

Partitioning of base metals between silicates, oxides, and a chloride-rich hydrothermal fluid. Part II. Some aspects of base metal fractionation during isothermal metasomatism

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Abstract—The distribution coefficients described in ILTON and EUGSTER (1990) are used in a simple isothermal fluid flow model to demonstrate that congruent exchange reactions involving the silicate rock fraction can enrich the geochemically scarce base metals relative to iron in more distal portions of chloride-rich metasomatic fluids.

INTRODUCTION

THE FORMATION of economically viable manganese, zinc, copper, cadmium and copper hydrothermal ore deposits depends on their enrichment relative to iron, as well as relative to other common rock-forming elements. Fractionation and enrichment can occur during magmatic vapor phase separation, during removal and acquisition by the fluid of the metals from rocks, and during the depositional event due to differing ore-mineral solubilities. Ore-grade metallization often requires the focusing of fluids that have interacted with large volumes of rock or magma, with subsequent precipitation of metals over compressed distances from high fluid fluxes with relatively low metal concentrations, or from lower fluid fluxes with relatively higher metal concentrations. In any case, hydrothermal ore deposits are the end products of a complex series of enrichment events that extend over wide ranges of temperature and pressure.

The present paper has modest goals and cannot address the complexity of ore formation. Instead, this contribution develops a simple isothermal model for the sulfur free or sulfide undersaturated system, that gives some physical meaning to the partition coefficients derived in ILTON and EUGSTER (1990). The model illustrates that congruent base metal exchange reactions between silicates and a flowing chloride-bearing hydrothermal fluid can strongly fractionate manganese, zinc, cadmium, copper and iron, either during metal acquisition by the fluid or rock. Given the proper conditions, strong fractionation can lead to the enrichment of manganese, zinc, copper, cadmium and copper *relative* to iron. The model may yield insights concerning the formation of distal zinc skarns, and manganese enrichment in distal skarns as well as in distal portions of skarns. Alternatively, fractionation

patterns that differ from those predicted would indicate, in part, either the influence of more complex physical conditions and reactions, perhaps involving the non-silicate rock-fraction, or that the partition coefficients need to be revised. It is stressed that the model does *not* address the question of *absolute* enrichment. Furthermore, the data and therefore the model is limited, and errors associated with the partition coefficients can be large.

DEVELOPMENT OF THE MODEL

The model illustrates the endmember case of isothermal, one dimensional fluid flow with trace base metal concentrations in the fluid and solid phases. The Mg-endmember serves as the reference component. Phases are conserved, and mineral/fluid interactions are restricted to congruent ion exchange reactions. (It is assumed that the fluid and aquifer are equilibrated with respect to major components.) Eventual inclusion of alteration and precipitation-dissolution reactions will require further experimental data. The model employs a form of chromatographic theory (*e.g.*, WILSON, 1940). The fluid and solid form an interconnected continuum, and the condition of instantaneous local equilibrium is imposed (THOMPSON, 1959). A pressure gradient forces the fluid from a reservoir of constant composition into an aquifer. The distribution coefficients are assumed to be invariant with respect to the pressure gradient required for fluid flow, and infiltration is the only transport mechanism (*i.e.* dispersion and diffusion are neglected). Our hypothetical system is undersaturated with respect to sulfides, the fluid is chloride-rich and the reactive minerals are phlogopite, tremolite, pyrope, and diopside. The partition coefficients are strictly associated with a 2 M KCL solution, $P = 2$ Kb, and $fO_2 \approx$ NNO. However, ILTON and EUGSTER (1989, 1990) argue they might be valid, for manganese and

zinc, over some range of chloride concentrations, pH, P , and fO_2 .

Regarding the geological literature, the reader is referred to KORZHINSKI (1970), HOFFMAN (1972), FLETCHER and HOFFMAN (1974), and BAUMGARTNER and RUMBLE (1988) for a detailed development of the relevant transport equations. An abbreviated derivation, closely following BAUMGARTNER and RUMBLE (1988) but with some variations on the theme, is presented here.

