Si_3O_{10}(OH)_2(ms) + 3Fe_3O_4(mt) + 6SiO_2(q) + 2KCl + 3H_2 \tag{8}$$

III. Congruent exchange.

$$KFe_3AlSi_3O_{10}(OH)_2(bi) + MgCl_2 \longrightarrow KMg_3AlSi_3O_{10}(OH)_2(bi) + 3FeCl_2 \tag{9}$$

IV. Incongruent exchange.

$$2KAlSi_3O_8(kf) + CaCl_2 \longrightarrow CaAl_2Si_2O_8(an) + 4SiO_2(q) + 2KCl \tag{10}$$
$$KFe_3AlSi_3O_{10}(OH)_2(bi) + NaCl \longrightarrow NaAlSi_3O_8(ab) + Fe_3O_4(mt) + KCl + H_2 \tag{11}$$

V. Melt-fluid exchange.

$$FeO(m) + 2HCl \longrightarrow FeCl_2 + H_2O \tag{12}$$

the magma will interact with the minerals of the already crystallized granite mantle and the wall rocks and will take up or release OFEs to the solution through a variety of release mechanisms, some of which are complex. Table I is an attempt to organize release reactions into five classes, with all equations written for the sake of simplicity with respect to major elements only. OFEs will be enriched in the chloride fluids, represented in Table I either by $FeCl_2$ or KCl. Congruent dissolution, incongruent dissolution and melt–fluid exchange all involve HCl-bearing fluids, that is fluids involved in acid alteration, while exchange reactions can also take place in near-neutral chloride solutions. As shown by Wang et al. (1984) for magnetite, mineral solubilities in neutral chloride solutions, even those with very high total chloride molalities, are expected to be much lower than in acid solutions. This conclusion was reached also by Barrett and Anderson (1982) for sulphide solubilities in NaCl solutions below 100 °C.

Congruent dissolution, by definition, leads to the destruction of the solid which interacts with the fluid, and hence all OFEs are released in the process. Silicates usually do not behave in this way because of the large solubility differences of their constituents. Oxides, on the other hand, dissolve congruently as illustrated by equations (1) and (2). These two reactions involve reduction also. Laboratory calibrations are available only for reaction (1), the dissolution of magnetite in chloride fluids (Chou and Eugster, 1977; Wang et al., 1984). Concentrations of $FeCl_2$ increase in the fluid with

increasing HCl (or total chloride), higher f_{H_2} or more reducing conditions, and decreasing temperature. No calibrations are available for reaction (2), one of the principal mechanisms for the release of Sn and similar elements. Nothing is known about Ti complexing in chloride fluids, but relations may be analogous to those of reaction (1). For the sake of simplicity, all reactions in Table I are formulated with respect to the uncharged, associated chloride species.

OFEs can be released through incongruent dissolution of their host minerals. Reactions (3)–(8) represent a number of typical examples. Reactions (3) and (4) are the acid alteration reactions calibrated by Hemley and Jones (1964), Shade (1974), and others. They lead to a decrease or elimination of alkali positions and hence release of OFEs which proxy for alkalis, such as Pb, Ag, Hg (ALC elements). Both reactions are important in the formation of porphyry copper deposits (Lowell and Guilbert, 1970) and play a significant role also in the deposition of cassiterite and other minerals of the Sn–W association. Reaction (5) has been included to illustrate the behaviour of ferromagnesian silicates free of aluminum, minerals such as olivine, pyroxene, actinolite, talc, serpentine. Such reactions are incongruent, because the release of ferrous iron and other bivalent octahedral cations (BOC elements) necessitates the precipitation of one or more solid phases. Except for the neutralization of HCl, they are similar to the incongruent exchange reaction (11).

In Table II I have summarized the Shannon–

Table II. Shannon-Prewitt radii for BOC, LHC and ALC elements.

I. **BOC elements** (bivalent octahedral cations similar in size and behavior
                      to ferrous iron: (26) Fe^{2+} 0.77(VI))

Ore-forming elements:		Non-ore-forming elements:	
(26) Fe^{2+}	0.77(VI)	(12) Mg^{2+}	0.72(VI)
(27) Co^{2+}	0.61(VI)	(3) Li^+	0.74(VI)
(28) Ni^{2+}	0.60(VI)		
(29) Cu^{2+}	0.73(VI)		
(30) Zn^{2+}	0.75(VI)		

II. **LHC elements** (large highly charged cations similar in size and behavior
                       to ferric iron: (26) Fe^{3+} 0.49(IV), 0.65(VI))

Ore-forming elements:		Non-ore-forming elements:	
(25) Mn^{3+}	0.65(VI)	(13) Al^{3+}	0.53(VI), 0.39(IV)
(26) Fe^{3+}	0.65(VI)	(22) Ti^{3+}	0.67(VI)
(33) As^{3+}	0.58(IV)		
(41) Nb^{4+}	0.69(VI)		
(42) Mo^{4+}	0.65(VI)		
(50) Sn^{4+}	0.69(VI)		
(51) Sb^{5+}	0.61(VI)		
(73) Ta^{4+}	0.66(VI)		
(74) W^{4+}	0.65(VI)		

III. **ALC elements** (cations capable of occupying alkali positions)

Ore-forming elements:		Non-ore-forming elements:	
(47) Ag^+	1.30	(11) Na^+	1.16(VIII)
(80) Hg^{2+}	1.14(VIII)	(19) K^+	1.60(XII)
(82) Pb^{2+}	1.49(XII)	(20) Ca^{2+}	1.12(VIII)

Prewitt crystal radii of the three OFE classes, realizing that ionic radius is but a crude guide to the melt–fluid–mineral behaviour of the elements and that other aspects such as electronegativity, crystal field behaviour, melt structure, ligand concentrations and complexing, Jahn–Teller and other effects must also be considered.

Reaction (6) is of fundamental importance for Sn–W deposits. It represents the conversion of biotite, a host for LHC, BOC, and ALC elements, to muscovite, a principal host for LHC elements. In the process, assuming aluminium conservation, the amount of mica is reduced and all of the BOC along with most of the ALC elements are released to the fluid. Transition elements, such as Fe and Mn, may avoid release by oxidation and thus changing to LHC elements. As we have mentioned earlier, the relative concentrations of LHC elements are often higher in muscovite, indicating that they are probably largely retained in the mica structure during the conversion. Reaction (7) is intended to point out that reduction is not essential for the release of $FeCl_2$ and Fe^{2+} from spinel and rhombohedral oxides, provided that concomitant oxidation occurs among the solid phases. Reaction (8) is the biotite-muscovite conversion (6) coupled with oxidation. In the presence of Ti, ilmenite acts as an additional host for LHC elements, further decreasing the likelihood of their release to the fluid. Many additional dissolution reactions can be formulated, depending on the particular situation under study.

