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PARTITIONING OF ZINC AMONG COMMON FERROMAGNESIAN MINERALS AND IMPLICATIONS FOR HYDROTHERMAL MOBILIZATION

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ABSTRACT

The partitioning behavior of zinc among several common ferromagnesian minerals has been determined from analyses of natural assemblages in order to examine the processes by which zinc is mobilized by hydrothermal fluids. In systems where metals are scavenged from crystalline rocks by through-flowing fluids, the important host minerals must be dissolved or must undergo cation-exchange reactions with the fluid. Whereas copper resides in sulfides, zinc resides in magnetite and, to a lesser extent, in biotite, clinopyroxene and olivine. Magnetite is known from petrographic studies to be more resistant to alteration than sulfides. For metals extracted from crystalline rocks, the Cu:Zn mass ratio may thus decrease with progressive alteration. Bulk chemical compositions of altered rocks associated with known ore deposits support this conclusion. In systems where metals are scavenged from cooling magmas by exsolving fluids, the metals are partitioned among melt, fluid and any crystals that have fractionated. For zinc, crystal fractionation may be an important sink if magnetite or biotite crystallize before fluid saturation. The zinc concentrations of magmatic fluids will thus be reduced. Unfortunately, quantitative evaluation of the effect is difficult owing to uncertainty in the mineral–melt partition coefficients for zinc.

Keywords: zinc, partitioning, hydrothermal, ore deposit, mobilization, trace element.

SOMMAIRE

La répartition du zinc parmi plusieurs minéraux ferromagnésiens répandus a été déterminée à partir de compositions d'assemblages naturels afin d'établir les processus de mobilisation du zinc en milieu hydrothermal. Dans les systèmes où les métaux sont lessivés de roches cristallines par une phase fluide en circulation, les minéraux les plus importants doivent être dissous, ou bien ils doivent échanger des cations avec la phase fluide. Tandis que le cuivre réside dans les sulfures, le zinc se trouve en grande partie dans la magnétite et, à un degré moindre, dans la biotite, le clinopyroxène et l'olivine. D'après les études pétrographiques, la magnétite serait plus résistante à l'altération que les sulfures. Dans le cas de Cu et de Zn extraits de roches cristallines, le rapport massique de Cu à Zn pourrait donc diminuer avec altération progressive. Les compositions globales de roches altérées associées à des gîtes minéraux connus étayent cette conclusion. Dans les systèmes où les métaux sont lessivés de magmas lors de leur refroidissement par une phase fluide exsolvée, les métaux sont répartis parmi magma, phase fluide, et toutes phases cristallines qui auraient été fractionnées. Dans le cas du zinc, le fractionnement de cristaux pourrait s'avérer important si la magnétite ou la biotite cristallisent avant le point de saturation du magma en phase volatile. La teneur en zinc de la phase fluide magmatique s'en trouvera donc diminuée. Malheureusement, une évaluation quantitative de cet effet est difficile à cause de l'incertitude des coefficients de partage du zinc entre phase minérale et magma.

(Traduit par la Rédaction)

Mots-clés: zinc, répartition, hydrothermal, gîte minéral, mobilisation, élément trace.

INTRODUCTION

The first step in the formation of many ore deposits is the mobilization of dispersed base metals by hydrothermal fluids. One way in which mobilization can occur is for fluids to leach metals from permeable rocks through which they flow. This mechanism is accepted by most investigators as being important in the formation of sediment-hosted stratiform–stratabound deposits (*e.g.*, Gustafson & Williams 1981, Walker 1989) and volcanogenic massive sulfide deposits (Franklin *et al.* 1981). A second way in which mobilization can occur is for metal-scavenging fluids to exsolve and separate from a body of magma. This mechanism is believed by many to be important in the formation of porphyry, skarn and some types of vein deposits (Stein & Hannah 1985, Sawkins 1990).