Mass balance requires that the rate of change for the concentration of base metal B , $\partial B/\partial t$, within a given volume be equal to the integral of the flux of B across the surface enclosing the volume. This is expressed by the continuity equation,

$$\partial B/\partial t = -\text{div } \vec{J} \quad (1)$$

for an infinitesimally small volume element dV . The total concentration of a base metal (B) in a given volume composed of minerals and fluid is given by

$$B = (1 - \beta) \sum_{n=1}^x m_n b^n + \beta m_f b^f \quad (2)$$

where β is the porosity completely filled by fluid, m_n and m_f are the number of moles of mineral n and fluid, respectively, per unit volume of pure rock and fluid, and b^n and b^f are the number of moles of the base metal in one mole of mineral n and fluid, respectively. Substituting equation 2 into equation 1 yields

$$\partial/\partial t[(1 - \beta) \sum_{n=1}^x m_n b^n + \beta m_f b^f] = -\text{div } \vec{J}. \quad (3)$$

Given the condition of instantaneous equilibrium, the composition of the fluid and a mineral are related by the distribution coefficient Kd . The base metals of interest are treated as trace elements, whereas magnesium is the major element in both the fluid and solid, such that the distribution coefficient $Kd = b^n \text{Mg}^n / b^f \text{Mg}^f$. Since the base metals are assumed to be trace elements, the distribution coefficients are independent of composition, $\text{Mg}^n / \text{Mg}^f = M$ is considered a constant and $b^n = b^n M / Kd$. Given unidirectional fluid flow, equation 3 can be modified to

$$\partial b^n / \partial t [(1 - \beta) \sum_{n=1}^x m_n M / Kd_n + \beta m_f] = -\partial \beta \bar{v} b^n / \partial Z \quad (4)$$

where the constant \bar{v} is the fluid velocity and $\beta \bar{v} b^n = \vec{J}$. Here, the porosity is completely accessible to infiltration. Solving equation 4 for the distance

traveled by the compositional front (Z) for the base metal of interest yields

$$Z = \beta \bar{v} t / [(1 - \beta) \sum_{n=1}^x m_n M / Kd_n + \beta m_f]. \quad (5)$$

For small porosities equation 5 reduces to

$$Z = \beta \bar{v} t / (M \sum_{n=1}^x m_n / Kd_n), \quad \text{and} \quad (6)$$

$$Z = \beta \bar{v} t / (m M / Kd) \quad (7)$$

for monomineralic aquifers. The result is substantively identical to equation 38 in BAUMGARTNER and RUMBLE (1988), where the rare isotope is treated as a trace element. Given the linear relationship between metal contents in the fluid and solid, pure infiltration forms compositional plateaus along the length of the aquifer, separated by sharp reaction fronts, whereas combined infiltration, dispersion, and diffusion develop compositional plateaus separated by diffuse fronts (FLETCHER and HOFFMAN, 1974). Consequently, for monomineralic aquifers, the relative distances (Z) traveled by the base metal compositional fronts are given by the ratios of their distribution coefficients:

$$Z(b)/Z(\text{Fe}) = \frac{\beta \bar{v} t / (m M / Kd [b - \text{Mg}])}{\beta \bar{v} t / (m M / Kd [\text{Fe} - \text{Mg}])} \quad (8)$$

$$= Kd [b - \text{Mg}] / Kd [\text{Fe} - \text{Mg}], \quad (9)$$

and because magnesium is common

$$Z(b)/Z(\text{Fe}) = Kd [b - \text{Fe}]. \quad (10)$$

Therefore, the relative positions of the fronts are given by the partition coefficients in ILTON and EUGSTER (1990).

Uncertainties associated with the model

The 95% confidence intervals for the positions of the fronts are identical to those associated with the distribution coefficients in Tables 3 and 4 from ILTON and EUGSTER (1990). The reader is reminded that the confidence intervals only reflect the variance of the data. Uncertainties regarding temperature estimates, compositional differences between minerals in experimental and natural assemblages, and lack of definitive proof of exchange equilibrium in the natural assemblages are not accounted for. Moreover, the minerals are modeled as near Mg-endmembers, whereas the Kds are derived from

more complex solid solutions. Copper and cadmium are modeled despite the large statistical uncertainties associated with their Kds . Although the positions of the copper and cadmium fronts are statistically inconclusive, the results are considered sufficiently informative to present.