Exchange reactions have also been separated into congruent and incongruent examples. In exchange processes, metal chlorides, such as NaCl, KCl, $FeCl_2$, take the place of HCl for the case of dissolution reactions. During congruent exchange (reaction 9), the same solid solution phase is present on both sides, but its composition is modified by exchange with the chloride fluid. For the sake of clarity, reaction (9) is formulated in terms of the end member components present in biotite. Reaction (9) has been calibrated by Schulien (1980) between 500 and 650 °C (see also Eugster and Gunter, 1981; Eugster and Ilton, 1983). At these temperatures, Mg is strongly fractionated into the solid, while Fe is enriched in the chloride fluid, with the fractionation more intense at higher temperature. The distribution constant for reaction (9) is

$$(K_D)_9 = \frac{(1 - x_{ann})m_{FeCl_2}}{x_{ann}(1 - m_{FeCl_2})}$$

where x_{ann} is the mole fraction of annite in biotite and m_{FeCl_2} is the molality of $FeCl_2$ in the fluid. At 600 °C, $K_D = 12.0$ and at 500 °C, $K_D = 7.75$. Figs. 3 and 4 illustrate the effect of such pronounced fractionation. Iron is extracted from the biotite very efficiently and only very Mg-rich phlogopites can coexist with $MgCl_2$-fluids. As fig. 4 indicates, $m_{FeCl_2} = m_{MgCl_2}$ for a biotite with $x_{ann} = 0.04$!

No data are available for the release of BOC elements from biotites by congruent exchange, but
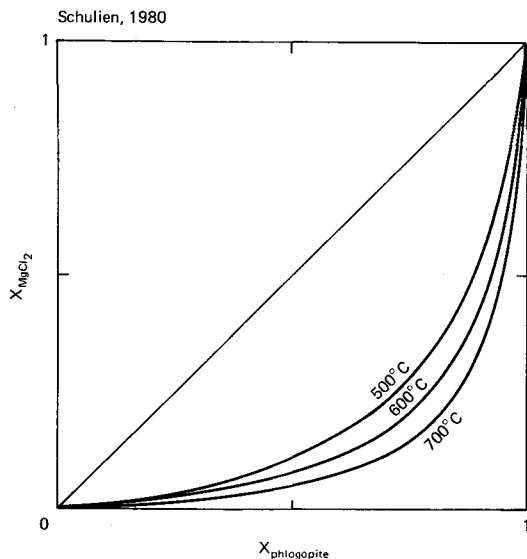
Schulien, 1980

FIG. 3. Mg–Fe fractionation between chloride fluids and biotites, 500, 600, 700 °C, 2 kbar. From Schulien (1980); see also Eugster and Ilton (1983).

the similarity between Cu^{2+}, Zn^{2+}, and Fe^{2+} lets us suspect that BOC elements will be fractionated into chloride fluids just as effectively as $FeCl_2$ is in the range 500–700 °C. At lower temperatures, as pointed out by Eugster and Ilton (1983), fractionation diminishes and in carbonates it is reversed around 350 °C, with Mg^{2+} enriched over Fe^{2+} in the fluid (Eugster, 1982). No data are available for silicates, but the same behaviour may be expected as indicated by the growth of Fe-rich silicates in diagenetic seawater-dominated Mg-rich fluids. Until laboratory calibrations become available, we may assume that exchange reactions such as reaction (9) represent an effective mechanism for the release of BOC elements, particularly at higher temperatures.

Incongruent exchange reactions are illustrated by reactions (10) and (11). Unlike solids are present as reactants and products, while LHC, BOC, and ALC elements are exchanged with the chloride fluid. Reaction (10) is used to show exchange between two feldspars and the consequent release of ALC elements, while reaction (11) illustrates the preferential liberation of BOC elements through the destruction of biotite by exchange coupled with oxidation. In the process, magnetite or ilmenite are precipitated, providing hosts for the LHC elements. Many more similar reactions can be formulated as well as various combinations of dissolution, exchange and redox processes. In Table III an attempt has been made to classify in a qualitative

manner the contrasting behaviour of the LHC, BOC, and ALC elements during release by a variety of reactions. The largest contrast exists between early acid + reducing and later acid–neutral + oxidizing conditions, the former presumably dominated by magmatic fluids and the latter by meteoric fluid influx.

Transport of ore-forming elements. The transport of OFEs in hydrothermal solutions has been discussed by Barnes (1979) in terms of the principal complexing agents chloride and bisulphide, and based on solubility data for the sulphides of Fe, Cu, Ni, Pb, and Hg. The most complete data for chloride complexing at elevated P and T has been presented by Seward (1976) based on solubility measurements on cerargyrite, AgCl. The following sequence of progressive complexing as a function of increasing chloride concentration was deduced:

$$Ag^+ \rightarrow AgCl \rightarrow AgCl^{2-} \rightarrow AgCl_3^{2-}.$$
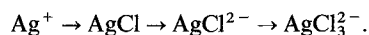
A number of other studies, including that by Seward (1984) on lead chloride, have shown that complexing reactions generally proceed to the right in response to increasing ligand concentration. Due to changes in the dielectric constant of water as a function of P and T (Helgeson and Kirkham, 1974; Eugster, 1981), increasing temperature and decreasing pressure have a similar effect.

Solubility measurements on magnetite, Fe_3O_4, in chloride fluids have been reported by Sweeton
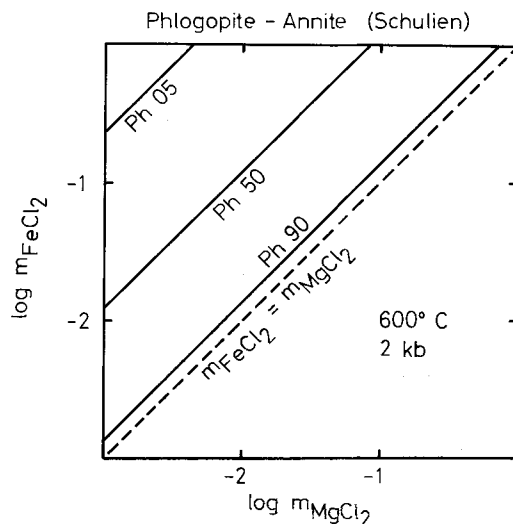
Phlogopite – Annite (Schulien)

FIG. 4. Effect of biotite–fluid fractionation on the composition of chloride fluids at 600 °C, 2 kbar pressure. Ph 05 is a biotite with a phlogopite mol fraction of 0.05. The dashed curve represents equal abundance of $MgCl_2$ and $FeCl_2$ in the fluid. 600 °C, 2 kbar, from Eugster and Gunter (1981), based on data of Schulien (1980).

Table III. Efficiency of OFE release mechanisms.

Reaction type and condition	LHC	BOC	ALC
1. Congruent dissolution at low pH and f_{O_2}	XXX	XXX	XXX
2. Incongruent dissolution, no oxidation	X	XXX	XX
3. Incongruent dissolution with oxidation	---	XXX	XX
4. Congruent exchange, neutral pH, no oxidation	X	X	---
5. Incongruent exchange, with oxidation	---	XXX	XX
6. Melt-fluid exchange with HCl production	XX	XX	X

LHC: large highly charged cations

BOC: bivalent octahedral cations

ALC: alkali and alkali-like cations

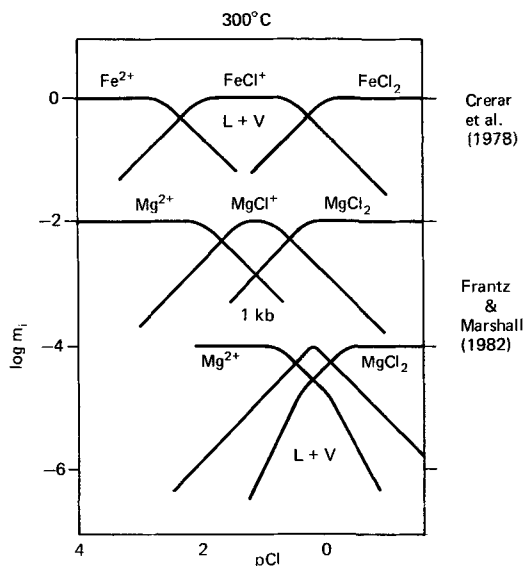XXX, XX, X, ---: strong, moderate, slight, no release, respectively.