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In order to understand either mechanism of mobilization in detail, one must know the mass balance of the base metals among the minerals ± melt at their source. There is general agreement that in crystalline rocks, the major reservoir for copper is sulfide minerals, and the major reservoir for lead is feldspars (Wedepohl 1972). Mobilization of copper and lead, then, requires that sulfides and feldspars either dissolve or undergo cation-exchange reactions with the hydrothermal fluids. There is wide disagreement, by contrast, on the important host minerals for zinc. Some authors favor sulfides (*e.g.*, Keays 1987), others favor magnetite (*e.g.*, Heinrichs *et al.* 1980), and still others favor hydrous silicates (*e.g.*, Ilton & Eugster 1990). The distribution of zinc between minerals and melt in a cooling magma also is poorly known.

The purpose of this paper is to give a quantitative prediction of the mass balance of zinc among the minerals found in common igneous and metamorphic rocks. The procedure that is used is to determine mineral–mineral distribution coefficients from published compositions of coexisting phases, and to calculate mass balance from modes of common rock-types. It is assumed in this exercise that the trace zinc contained in common crystalline rocks is held in solid solution in the common ferromagnesian phases. There is a large body of analytical data supporting this assumption (Wedepohl 1972, Heinrichs *et al.* 1980, Dissanayake & Vincent 1972). The mineral–mineral distribution coefficients derived in this work do not yield new estimates of mineral–melt partition coefficients for zinc. They are used, however, to critically evaluate the mineral–melt coefficients that have been published by other investigators.

The mass-balance calculations have implications for the efficiency of zinc removal from crystalline rocks during alteration, and thus bear on the total mass of metal available to hydrothermal systems. They also reveal, by comparison with copper, a mechanism by which zinc and copper can be fractionated from one another as they are extracted from their source. The specific metal-releasing reactions operating in crystalline source-rocks may thereby affect the metal ratios observed in distant ore deposits.

THERMODYNAMIC BACKGROUND

This work considers only assemblages for which both zinc and major-element concentrations have been reported. These data present two advantages. The first is that partitioning can be examined for dependence on compositional parameters other than zinc concentration. The second is that the partitioning can be viewed as simple exchange-reactions for which the thermodynamic basis is well established (*e.g.*, Kretz 1961). For example, zinc partitioning between clinopyroxene and olivine can be expressed by the reaction:

$$\begin{aligned}&\mathrm{Ca(Fe,Mg)Si_2O_6} + 1/2\ \mathrm{Zn_2SiO_4} = \\ &\mathrm{CaZnSi_2O_6} + 1/2\ \mathrm{(Fe,Mg)_2SiO_4}.\end{aligned} \tag{1}$$

The distribution coefficient for Reaction 1 is:

$$K_D(\mathrm{Cpx–Ol}) = \frac{X_{\mathrm{CaZnSi_2O_6}}(1-X_{\mathrm{Zn_2SiO_4}})}{(1-X_{\mathrm{CaZnSi_2O_6}})X_{\mathrm{Zn_2SiO_4}}}$$

where X is mole fraction of the zincian component calculated from the mineral's composition. For this paper, analogous exchange-reactions and distribution coefficients have been defined for other mineral pairs using the zincian end-members listed in Table 1.

If chemical equilibrium is achieved, then K_D will be independent of zinc concentration if (1) the phases are ideal crystalline solutions, and (2) zinc is sufficiently dilute that the phases obey both Henry's law and Raoult's law. In either case, K_D can potentially vary with pressure (P), temperature (T), or the compositions of the phases in terms of major elements (X). The effects of P are predicted to be small owing to the small changes in volume of the exchange reactions. For example, K_D for Reaction 1 would change by 10–20% for a 5 kbar change in P [phases assumed to be ideal solutions, molar volumes from Robie *et al.* (1966) and Essene & Peacor (1987)]. Variations of this magnitude are comparable to the variations expected from analytical error in most cases.

The effects of T are more difficult to predict because enthalpy changes for exchange reactions cannot be calculated with sufficient precision using calorimetric data.