MONOMINERALIC AQUIFERS

Silicates as sinks for base metals

At $t = 0$, assume that the aquifer, composed of either phlogopite, tremolite, diopside or pyrope is undersaturated with respect to the concentrations of base metals in the reservoir fluid. Further, for clarity and simplicity, we assume the special case of base metal concentration = 0 in the aquifer at $t = 0$. As infiltration proceeds, the metals are stripped from the *fluid* with varying degrees of efficiency; iron is removed from the fluid most efficiently, followed by manganese, zinc, cadmium, and copper. At 500°C, the relative distances (Z) traveled by the fronts are— $\sim Z(\text{Fe}):6Z(\text{Mn}):40Z(\text{Zn}):1600Z(\text{Cd}):3600Z(\text{Cu})$ for a phlogopite aquifer, and $Z(\text{Fe}):7Z(\text{Mn}):70Z(\text{Zn}):1200Z(\text{Cd}):11000Z(\text{Cu})$ for a tremolite aquifer, using the distribution coefficients in Tables 1 and 2 from ILTON and EUGSTER (1990). The fractionation pattern is illustrated in Fig. 1.

The copper and iron fronts travel the fastest and slowest, respectively. If the iron front has progressed 0.1 km, then the manganese, zinc, cadmium, and copper fronts traveled 0.6, 4.0, 160 and 360 km, and 0.7, 7.0, 120, and 1100 km for phlogopite and tremolite aquifers, respectively. Since the fronts travel at different velocities, the distance *between* the fronts increases with time. Therefore, compared to the reservoir, the leading fluid packets are enriched in copper, cadmium, zinc, and manganese relative to iron.

If such a fluid reaches a distal reactive rock such as a carbonate, which removes the metals without further fractionation, then the enrichment sequence would be copper followed by cadmium \rightarrow zinc \rightarrow manganese \rightarrow iron. Iron starts to precipitate *only* when the iron front crosses the carbonate unit. A very high fluid flux would overwhelm the exchange capacity of the aquifer, and would simply impose the base metal composition of the reservoir on the carbonate unit. Alternatively, if the fluid supply is exhausted shortly after the zinc and manganese fronts cross the carbonate boundary, then zinc, manganese, cadmium, and copper will be enriched relative to iron at that site, compared to the reservoir.

Longer fluid path lengths, prior to deposition, will increase the separation of the fronts, and

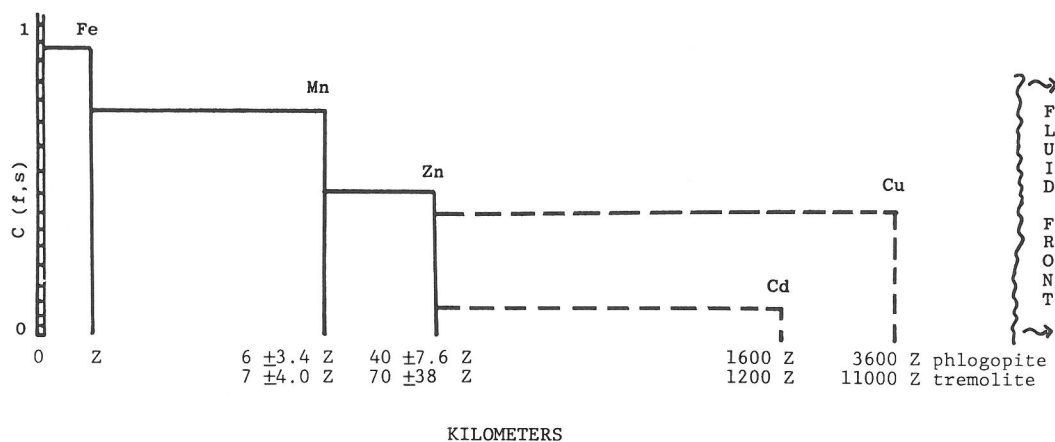


FIG. 1. Schematic diagram illustrating the development of base metal compositional fronts, at 500°C, during infiltration of a chloride-rich fluid into an aquifer containing phlogopite or tremolite. The reservoir fluid is Mg-rich, but contains trace concentrations of Fe, Mn, Zn, Cd, and Cu, whereas initially there are no base metals in the aquifer. The base metals are stripped from the *fluid* as infiltration proceeds. The vertical axis represents the concentrations of the metals in both the fluid and solid (the fluid and solid scales differ). The horizontal scale marks distance from the fluid source. As discussed in the text, the relative positions of the fronts are given by the distribution coefficients. The 95% confidence intervals are given for the positions of the fronts. The Cu and Cd fronts are dashed as a reminder of the large uncertainties associated with their positions (see ILTON and EUGSTER, 1990, for details).

thereby increase the likelihood and degree of minor base metal enrichment relative to iron, in distal portions of the metasomatic system. Greater porosities or channelized fluid flow would require longer fluid path lengths to achieve the same degree of fractionation.