FIG. 5. Dissociation of iron and magnesium chloride species as a function of total chloride molality (chlorinity), plotted as the negative logarithm of m_{Cl}, p_{Cl}, at 300 °C. Curves are shown for a total log iron molality of 0 (pressure of liquid + vapour), a total log Mg molality of −2 (1 kbar pressure) and of −4 (pressure of liquid + vapour). Data from Crerar et al. (1978) and Frantz and Marshall (1982), see also Eugster and Ilton (1983).

and Baez (1970), Chou and Eugster (1977), Eugster and Chou (1979), Crerar et al. (1978), Tremaine and LeBlanc (1980), and Wang et al. (1984). From these data, we can suggest the sequence

$$Fe^{2+} \rightarrow FeCl^{+} \rightarrow FeCl_2 \rightarrow FeCl_3^{-}$$
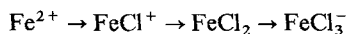
all of which have been inferred to exist. Abundance diagrams presented in fig. 5 are based on the data of Crerar et al. (1978) for Fe and of Frantz and Marshall (1982) for Mg. Curves are drawn for arbitrary, constant metal molalities, with log m chosen at 0 for Fe at the pressure of the liquid + vapour curve, at −2 for Mg at 1 kbar, and at −4 for Mg at the $L + V$ pressure. Fig. 6 shows schematic curves for a BOC element, the upper diagram drawn for a constant metal molality, the latter for a fixed molality of $MeCl_2$, such as that defined by a mineral solubility.

At lower temperatures, Fe^{2+} and $FeCl^{+}$ are the major solute species, but at 500 °C and above, Chou and Eugster (1977) have shown that $FeCl_2$ is dominant. As indicated by Wang et al. (1984), iron concentration in acid solutions based on magnetite dissolution is directly proportional to the HCl molality of the reacting fluid, as given by

$$1/3 Fe_3O_4 + 2HCl \rightarrow FeCl_2 + H_2O + 1/6 O_2$$
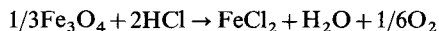
that is $FeCl_2$ molality is half the molality of the HCl neutralized in the dissolution reaction. In NaCl
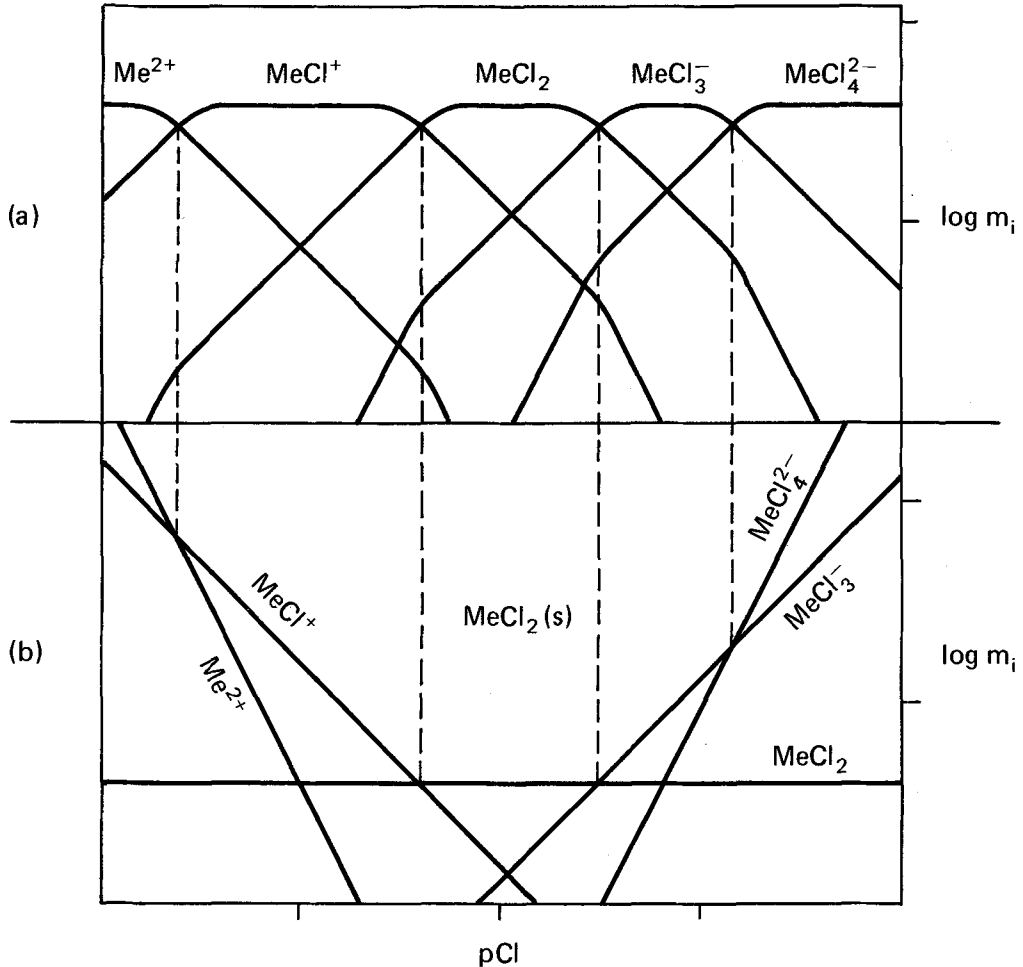
FIG. 6. Comparison of a Bjerrum diagram (top) with a solubility diagram (bottom) for a $MeCl_2$ system, with species abundances plotted against p_{Cl}, the negative logarithm of the total chloride molality. In the top diagram, total metal molality is constant, while species abundances in the bottom diagram are controlled by the solubility of a metal chloride or oxide mineral. From Eugster and Ilton (1983).

solutions, on the other hand, Wang *et al.* (1984) found much lower magnetite solubilities, due to the stability of the NaCl complex. Total iron concentrations were found to be less than 10^{-4} moles/l and at 600 °C the major iron species is inferred to be $FeCl_3^-$. Speciation data for iron are still incomplete and the magnitudes of the dissociation constants remain uncertain, but there is little doubt now that high NaCl concentrations are not sufficient to produce ore-forming solutions. Adequate OFE concentrations can be acquired only by solutions which initially had high enough HCl molalities to ensure OFE release and complexing by chloride.