Enthalpy data also are lacking for several of the end-members listed in Table 1. Sufficient data are available though for an order-of-magnitude estimate of the T effect on orthopyroxene–olivine exchange. The K_D value is predicted to change by a factor of about 2 from 700 to 1200°C [phases assumed to be ideal, enthalpy data from Berman (1988) and Wagman *et al.* (1982)]. The effects of T also can be evaluated empirically if T of equilibration can be determined for mineral pairs with known zinc contents. This exercise is carried out below for garnet – clinopyroxene.

TABLE 1. MINERAL ABBREVIATIONS AND ZINCIAN END-MEMBERS

Mineral	Abbrev.	Zincian End-Member
Olivine	Ol	Zn_2SiO_4
Orthopyroxene	Opx	$ZnSiO_3$
Clinopyroxene	Cpx	$CaZnSi_2O_6$
Garnet	Grt	$Zn_3Al_2Si_3O_{12}$
Biotite	Bt	$KZn_3AlSi_3O_{10}(OH)_2$
Clinoamphibole	Cam	$Ca_2Zn_5Si_8O_{22}(OH)_2$
Magnetite	Mag	$ZnFe_2O_4$
Al-spinel	Spl	$ZnAl_2O_4$
Ilmenite	Ilm	$ZnTiO_3$

Compositional effects on zinc partitioning are sought in the following sections. For mineral pairs with sufficient data, multiple linear regression analysis was carried out to determine whether K_D varies with the abundances of specific elements or cations. In addition to compositional parameters, P and T were included in the regression analysis of garnet – clinopyroxene partitioning.

In this paper, zinc partitioning is cast in terms of both K_D, the distribution coefficient, and D, the Nernst partition coefficient. For Reaction 1, the Nernst partition coefficient is given by:

$$D_{\mathrm{Cpx-Ol}} = \frac{\text{wt\% Zn in Cpx}}{\text{wt\% Zn in Ol}}$$

The D value is a more useful quantity for comparing mineral–mineral partitioning with mineral–melt partitioning.

PRESENTATION AND EVALUATION OF DATA

Analytical data are available for nine common ferromagnesian minerals, olivine, orthopyroxene, clinopyroxene, garnet, clinoamphibole, biotite, magnetite, ilmenite and aluminous spinel, coexisting in various combinations in a variety of rock types (Annersten & Ekström 1971, Dissanayake & Vincent 1972, Graybeal 1973, Dupuy *et al.* 1980, Bodinier *et al.* 1987, Sorensen & Grossman 1989, O'Reilly *et al.* 1991, Smith *et al.* 1991, Hickmott *et al.* 1992). Analytical error varies among the studies. Where it is stated, the precision of the atomic absorption data (Dissanayake & Vincent 1972, Graybeal 1973, Dupuy *et al.* 1980) is ±8% or better. Annersten's & Ekström's (1971) atomic absorption data are assumed to have similar reproducibility. The neutron activation data of Sorensen & Grossman (1989) have an estimated precision of ±10%, and the results of the spectrographic analyses of DeVore (1955a, b), a precision of ±20%. The precision of the proton microprobe data is estimated to be ±6% (O'Reilly *et al.* 1991, Smith *et al.* 1991) or ±10% (Hickmott *et al.* 1992), and the precision of the electron-microprobe data (Bodinier *et al.* 1987) is about ±30% (for zinc).

The nine minerals taken as pairs give rise to thirty-six independent exchange-reactions of the type given as Reaction 1. The partitioning of zinc can be determined empirically from the published analytical results for twenty-four of the thirty-six reactions. The data are displayed graphically in Figure 1, and mean values of K_D and D are given in Table 2.