Other silicates, such as chlorite and talc, may cause similar fractionation (see Tables 1 and 2 in ILTON and EUGSTER, 1990).

The fact that copper is usually proximal, for those parts of metasomatic systems usually sampled, is consistent with copper mobility controlled by more complex reactions involving sulfides. Alternatively, given the large uncertainty associated with $Kd(\text{Cu}/\text{Fe})$, the relative position of the copper front is *not* well defined.

At 700°C, partition coefficients (see Table 1 in ILTON and EUGSTER, 1990) yield metasomatic fronts for manganese and iron in aquifers composed of phlogopite, tremolite, diopside, or pyrope, as shown in Fig. 2. The manganese front leads the

iron front for phlogopite-, tremolite- and diopside-rich rocks. The sense of fractionation, however, is reversed by an aquifer composed of pyrope, where distal portions of the fluid are enriched in manganese relative to iron. Pyrope/almandine-rich garnets may be the only common rock-forming silicate to produce such fractionation. Although the model is limited, it may yield insights concerning the fractionation of manganese and iron in reducing skarn environments, such as deeper level tungsten skarns associated with almandine/pyrope-rich garnets, compared to higher level more oxidizing skarn environments associated with andradite-rich garnets.

Skarns distal to possible but unknown plutonic fluid sources (distal skarns), such as the Paymaster skarn (MEINERT, 1980), characteristically are associated with zinc deposits, and silicates unusually enriched in manganese (EINAUDI *et al.*, 1981). BURT (1977), MEINERT (1980, 1984, 1987), and YUN and EINAUDI (1982) have suggested that extended fluid interaction with non-carbonate rock prior to contact with a carbonate unit may be responsible for the high degree of zinc and manganese enrichment in distal skarns and more distal portions of skarns. The model presented here, although broadly consistent with their interpretations, assuming gentle temperature gradients, is obviously too limited and simplistic for direct application. It does suggest, however, that simple exchange reactions between flowing chloride-rich hydrothermal fluids and silicates may enhance, under certain conditions, such fractionation and enrichment. Obviously, proximal precipitation of chalcopyrite could produce similar enrichment of manganese and zinc, relative to iron, in distal skarns. Complex reactions involving ore minerals such as sphalerite, pyrrhotite, and pyrite may also strongly influence base metal fractionation and enrichment patterns in distal skarns.

MEINERT (1984) has documented distal clinopyroxenes (cpx) from the Iron Hill skarn, British Columbia that are unusually enriched in manganese. Furthermore, the cpx rims have higher Fe/Mn ratios than the cores. Apparently, the fluids had to flow through a considerable thickness of volcanic rock before encountering a limestone unit and precipitating Mn-enriched cpx. Given the data, MEINERT (1984) suggested that distal cpx formed from fluids that evolved from higher Mn/Fe ratios to lower Mn/Fe ratios. This is broadly consistent with the fractionation predicted by the model, where the Fe-rich front follows the Mn-rich front. Thus, it is possible that ion exchange reactions could be partially responsible for such patterns of manganese enrichment. Alternatively, more complex reactions involving precipitation of iron-rich minerals such

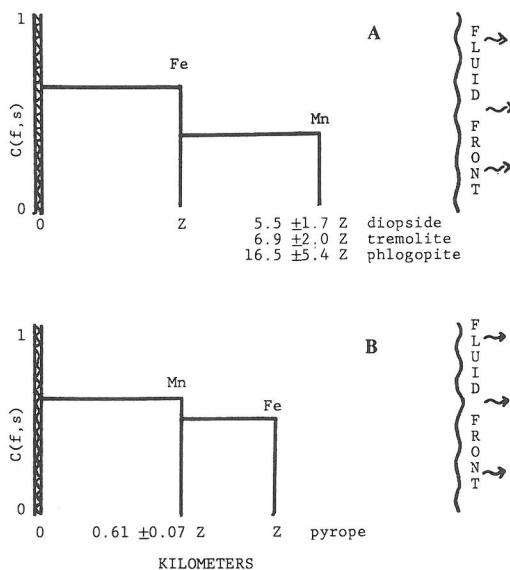


FIG. 2. Schematic diagrams illustrating the development of base metal compositional fronts, at 700°C, during infiltration of a chloride-rich fluid into an aquifer containing (A) phlogopite, tremolite, or diopside and (B) pyrope. The reservoir fluid is Mg-rich, but contains trace concentrations of Fe, Mn, Zn, Cd, and Cu, whereas initially there are no base metals in the aquifer. The base metals are stripped from the fluid as infiltration proceeds. The vertical axis represents the concentrations of the metals in both the fluid and solid (the fluid and solid scales differ). The horizontal scale marks distance from the fluid source. As discussed in the text, the relative positions of the fronts are given by the distribution coefficients. The 95% confidence intervals are given for the positions of the fronts.