Information on speciation of other OFEs is scarce. Data on the solubility of copper sulphides in chloride solutions and relevant dissociation constants are given in Crerar and Barnes (1976). Anderson (1973) and Barrett and Anderson (1982) reported sphalerite solubilities in chloride solutions, while galena solubility was measured by Nriagu and Anderson (1971), Anderson (1973), Yurchenko *et al.* (1976), Barrett and Anderson (1982), and others. Few of these data are complete enough to allow calculation of the relevant dissociation and speciation constants.

Information on LHC element transport in

chloride fluids is scarcer still. Patterson *et al.* (1981) reviewed data on cassiterite solubility and concluded:

Recent work on cassiterite solubility ... has largely been directed toward highly alkaline conditions under which tin deposits were thought to have formed (Barsukov, 1957). Oxygen fugacity was not specifically controlled ... and the valence state was ... assumed to be Sn^{4+}. (pp. 424–5.)

Wilson and Eugster (1984) have clearly documented that for f_{O_2} conditions up to and including HM, tin valence in chloride solutions is 2, that is cassiterite dissolution is a reduction reaction. Under the conditions of our experiments, 500–600 °C, no NaCl present, $SnCl^+$ is the dominant solute. Under appropriate conditions, we may expect to encounter Sn^{2+}, $SnCl_2$, as well as $SnCl_3^-$. Our experimental results are in contrast with the extrapolations of Eadington (1983) based on 25 °C data.

We also must consider the possibility that some LHC elements are carried as acids or sodium complexes, particularly in NaCl-rich solutions. This will be important particularly for tungsten and arsenic. Krauskopf (1970) has stated:

... it seems clear that tungsten is carried in ore-forming solutions chiefly as tungstate ion, tungstic acid, sodium tungstate, or a heteropolyacid, the relative amounts of these depending on temperature, pH, and the silica content of the solutions. From such fluids tungsten is deposited as wolframite if limestone is absent and Ca^{2+} is low, or as scheelite if limestone is present. ...

Since then, Bryzgalin (1976) has measured the solubility of H_2WO_4 in NaCl and KCl brines at 300–400 °C, but without controlling f_{H_2} or f_{HCl}. These experiments need to be repeated under controlled conditions. Wesoloski *et al.* (in press) studied hydrolysis equilibria of tungsten in aqueous sodium chloride solutions spectroscopically to 300 °C and concluded that WO_4^{2-}, HWO_4^-, and H_2WO_4 are the major species. Sodium tungstate solutes were not found to be significant.

Many laboratory calibrations will be required before we can evaluate the transport of ore-forming elements quantitatively. This includes information on mineral solubilities as well as on dissociation constants. Until such data become available, we cannot assess the relative importance of various suggested depositional mechanisms, such as decreasing temperature, increasing pH, dilution by meteoric waters, boiling, and others.

For the subsequent formulation of depositional mechanisms we represent the iron solutes by $FeCl_2$, though the actual species may be Fe^{2+}, $FeCl^+$, $FeCl_2$, $FeCl_3^-$, or higher complexes, or any mixture thereof. There is no doubt, however, that the solutes will be ferrous species of f_{O_2}s as high as those of
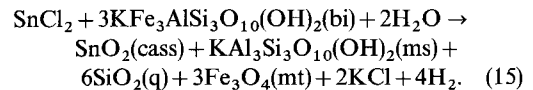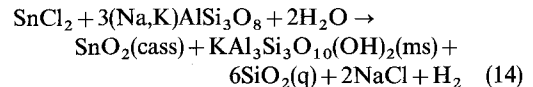
magnetite + hematite (see Chou and Eugster, 1977). In the presence of cassiterite, the dominant tin species will be bivalent tin, Sn^{2+}, $SnCl^+$, or $SnCl_2$ represented by $SnCl_2$. Similarly, we will use CuCl, $ZnCl_2$, and $PbCl_2$ to indicate the dominant Cu, Zn, and Pb solutes (see also Barnes, 1979). For tungsten we will use tungstic acid, H_2WO_4, as the representative carrier.

Deposition of ore minerals. The chemical reactions involved in the deposition of Sn–W ores depend largely on the nature of the country rock. In every case, however, metal chloride solutes are converted to oxide or sulphide minerals, liberating HCl or H^+ in the process. For deposition to continue, this acidity must be absorbed by the wall rock. In carbonate rocks, neutralization is readily achieved through carbonate dissolution and the production of $CaCl_2$ brines. Schematically:

$$SnCl_2 + CaCO_3(cc) + H_2O \rightarrow SnO_2(cass) + CaCl_2 + CO_2 + H_2. \quad (13)$$
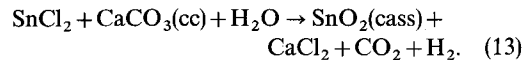
The dissolution of calcite obviously aids in the precipitation of cassiterite, and the importance of $CaCl_2$ has been documented by Kwak and Tan (1981) for fluid inclusions from Sn–W deposits. Because of the valence change of tin, cassiterite deposition also must involve oxidation, an effect which careful study on the hand specimen scale should reveal.

In schists, the dominant mechanisms for acid neutralization at the temperature of initial deposition are the conversion of feldspar to muscovite (Hemley and Jones, 1964), or of biotite to muscovite:

$$SnCl_2 + 3(Na,K)AlSi_3O_8 + 2H_2O \rightarrow SnO_2(cass) + KAl_3Si_3O_{10}(OH)_2(ms) + 6SiO_2(q) + 2NaCl + H_2 \quad (14)$$

$$SnCl_2 + 3KFe_3AlSi_3O_{10}(OH)_2(bi) + 2H_2O \rightarrow SnO_2(cass) + KAl_3Si_3O_{10}(OH)_2(ms) + 6SiO_2(q) + 3Fe_3O_4(mt) + 2KCl + 4H_2. \quad (15)$$

The efficacy of these reactions is documented in the Portuguese Sn–W deposits of Panasqueira and Argozelo, where cassiterite crystals hosted in quartz veins are surrounded by a selvage of coarse muscovite flakes oriented perpendicular to the cassiterite crystal faces (Wilson *et al.*, 1983, see also fig. 7). Oxidation is also associated with these reactions. Depending on the specific mineralogy of the wall rock involved and the temperature range, many other neutralization reactions are possible.

Feldspar–mica and mica–mica reactions are relatively slow and it is likely that they are the rate-controlling step during cassiterite precipitation in schist-hosted quartz veins. In skarn environments, decarbonation and oxidation reactions
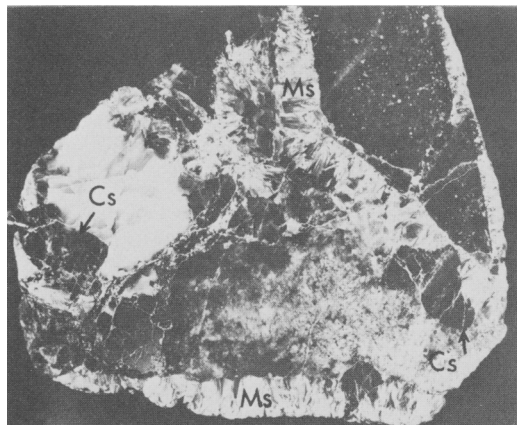
FIG. 7. Polished slab of a quartz vein, carrying cassiterite and arsenopyrite. Note the coarse muscovite fringes separating the schist of the country rock from the vein. Vinheiros Mine, Vale das Gatas, near Vila Real, Portugal ($\times \frac{1}{2}$).

probably assume that function, but detailed textural and compositional studies are necessary to verify these suggestions.