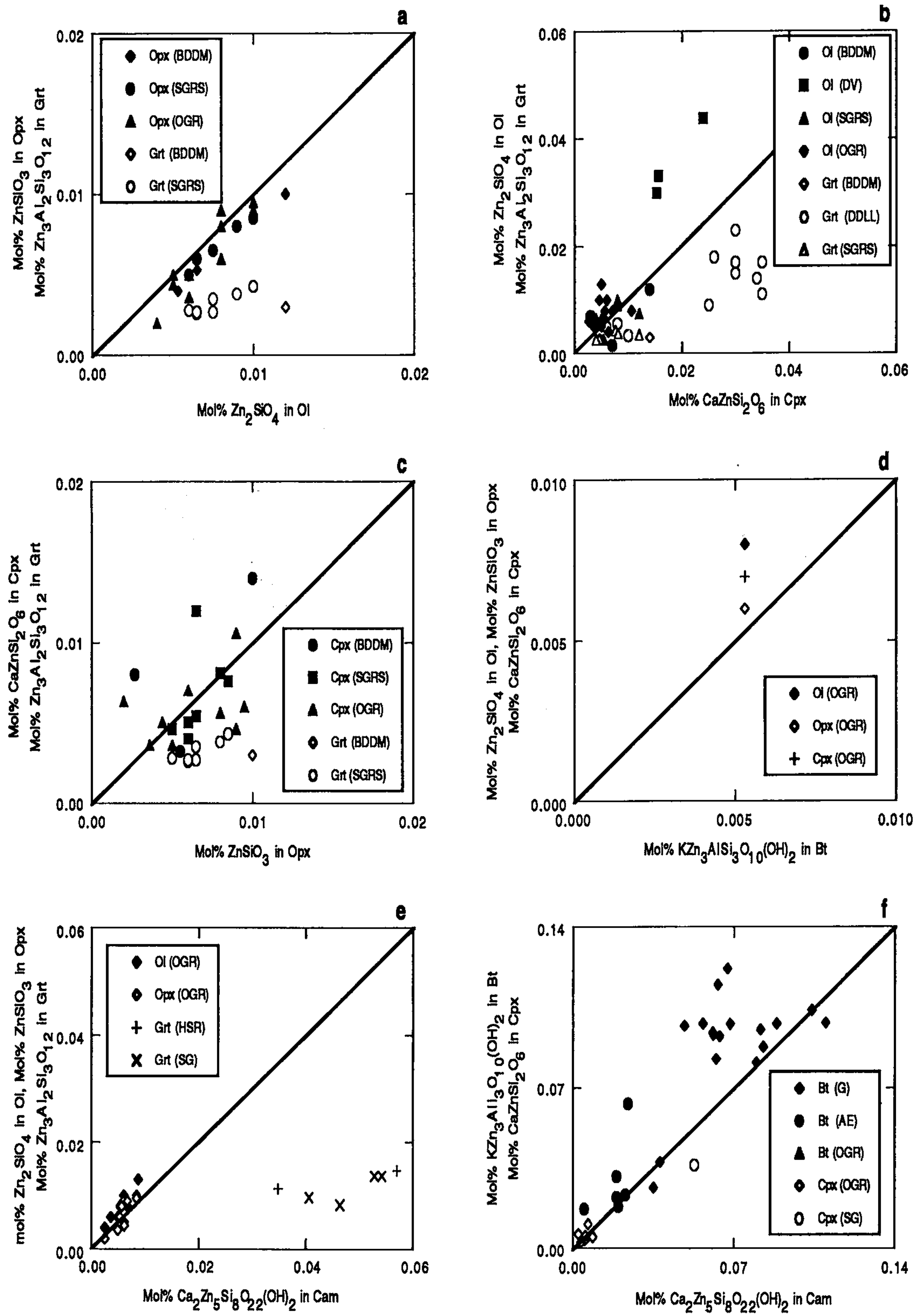
For fifteen of the minerals pairs, sufficient data are available to test for compositional effects on zinc partitioning. Multiple linear regression analysis was carried out in which K_D values were fit by the method of least squares using cation concentrations as variables. The cations considered as variables are listed in Table 3. Compositional parameters were judged to have a significant effect on K_D if their inclusion in the regression resulted in a reduction of the sum of squared residuals that is significant at the 95% confidence level.