as andradite in relatively proximal locations (YUN and EINAUDI, 1982), decreasing fO_2 , and decreasing temperature (MEINERT, 1987; ILTON and EUGSTER, 1990) may be the primary cause of extreme manganese enrichment in distal portions of the skarn.

In the foregoing analysis, the base metals have been modeled as trace elements, and magnesium served as a reference frame. This approach yielded simple analytical solutions to the transport equations. Some metasomatic fluids, however, may contain high concentrations of metals. Further, silicates in metasomatic systems are often zoned. Consequently, magnesium eventually needs to be included in a more generalized transport model, that treats non-trace concentrations of base metals, and that allows for non-equilibrium partitioning. Treating the base metals as "major" elements would effect the model quantitatively, but *not* necessarily qualitatively. Since magnesium is preferentially partitioned into silicates relative to iron (EUGSTER and ILTON, 1983), one might expect magnesium to be depleted relative to iron in distal fluids. Once again this is in qualitative agreement with the skarn literature (*e.g.*, BURT, 1977; DICK and HODGESON, 1982). Enlarging the data base may eventually allow one to couple the partition coefficients with alteration and precipitation-dissolution reactions oc-

curing along various temperature and pressure paths.

Silicates as sources of base metals

This model is identical to the model of the previous section, except the initial conditions are reversed, such that the reservoir fluid contains initial base metal concentration = 0, whereas the aquifer contains trace concentrations of base metals. As infiltration proceeds, the base metals are stripped from the *aquifer* with varying degrees of efficiency. Given an arbitrary amount of fluid flux, copper is stripped from the greatest rock volume, followed in descending order by cadmium, zinc, manganese, and iron (Fig. 3). Enrichment patterns in the fluid are spatially zoned. For example, there is no zinc in the fluid and rock *up to* the zinc front, whereas, compared to the original rock, zinc is enriched in the fluid relative to manganese and iron *between* the zinc front and fluid front. In this scenario, a distal carbonate unit would record an abrupt decrease or cessation of base metal precipitation as its associated stripping front encountered the reactive rock.

Despite the manifest differences between silicates acting as sources vs sinks of base metals, the stripping fronts travel with velocities directly propor-