Wolframite deposition is somewhat more complex, because it also involves $FeCl_2$ and $MnCl_2$. For the precipitation of ferberite, we can write

$$Na_2WO_4 + FeCl_2 \rightarrow FeWO_4(wolf) + 2NaCl. \quad (16)$$
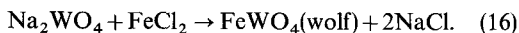
No acidity is created by this reaction and indeed, at Panasqueira wolframite crystals in quartz veins are generally not armoured by muscovite as is commonly the case for cassiterite. Furthermore, wolframite often is distributed randomly throughout the quartz veins, whereas cassiterite is enriched at the vein–wall-rock contact.
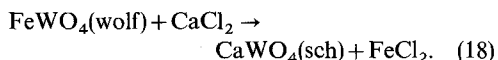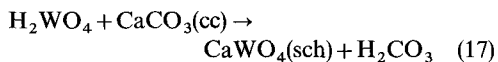
Appropriate solubility determinations for ferberite and huebnerite are not yet available, but judging from wolframite deposits, both phases must be quite insoluble. Hence we should not expect the solutes H_2WO_4 and $FeCl_2$ or $MnCl_2$ to travel in the same solution, unless we invoke large temperature gradients or mixing of waters. It is tempting to suggest that H_2WO_4 derives from the hydrothermal fluids associated with the granite batholith, while $FeCl_2$ and $MnCl_2$ are produced by acid alteration of the country rock through reactions such as

$$3Fe_3O_4(mt) + 18HCl + 3H_2 \rightarrow$$
$$9FeCl_2 + 12H_2O. \quad (1)$$
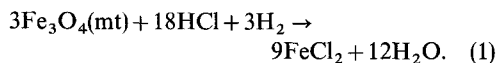
Whenever the concentration of $FeCl_2$ and $MnCl_2$ contributed by the country rock is sufficient to exceed the wolframite solubility product, deposition ensues. Through the requirement of acid

alteration, wolframite deposition thus is linked to the precipitation of the other minerals of the Sn–W association. Convincing mechanisms for the transport of $FeCl_2$ in the presence of H_2S or SO_2 have not been documented. Consequently it is not surprising that wolframite in quartz veins is not normally associated with large quantities of co-genetic sulphides, but the detailed relationships need further clarification.
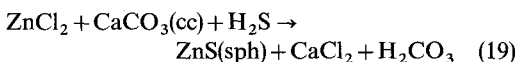
In the presence of carbonate rocks, scheelite is the normal tungsten mineral rather than wolframite. This can be accounted for either by a precipitation or an exchange reaction:

$$H_2WO_4 + CaCO_3(cc) \rightarrow$$
$$CaWO_4(sch) + H_2CO_3 \quad (17)$$

$$FeWO_4(wolf) + CaCl_2 \rightarrow$$
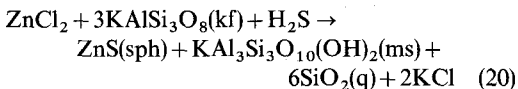$$CaWO_4(sch) + FeCl_2. \quad (18)$$

In many deposits, scheelite has been reported as a late-stage alteration product after wolframite, documenting the importance of the exchange reaction.

Next we turn to the formation of the sulphide ores. Depending on T and f_{O_2}, the dominant sulphur species in the hydrothermal fluid will be H_2S or SO_2, but for the sake of simplicity all reactions will be formulated with respect to H_2S.
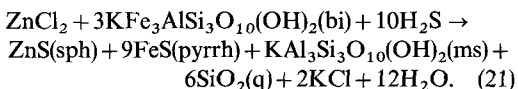
Sulphide precipitation in carbonate rocks can be represented by

$$ZnCl_2 + CaCO_3(cc) + H_2S \rightarrow$$
$$ZnS(sph) + CaCl_2 + H_2CO_3 \quad (19)$$

and in schists by

$$ZnCl_2 + 3KAlSi_3O_8(kf) + H_2S \rightarrow$$
$$ZnS(sph) + KAl_3Si_3O_{10}(OH)_2(ms) +$$
$$6SiO_2(q) + 2KCl \quad (20)$$

or by

$$ZnCl_2 + 3KFe_3AlSi_3O_{10}(OH)_2(bi) + 10H_2S \rightarrow$$
$$ZnS(sph) + 9FeS(pyrrh) + KAl_3Si_3O_{10}(OH)_2(ms) +$$
$$6SiO_2(q) + 2KCl + 12H_2O. \quad (21)$$

Similar reactions can be formulated for chalcopyrite, pyrite, pyrrhotite, galena, jamesonite, and the other sulphosalts. In every case a neutralization reaction is involved here as it is with the oxide ores, which consumes the HCl or H^+ produced by the sulphide precipitation, represented by:

$$ZnCl_2 + H_2S \rightarrow ZnS(sph) + 2HCl.$$
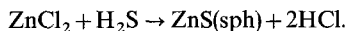
However, the source of the H_2S necessary for the sulphide precipitation represents a unique problem and one which clearly separates conditions for oxide deposition from those for sulphide deposition.

Four principal sulphur sources can be envisaged: (1) granitic melt and granite minerals; (2) sulphides

disseminated in the country rock; (3) organic sulphur of the country rock; (4) sulphates of the country rock.

There is good isotopic evidence that most or at least some of the sulphur in Sn–W deposits is of magmatic derivation (see So *et al.*, 1983; Collins, 1981; Patterson *et al.*, 1981; Kelly and Rye, 1979). As pointed out by Burnham and Ohmoto (1980), S-type magmas may contain as much H_2S as I-type magmas do, but their SO_2 and hence total sulphur contents are much lower because of their reduced state. Ishihara (1981) notes that in S-type, or ilmenite series magmas

sulfur seems to crystallize as pyrrhotite ... and does not move out from the silicate melts to form large-scale sulfide ore deposits. (p. 479.)

Although this conclusion has limited validity, the concept of locking up sulphur in disseminated sulphides in the cooling granite is very important. Not surprisingly, carbonate hosted Sn–W deposits can be quite rich in sulphides, such as the Dachang ore field of SE China (Zhang and Xilin, 1981; Wilson *et al.*, 1983) or the Mt. Bischoff and Renison Bell deposits of Tasmania (Newnham, 1975; Groves, 1972, 1977; Patterson *et al.*, 1981). At Dachang I have related sulphide deposition to an evaporitic facies of the Devonian host carbonates represented by many transgressive–regressive sabkha sequences capped by chicken-wire texture with the anhydrite nodules now replaced by calcite ('little-bean limestone' in the local terminology) (Eugster, 1983). Reduction of the sulphate can be accomplished readily by interaction with methane produced from organic matter:

$$CaSO_4 + CH_4 \rightarrow CaCO_3 + H_2S + H_2O.$$
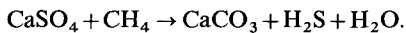
The H_2S liberated in this process then becomes available for transport to the depositional sites. This transport must be accomplished by a fluid path different from the path supplying the BOC elements. These waters may well be cooler, less saline and influenced by meteoric waters. Based on isotopic evidence, Patterson *et al.* (1981) have postulated mixing of magmatic aqueous fluids with contemporary heated groundwater for the Renison Bell deposit, Tasmania.