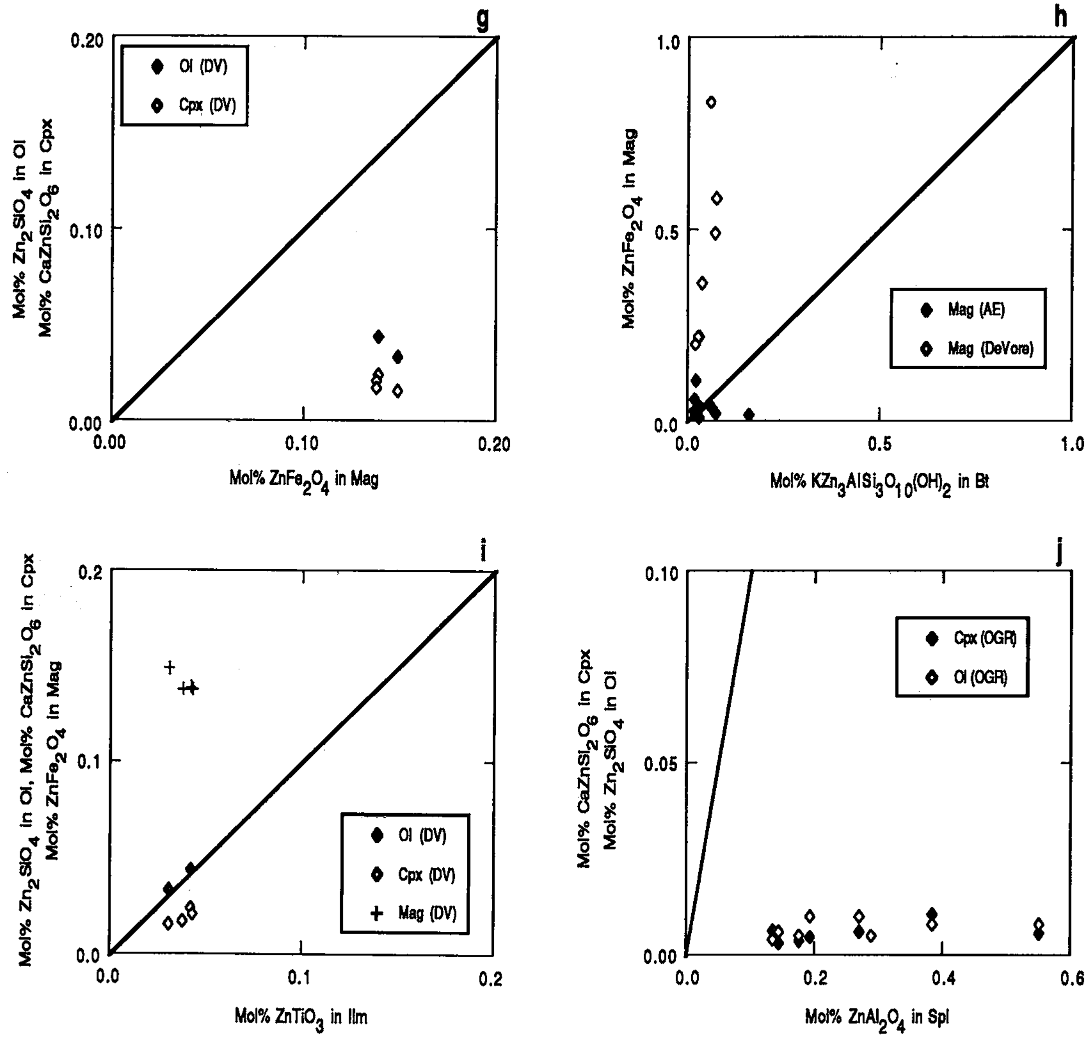
Only two mineral pairs, orthopyroxene – olivine and clinoamphibole – biotite, have significant detectable compositional dependencies, both on Zn (Table 3). The apparent lack of dependencies for the other mineral pairs may be a result of the restricted range of rock types, mostly mafic and ultramafic, for which zinc concentrations are available (Table 3). There is a need for analytical data from a broader range of rock types, particularly felsic metamorphic and igneous rocks, in order to more rigorously test for compositional effects.