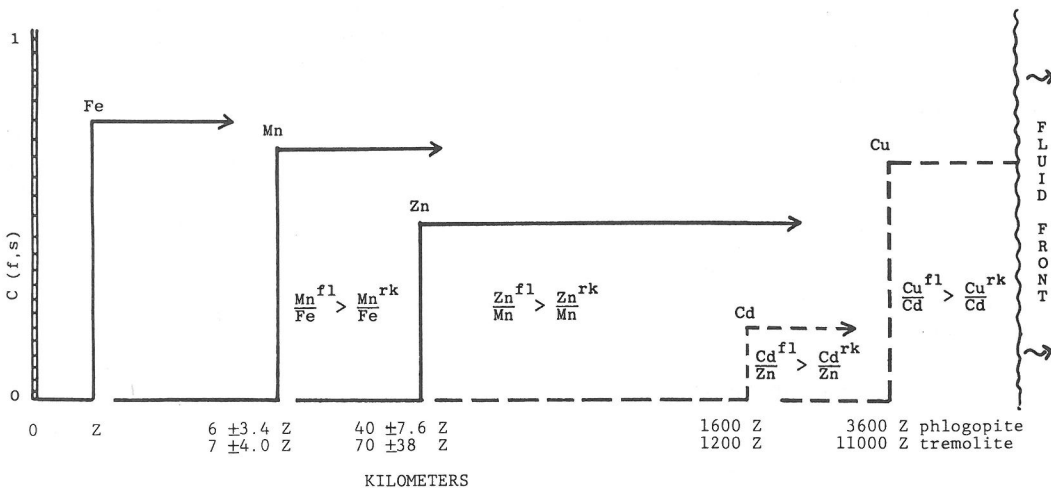


FIG. 3. Schematic diagram illustrating the development of base metal compositional fronts, at 500°C, during infiltration of a chloride-rich fluid into an aquifer composed of phlogopite or tremolite. The reservoir fluid is Mg-rich, but contains no base metals, whereas initially the aquifer contains trace concentrations of Fe, Mn, Zn, Cd, and Cu. The base metals are stripped from the *aquifer* as infiltration proceeds. The vertical axis represents the concentrations of metals in both the fluid and solid (the fluid and solid scales differ). The horizontal scale marks distance from the fluid source. As discussed in the text, the relative positions of the fronts are given by the distribution coefficients. The 95% confidence intervals are given for the positions of the fronts. The Cu and Cd fronts are dashed as a reminder of the large uncertainties associated with their positions (see ILTON and EUGSTER, 1990, for details).

tional to the distribution coefficients. Consequently, the implications for enrichment are similar to those described in the previous model, where in this case too much fluid flow strips the entire aquifer of base metals, and simply imposes the base metal composition of the aquifer on the the carbonate unit. In which case no relative enrichment occurs.

POLYMINERALIC AQUIFERS

Equation 6 gives the position of the compositional front for a polymineralic aquifer. The relative position of two fronts is given by

$$Z(b)/Z(\text{Fe}) = \left(\sum_{n=1}^x X_n/Kd_n^{\text{Fe-Mg}} \right) / \left(\sum_{n=1}^x X_n/Kd_n^{\text{b-Mg}} \right). \quad (11)$$

Therefore, the relative positions of the fronts are a simple function of the distribution coefficients and mole fractions (X) of each mineral in the aquifer. Since the silicates exhibit similar partitioning behavior, the combination of biotite, amphibole, pyroxene, and perhaps chlorite, and talc, would effect the model quantitatively, but *not* necessarily qualitatively (see Tables 1 and 2 in ILTON and EUGSTER, 1990). The addition of significant almandine-pyrope garnet, however, could reverse the fractionation behaviors of manganese and iron. Within the context of the present model, base metal-Mg partition coefficients would need to be calculated in order to predict the relative positions of the fronts in polymineralic aquifers. Although this would be possible to do, errors would be increased and the fractionation *pattern* would not change significantly.

CONCLUSION

The simple model presented here, although preliminary and limited, yields insights concerning natural processes that enrich the minor and trace base metals relative to iron.

The common rock-forming silicates and oxides tend to partition the geochemically scarce base metals, relative to iron, into chloride-rich hydrothermal-metamorphic fluids. Iron is partitioned into the fluid relative to magnesium (EUGSTER and ILTON, 1983). A possible exception for manganese is almandine-garnet. It is interesting to note that, in general, the less abundant the base metal the greater its partitioning into the fluid.

Consequently, exchange reactions between flowing Cl-rich hydrothermal fluids, and rock-forming silicates tend to enrich ($\text{Cu} > \text{Cd}$) \gg $\text{Zn} \gg \text{Mn} \gg \text{Fe} \gg \text{Mg}$ in more distal portions of the fluid. Copper

and cadmium are bracketed because of the large uncertainties associated with their partition coefficients (see ILTON and EUGSTER, 1990). Longer fluid path lengths and smaller porosities increase the degree of fractionation and possibilities for enrichment of the less abundant base metals relative to iron.

The degree to which this is not the case could reflect a violation of one or more of the conditions and simplifying assumptions built into the model, including differing ore mineral solubilities during deposition, and the percentage of base metals in the whole-rock *not* contained in the Fe-Mg oxide-silicate fraction.

The application of any such model requires, among other things, rigorous identification of the host phases and site occupancies for the base metal of interest; not necessarily a trivial matter when dealing with trace-minor concentrations and hydrothermally altered assemblages. As discussed in ILTON and EUGSTER (1990) the transmission electron microscope (TEM) is a powerful tool for addressing this problem. In fact TEM observations cast doubt on the validity of such modeling for copper (ILTON and VEBLEN, 1988).

Although the results have indicated some tendencies with respect to congruent exchange reactions, more rigorous isothermal models, as well as more general models involving T - P gradients, and alteration and precipitation-dissolution reactions, require further experimental and natural data covering a wider range of minerals and conditions (P , T , and fluid-solid compositions).

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