In the absence of evaporites the main sulphur reservoirs of the country rocks must be either organic matter or disseminated sulphides. This may be the case for instance for the Cambro–Silurian host schists of the Portuguese Sn–W deposits. Obviously, the abundance of sulphides found in association with a particular cassiterite and wolframite deposit is primarily a function of the combined amount of sulphur supplied by the granitic fluids and the country rock.

The deposition of arsenopyrite, FeAsS, commonly associated with cassiterite and wolframite, poses a problem intermediate between oxide and sulphide ores. Like W, transport of this typical LHC element must occur either as H_2AsO_4 or Na_2AsO_4. Deposition also requires $FeCl_2$ and, in addition, H_2S, according to a reaction such as

$$Na_2AsO_4 + FeCl_2 + H_2S + 3H_2 \rightarrow$$
$$FeAsS(aspy) + 2NaCl + 4H_2O. \quad (22)$$
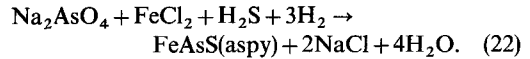
Not surprisingly, arsenopyrite is one of the earliest of the sulphides deposited in Sn–W deposits.

Acquisition of BOC, LHC, and ALC elements during partial melting of crustal rocks. If we can generalize from the findings of Ishihara (1981) from Japanese to Sn–W granites in general, we may expect sedimentary materials to make up a significant portion of the crustal material involved in the partial melting process leading to the separation of the granitic magma. The additional material will be of metamorphic and igneous origin and some of it may have participated in previous cycles of partial melting. Sediments include oxidized clastic fractions which carry LHC elements in feldspars and micas, as well as oxidized chemical sediments such as Mn nodules which have enhanced contents of Mo, Sn, and W. Sphene and ilmenite are carriers of Nb, Ta, and As, as well as the other LHC elements Mo, Sn, and W. The reduced or carbonaceous portion of the sediments is important as a host for LHC elements in the form of sulphides, but data on their abundance are scarce. ALC elements such as Pb, Ag, Eu, Sb are also enriched in reduced sediments, with particularly high values in coals. BOC elements Zn, Mn, and Fe are supplied by carbonaceous shales in the form of organic chelates (Disnar, 1981) or as sulphides, ZnS, MnS, and FeS. Finally, ferromagnesian silicates of the igneous and metamorphic fractions such as pyroxenes, amphiboles, biotites, garnets, and staurolite are important sources for BOC elements.

Release of BOC, LHC, and ALC elements from the solids to the partial melt in process of formation is essentially the inverse of the enrichment of those elements in the residual melt during crystallization in the upper crust, except that a separate vapour phase is not involved. H_2O, HCl, and elements such as Fe, Mn, Zn, and Cu will be enriched in the melt fraction, although no data are available on details of the fractionation between solids and an aqueous, chloride-bearing melt. Koster Van Groos and Wyllie (1969) found the maximum NaCl content of albite liquids at 1 kbar to be 0.3 wt. % NaCl in the presence of H_2O. In their experiments, a separate vapour phase was present, promoting fractionation into the fluid. It is possible that higher NaCl solubility could be achieved in hydrous silicate

melts undersaturated with respect to an aqueous fluid. On the other hand, initial concentrations as low as 0.3% probably suffice, with the aid of boiling, to provide all the HCl necessary for the release of OFEs after emplacement of the melt.

None of the very general and qualitative relations mentioned here fully answer the basic question of why certain orogenic granites eventually produce Sn–W deposits while others are barren. Source rock composition obviously is an essential aspect. The presence of NaCl either dissolved in the granitic magma or in the form of an immiscible chloride melt also appears to be a crucial ingredient. It seems clear why Sn–W deposits are associated with granites, because both depend on crustal material for their essential source. Specifically, LHC elements because of their higher valence in oxygen-dominated lattices and their ability to form sulphides, can be enriched in the oxidized as well as the organic-rich fractions of sediments. It is interesting to note that in their oxidized form LHC elements follow Ti, with sphene and ilmenite as important hosts, but Ti does not form an insoluble natural sulphide. Hence, in shales, ferric iron is a better guide to the behaviour of LHC elements.

The reasons why some provinces are particularly rich in tin remain to be elucidated. Recently, Lehmann (1982) and Pollard et al. (1983) have debated models based on magmatic differentiation and on geochemical heritage.

Summary. Differences in the release behaviour of LHC and BOC elements make it possible to account for the observed separation in space and time of oxide (cassiterite, wolframite) and sulphide (pyrite, pyrrhotite, sphalerite, galena) ores. Early acid alteration under neutral to reducing conditions favours LHC abundances in the fluids, while later, more oxidizing conditions favour BOC abundances. This conclusion is supported by the results of Mercolli et al. (in press) on OFE behaviour during the greenschist alteration of the Aare granite and the formation of cleft minerals. In that study LHCs were found to be moderately and BOCs nearly totally depleted in the altered granite, in agreement with the oxidized meteoric fluids thought to be responsible for the alteration. Oxidizing conditions will also be required for those cases where magmatic sulphur is to be provided by dissolution of the sulphides disseminated in the granites.

Transport is envisaged to occur primarily in the form of mono- and bivalent metal chlorides and their dissociation products, except for W and As, which may be carried as acids or as sodium complexes. Chloride is thought to be the major anion and initially is acquired as NaCl by the granitic melt during the partial melting process in the lower crust. After emplacement in the upper crust, boiling occurs in the H_2O-saturated carapace, with HCl produced by a hydrolysis reaction enriched in the aqueous fluid. Initial neutralization of this acid takes place through the OFE release mechanisms by interaction with granitic minerals, residual melt, and wall-rock minerals. Deposition of ores occurs in response to reactions with the country rock or to gradients in T, P, and salinity. This deposition releases HCl for the second time and the acid is neutralized either by dissolution of carbonates or the conversion of biotite or feldspar to muscovite, releasing metal chlorides to the fluid. This chloride cycle is illustrated schematically in fig. 8. The crucial difference between mineralized and barren batholiths may be linked to the presence or absence of NaCl, either dissolved in the silicate liquid or included as an immiscible melt. This contention is readily accessible to experimental verification.