For garnet – clinopyroxene, the zinc partitioning also was examined for P and T effects. Equilibration P for the samples, obtained from the original papers (Dupuy *et al.* 1980, Smith *et al.* 1991), ranged from 10 to 40 kbar and was found to have no detectable effect on K_D in regression analyses. A temperature effect was sought by plotting $\ln K_D$ *versus* $1/T$ using the results of the garnet – clinopyroxene Fe–Mg exchange geothermometer of Ellis & Green (1979). Equilibration T for the samples was found to range from 710 to 1318°C, and had no detectable effect on the partitioning.

The magnetite – biotite partitioning shows an unusually wide range of K_D, 0.09–4.8 [see data of Annersten & Ekström (1971) in Fig. 1h]. Because these two minerals are important hosts of zinc in many rocks, the partitioning behavior warrants further evaluation. The minerals, from intermediate-grade metamorphic rocks from Grängesberg, Sweden, span broad ranges of composition. The samples of biotite are $\mathrm{Na_{0-0.14}K_{0.73-0.95}Mg_{0.92-2.99}Fe_{0.05-1.84}Mn_{0-0.03}Ti_{0-0.09}{}^{VI}Al_{0-0.11}{}^{IV}Al_{0.90-1.24}Si_{2.76-3.10}O_{10}(OH)_2}$, with 84–748 ppm Zn. The samples of magnetite contain up to 1980 ppm Ti and 2890 ppm V, and have 23–297 ppm Zn. Multiple regression analysis shows that no compositional parameters have a significant detectable effect on the partitioning. Variation in metamorphic P and T also cannot account for the range in K_D inasmuch as the samples were collected over a small area of uniform metamorphic grade (Annersten & Ekström 1971).

Data from other studies suggest that the observed variation in K_D may reflect disequilibrium. DeVore (1955a, b) reported results of spectrographic analyses of coexisting biotite and garnet in metapelites. Zinc partitioning between biotite and fictive magnetite can be estimated from these data using K_D values for garnet – clinopyroxene and magnetite – clinopyroxene (from Table 2). The results imply that magnetite strongly partitions zinc over biotite, and that K_D is about 9 (Fig. 1h). Also, Johnson (1991) determined magnetite – biotite partitioning by electron-microprobe


a
Opx (BDDM)
Opx (SGRS)
Opx (OGR)
Grt (BDDM)
Grt (SGRS)
0.02
0.01
0.00
0.00
0.01
0.02
Mol% ZnSiO$_3$ in Opx
Mol% Zn$_3$Al$_2$Si$_3$O$_{12}$ in Grt
Mol% Zn$_2$SiO$_4$ in Ol
b
Ol (BDDM)
Ol (DV)
Ol (SGRS)
Ol (OGR)
Grt (BDDM)
Grt (DDLL)
Grt (SGRS)
0.06
0.04
0.02
0.00
0.00
0.02
0.04
0.06
Mol% Zn$_2$SiO$_4$ in Ol
Mol% Zn$_3$Al$_2$Si$_3$O$_{12}$ in Grt
Mol% CaZnSi$_2$O$_6$ in Cpx
c
Cpx (BDDM)
Cpx (SGRS)
Cpx (OGR)
Grt (BDDM)
Grt (SGRS)
0.02
0.01
0.00
0.00
0.01
0.02
Mol% CaZnSi$_2$O$_6$ in Cpx
Mol% Zn$_3$Al$_2$Si$_3$O$_{12}$ in Grt
Mol% ZnSiO$_3$ in Opx
d
Ol (OGR)
Opx (OGR)
Cpx (OGR)
0.010
0.005
0.000
0.000
0.005
0.010
Mol% Zn$_2$SiO$_4$ in Ol, Mol% ZnSiO$_3$ in Opx
Mol% CaZnSi$_2$O$_6$ in Cpx
Mol% KZn$_3$AlSi$_3$O$_{10}$(OH)$_2$ in Bt
e
Ol (OGR)
Opx (OGR)
Grt (HSR)
Grt (SG)
0.06
0.04
0.02
0.00
0.00
0.02
0.04
0.06
mol% Zn$_2$SiO$_4$ in Ol, Mol% ZnSiO$_3$ in Opx
Mol% Zn$_3$Al$_2$Si$_3$O$_{12}$ in Grt
Mol% Ca$_2$Zn$_5$Si$_8$O$_{22}$(OH)$_2$ in Cam
f
Bt (G)
Bt (AE)
Bt (OGR)
Cpx (OGR)
Cpx (SG)
0.14
0.07
0.00
0.00
0.07
0.14
Mol% KZn$_3$AlI$_3$O$_{10}$(OH)$_2$ in Bt
Mol% CaZnSi$_2$O$_6$ in Cpx
Mol% Ca$_2$Zn$_5$Si$_8$O$_{22}$(OH)$_2$ in Cam



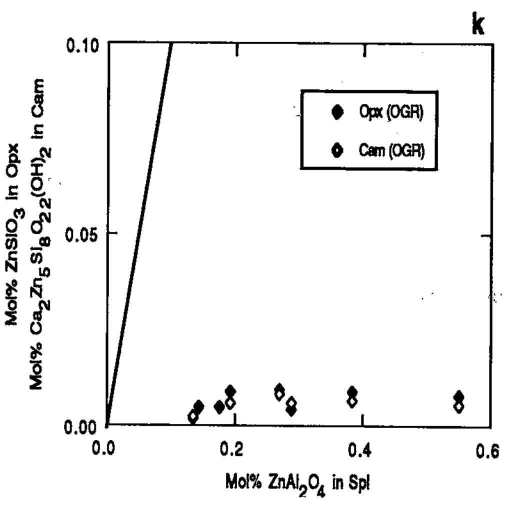


FIG. 1. Distributions of trace zinc between coexisting minerals in common rocks. On plots of this type, samples with the same K_D value will to a close approximation define a line passing through the origin. Reference lines represent equal partitioning. The mineral pairs for which data are available are (a) Opx–Ol and Grt–Ol, (b) Cpx–Ol and Grt–Cpx, (c) Cpx–Opx and Grt–Opx, (d) Bt–Ol, Bt–Opx and Bt–Cpx, (e) Cam–Ol, Cam–Opx and Cam–Grt, (f) Cam–Bt and Cam–Cpx, (g) Mag–Ol and Mag–Cpx, (h) Mag–Bt (see text), (i) Ilm–Ol, Ilm–Cpx and Ilm–Mag, (j) Spl–Cpx and Spl–Ol, and (k) Spl–Opx and Spl–Cam. Sources of data: BDDM Bodinier *et al.* (1987), SGRS Smith *et al.* (1991), OGR O'Reilly *et al.* (1991), DV Dissanayake & Vincent (1972), DDLL Dupuy *et al.* (1980), HSR Hickmott *et al.* (1992), SG Sorensen & Grossman (1989), G Graybeal (1973), AE Annersten & Ekström (1971), and DeVore, DeVore (1955a, b).

TABLE 2. AVERAGE VALUES OF K_D (UPPER VALUES) AND D (LOWER VALUES) FOR ZINC PARTITIONING OBSERVED IN NATURAL ASSEMBLAGES*

Mineral A	Mineral B						
	Ol	Opx	Cpx	Grt	Bt	Cam	Mag
Opx	0.86(0.14) 0.62(0.08)						
Cpx	0.92(0.76) 0.32(0.25)	1.0(0.6) 0.48(0.29)					
Grt	0.40(0.07) 0.21(0.03)	0.46(0.08) 0.34(0.04)	0.52(0.16) 0.79(0.23)				
Bt	0.66 0.34	0.88 0.63	1.5 2.2				
Cam	0.76(0.18) 0.33(0.08)	0.98(0.30) 0.56(0.17)	1.2(0.4) 1.6(0.5)	4.2(0.8) 3.5(1.0)	0.79(0.25) 0.69(0.22)		
Mag	3.8 2.8		7.5(1.4) 7.2(1.3)		9.3(2.7) 5.0(1.3)		
Ilm	0.94 0.54		2.0(0.2) 1.5(0.1)				0.27(0.05) 0.21(0.04)
Spl	39(18) 17(7)	45(20) 27(12)	50(22) 65(25)			54(24) 53(20)	

Note: Numbers in parentheses are standard deviations calculated where there were sufficient data.