Sulphur necessary for sulphide deposition may be derived from a variety of sources. If magmatic H_2S is invoked, decrease of salinity by mixing with meteoric waters is a likely precipitation mechanism. For wall-rock sulphur, oxidation is required

D. ORE DEPOSITION

$$MeCl_2 + H_2S \longrightarrow MeS + 2\ HCl$$

$$Bi + 2\ HCl \longrightarrow Ms + Q + 2\ KCl$$

$$Cc + 2\ HCl \longrightarrow CaCl_2 + H_2CO_3$$

C. TRANSPORT

$$2\ HCl + silicates \longrightarrow MeCl_2 + H_2O$$

B. HCl PRODUCTION

$$2\ NaCl(m) + H_2O(f) \longrightarrow$$

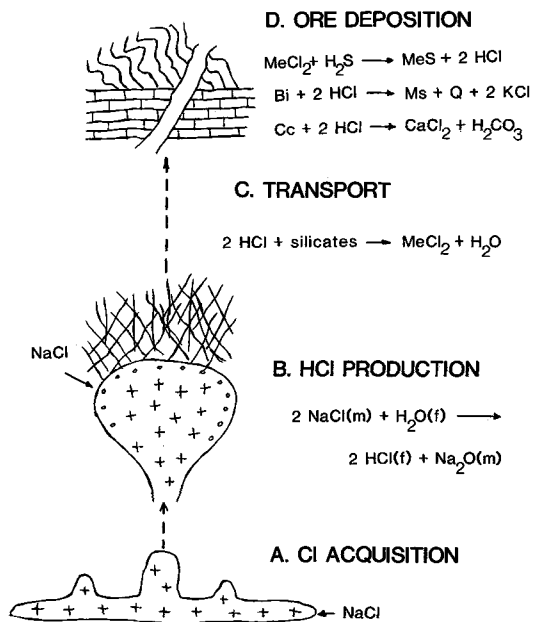$$2\ HCl(f) + Na_2O(m)$$

NaCl

A. Cl ACQUISITION

NaCl

FIG. 8. The chloride cycle, from acquisition of NaCl by the silicate melt to HCl production during boiling of the magma, followed by release of OFEs and initial HCl neutralization, followed by deposition of ores in schists or carbonates, coupled with second HCl production and final neutralization.

for disseminated sulphides or organic sulphur and reduction for evaporite sulphates.

The model developed in this paper is not intended to explain the depositional processes responsible for any particular Sn-W ore body, but it does, hopefully, contain the elements necessary to construct such an explanation. Information on the spacial and temporal sequence of mineral assemblages, and mineral compositions, on depositional temperatures, on type and extent of wall-rock interaction, on composition of fluids, and on isotopic exchanges must be provided in any particular instance. The model provides a framework for the effective collection of such data. In addition measurements on mineral solubilities and exchange constants, solute speciations, and many other aspects are needed to improve our understanding of these fascinating deposits which form in continental geothermal systems. There seems to be little need to point out the scientific and practical advantages of such an improved understanding.

REFERENCES

Anderson, G. M. (1973) *Econ. Geol.* **68**, 480–92.

Bacon, C. R., Macdonald, R., Smith, R. L., and Baedecker, P. A. (1981) *J. Geophys. Res.* **86**, 10223–41.

Bailey, D. K., and Macdonald, R. (1975) *Mineral. Mag.* **40**, 405-14.

Banks, N. G. (1974) *J. Res. U.S. Geol. Surv.* **2**, 195–211.

Barnes, H. L., ed. (1979) *Geochemistry of Hydrothermal Ore Deposits.* New York, John Wiley, 798 pp.

Barrett, T. J., and Anderson, G. M. (1982) *Econ. Geol.* **77**, 1923–33.

Barsukov, V. L. (1957) *Geochem.* **1**, 41 52.

Bryzgalin, O. V. (1976) *Geochem. Int.* **13**, 155-9.

Burnham, C. W. (1979) In *Geochemistry of Hydrothermal Ore Deposits* (H. L. Barnes, ed.). New York, John Wiley, 71–136.

——(1981) *Arizona Geol. Soc. Digest*, **14**, 71-7.

——and Ohmoto, H. (1980) In *Granitic Magmatism and Related Mineralization* (S. Ishihara and S. Takenouchi, eds.) Mining Geology Japan Spec. Issue 8, 1–11.

Candela, P. A., and Holland, H. D. (1984) *Geochim. Cosmochim. Acta*, **48**, 373 80.

Chou, I-M., and Eugster, H. P. (1977) *Am. J. Sci.* **277**, 1296-314.

Chivas, A. R. (1981) *Contrib. Mineral. Petrol.* **78**, 389 403.

—— Bikun, J. V., Sheridan, M. F., and Burt, D. M. (1984) *Am. Mineral.* **69**, 223-36.

Christiansen, E. H., Burt, D. M., Sheridan, M. F., and Wilson, R. T. (1984) *Contrib. Mineral. Petrol.* **83**, 16 30.

Clark, A. H., Palma, V. V., Archibald, D. A., Farrar, E., Arenas, M. J. F., and Robertson, R. C. R. (1983) *Econ. Geol.* **78**, 514 20.

Collins, P. L. F. (1981) Ibid. **76**, 365–92.

Crecraft, H. R., Nash, W. P., and Evans, S. H. (1981) *J. Geophys. Res.* **86**, 10303–20.

Crerar, D. A., and Barnes, H. L. (1976) *Econ. Geol.* **71**, 772–94.

—— Susak, N. J., Borcsik, M., and Schwartz, S. (1978) *Geochim. Cosmochim. Acta* **42**, 1427 -37.

Disnar, J. R. (1981) Ibid. **45**, 363 79.

Durasova, N. A. (1967) *Geochem. Int.* **4**, 671–81.

Eadington, P. J. (1983) *Hydrothermal Reactions* (S. Somiya, ed.). Tokyo, 335–45.

Eugster, H. P. (1981) *Chemistry and geochemistry of solutions at high temperature and pressure: Physics and Chemistry of the Earth* (F. E. Wickman and D. T. Richard, eds.). New York, Pergamon Press, **13** and **14**, 461-507.

——(1982) *High-Pressure Researches in Geoscience* (W. Schreyer, ed.). Stuttgart, Schweizerbart, 501 18.

——(1983) *Geol. Soc. Am. Abstracts with Programs*, 568.

——and Chou, I-Ming (1979) *Econ. Geol.* **74**, 763–74.

——and Gunter, W. D. (1981) *Bull. Mineral.* **104**, 817-26.

——and Ilton, E. S. (1983) *Adv. Phys. Geoch.* (S. Saxena and A. B. Thompson, eds.). Springer–Verlag, **3**, 115-40.

——and Jones, B. F. (1979) *Am. J. Sci.*, **279**, 609- 31.

Evans, A. M. (1982) *Metallization associated with acid magmatism*, John Wiley, New York, 385 pp.

Frantz, J. D., and Marshall, W. L. (1982) *Am. J. Sci.* **282**, 1666 93.

—— and Eugster, H. P. (1973) Ibid. **273**, 268 86.

Fryer, B. J., and Edgar, A. D. (1977) *Contrib. Mineral. Petrol.* **61**, 35–48.

Gilzean, M. N., and Brimhall, G. H. (1983) *Geol. Soc. Am. Abstracts with Programs*, 581.

Graybeal, F. T. (1973) *Econ. Geol.* **68**, 785 98.

Groves, D. I. (1972) Ibid. **67**, 445 -57.

——(1977) *Tasmania Geol. Survey Bull.* **55**, 7- 116.

Gunow, A. J., Ludington, S., and Munoz, J. L. (1980) *Econ. Geol.* **75**, 1127 -37.

Gunter, W. D., and Eugster, H. P. (1978) *Contrib. Mineral. Petrol.* **66**, 271 81.

————(1980) Ibid. **75**, 235–50.

Haapala, I., and Kinnunen, K. (1979) *Econ. Geol.* **74**, 1231-8.

Handy, A. H., and Hahl, D. C. (1966) *Utah Geol. Soc. Guidebook* **20**, 135 51.

Helgeson, H. C., and Kirkham, D. H. (1974) *Am. J. Sci.* **274**, 1089 98.

Hemley, J. J. (1959) Ibid. **257**, 241 70.

——and Jones, W. R. (1964) *Econ. Geol.* **59**, 538–69.

Hildreth, W. (1979) *Geol. Soc. Am. Sp. Pap.* **180**, 43 75.

Holland, H. D. (1972) *Econ. Geol.* **67**, 281–301.

Ishihara, S., ed. (1980) *Granitic Magmatism and Related Mineralization.* Japan Soc. Mining Geol. Spec. Issue 8, Tokyo, 247 pp.

——(1981) *Econ. Geol. 75th Ann. Vol.*, 458–84.

Jackson, N. J., Halliday, A. N., Sheppard, S. M. F., and Mitchell, J. G. (1982) In *Metallization Associated with Acid Magmatism* (A. M. Evans, ed.). John Wiley, New York, 137–79.

Kelly, W. C., and Rye, R. O. (1979) *Econ. Geol.* **74**, 1721–819.

——and Turneaure, F. S. (1970) Ibid. **65**, 609–80.

Kilinc, I. A., and Burnham, C. W. (1972) Ibid. **67**, 231–5.

Koster Van Groos, A. F., and Wyllie, P. J. (1969) *J. Geol.* **77**, 581–605.

Krauskopf, K. B. (1970) *Tungsten.* In *Handbook of Geochemistry* 74-F. (K. H. Wedepohl, ed.). New York, Springer-Verlag.

Kwak, T. A. P., and Askins, P. W. (1981*a*) *Geol. Soc. Austral.* **28**, 123–36.

——-——(1981*b*) *Econ. Geol.* **76**, 439–67.

——and Tan, T. H. (1981) Ibid. **76**, 955–60.

Lehmann, J. D. (1982) Ibid. **77**, 50–69.

Lowell, J. D., and Guilbert, J. M. (1970) Ibid. **65**, 337–408.

Mahood, G. (1981) *Contrib. Mineral. Petrol.* **77**, 129–49.

——and Hildreth, W. (1983) *Geochim. Cosmochim. Acta*, **47**, 11–30.

Manning, D. A. C. (1981) *Contrib. Mineral. Petrol.* **76**, 206–15.

Mercolli, I., Schenker, F., and Stalder, H. A. (In press) Geochemie der Veranderungen von Granit durch hydrothermale Lösungen. *Schweiz. Mineral. Petrol. Mitt.*

Munoz, J. L., and Eugster, H. P. (1969) *Am. Mineral.* **54**, 943–59.

——and Ludington, S. D. (1974) *Am. J. Sci.* **274**, 396–413.

——and Swenson, A. (1981) *Econ. Geol.* **76**, 2212–21.

Neiva, A. M. R. (1982) In *Metallization associated with acid magmatism.* (A. M. Evans, ed.). New York, John Wiley, 243–59.

Newnham, L. A. (1975) In *Economic Geology of Australia and Papua, New Guinea,* **1**, *Metals.* (C. L. Knight, ed.). Melbourne, Australian Inst. Mining Metallurgy, Mon. 5, 581–4.

Nriagu, J. O., and Anderson, G. M. (1971) *Chem. Geol.* **7**, 171–83.

Patterson, D. J., Ohmoto, H., and Solomon, M. (1981) *Econ. Geol.* **76**, 393–438.

Pollard, P. J., Taylor, R. G., and Coff, C. (1983) Ibid. **78**, 543–5.

Rettig, S. L., Jones, B. F., and Risacher, F. (1980) *Chem. Geol.* **30**, 57–79.

Richardson, C. K., and Holland, H. D. (1979) *Geochim. Cosmochim. Acta,* **43**, 1313–25.

Ryabchikov, I. D., Orlova, G. P., Efimov, A. S., and Kalenchuk, G. E. (1980) *Geokhimia*, **8**, 1320–6.

——Rekharsky, V. I., and Kudrin, A. V. (1981) Ibid. **9**, 1243–6.

Ryerson, J. J., and Hess, P. C. (1978) *Geochim. Cosmochim. Acta*, **42**, 921–32.

Schulien, S. (1980) *Contrib. Mineral. Petrol.* **74**, 85–93.

Seward, T. M. (1976) *Geochim. Cosmochim. Acta*, **40**, 1329–41.

——(1984) Ibid. **48**, 121–34.

Shade, J. W. (1974) *Econ. Geol.* **69**, 218–28.

Shelton, K. L., and So, C. S. (1983) *Geol. Soc. Am. Abstracts with Programs*, 685.

Sillitoe, R. H., Halls, C., and Grant, J. N. (1975) *Econ. Geol.* **70**, 913–27.

Simmons, S. F., and Sawkins, F. J. (1983) Ibid. **78**, 521–6.

So, C.-H., Shelton, K. L., and Rye, D. M. (1983) Ibid. **78**, 157–63.

Strubel, G., and Schaefer, B. (1975) *Geochemie der Lagerstattenbildung und -prospektion*, GDMB-DMG Symposium, Feb. 1974, Karlsruhe.

Sweeton, F. G., and Baez, C. F. (1970) *J. Chem. Thermodyn.* **2**, 479–500.

Taylor, R. G. (1979) *Geology of tin deposits: Devel. Econ. Geol.* **11**. New York, Elsevier, 543 pp.

Taylor, R. P., Strong, D. F., and Fryer, B. J. (1981) *Contrib. Mineral. Petrol.* **77**, 267–71.

Tremaine, P. R., and LeBlanc, J. C. (1980) *J. Sol. Chem.* **9**, 415–42.

Wang, S., Eugster, H. P., and Wilson, G. A. (1984) *Geol. Soc. Am. Abstracts with Programs*, 686.

Watson, E. B. (1976) *Contrib. Mineral. Petrol.* **56**, 119–34.

Wedepohl, K. H. (1969) *Handbook of Geochemistry.* New York, Springer-Verlag.

Wesoloski, D., Drummond, S. E., Mesmer, R. E., and Ohmoto, H. (In press) *Geochim. Cosmochim. Acta.*

Wilson, C. A., and Eugster, H. P. (1984) *Geol. Soc. Am. Abstracts with Programs*, 696.

——-——Neiva, A. M. R., Cotelo Neiva, J. M., Wang, S. Y., and Zhang, C. K. (1983) Geol. Ass. Canada meeting, Vancouver 1983.

Yurchenko, N. E., Kolonin, G. R., Shironosova, G. P., and Aksenova, T. P. (1976) *Russ. J. Inorg. Chem.* **21**, 1682–5.

Zaw, U. K., and Thet, D. K. M. (1983) *Econ. Geol.* **78**, 530–4.

Zhang, Z., and Xilin, L. (1981) *Geochemica*, **1**, 74–86.