*K_D=$((X_{Zn}/(1\text{-}X_{Zn}))^{\text{Min A}}/((X_{Zn}/(1\text{-}X_{Zn}))^{\text{Min B}})$, D=(wt% Zn in A)/(wt% Zn in B). See Table 1 for zincian end-members used to calculate X_{Zn}.

analysis of a granulite-facies metamorphic assemblage from Sterling Hill, New Jersey. The K_D value was found to be 8.0. The Sterling sample is not directly comparable to the Grängesberg samples because zinc is present as a minor element rather than at trace levels. Nevertheless, the results support the conclusion that magnetite strongly partitions zinc over biotite in an equilibrium assemblage.

It is difficult to account for the apparent disequilibrium in the Grängesberg samples without additional information. Annersten & Ekström (1971) noted the presence of postmetamorphic intrusions of granitic pegmatite near their sample locations, and it is possible that the minerals underwent compositional changes during postmetamorphic reheating or metasomatism. The biotite would have been particularly susceptible to such compositional changes, inasmuch as micas readily undergo subsolidus replacement and unmixing reactions (*e.g.*, Yau *et al.* 1984, Ferrow *et al.* 1990). In Table 2, the values of K_D and D listed for magnetite – biotite are those derived from the data of DeVore (1955a, b). They are somewhat more uncertain than the values for other mineral pairs because they are not based on analyses of minerals coexisting in the same rocks.

How generally applicable are the coefficients in Table 2 to rocks? A first consideration is the accuracy and precision with which the coefficients are known. There is wide scatter in the data for some mineral pairs (*e.g.*, biotite – clinoamphibole, clinopyroxene – orthopyroxene), which does not appear to be due to compositional effects. The scatter is also unlikely to be due to systematic P–T effects because data for samples of the same lithology with similar conditions of equilibration can also show wide scatter (see clinopyroxene – orthopyroxene partitioning in peridotites in Fig. 1c). The scatter is presumably a result of disequilibrium in some samples, possibly reflecting compositional changes due to subsolidus re-equilibration or metasomatism, or analytical difficulties.

A second consideration is the extrapolation of the coefficients to rock compositions and P–T conditions different from those for which the data were obtained. Use of the coefficients at higher or lower P is justified on theoretical grounds by the small changes in volume of the (Fe,Mg)-for-Zn exchange reactions. The lack of an observable dependence on P for garnet – clinopyroxene partitioning, the only mineral pair for which there is independent geobarometry, supports this view. The validity of the coefficients at higher or lower T than the rocks in which they were determined is more difficult to evaluate. Data for a range of equilibration T are available only for garnet – clinopyroxene and clinoamphibole – biotite. There does not appear to be a strong dependence on T in either case; whether there is a strong dependence for other mineral pairs is unknown.

Extrapolation of the coefficients to greatly different mineral compositions also is uncertain. Orthopyroxene – olivine and clinoamphibole – biotite coefficients were found to depend weakly on zinc content. The use of mean coefficients for these two mineral pairs (Table 2) is sufficiently accurate for the purposes of this paper where zinc concentrations are below a few hundred ppm, but care should be taken in extrapolations to higher concentrations. With respect to the major-element compositions of the minerals, no significant compositional dependencies were observed. It is important to note, however, that the composition ranges for which zinc data are available are quite

TABLE 3. DATA USED TO CALCULATE K_D AND D VALUES AND TO EVALUATE POSSIBLE COMPOSITIONAL EFFECTS

Mineral Pair	No. Pairs Analyzed	Rock Types Analyzed	Multiple Regression Parameters	Observed Compositional Effects
Opx-Ol	20	peridotite, lherzolite	^{IV}Al,^{VI}Al,Ti,Cr,Fe,Mg,Ca,Zn in Opx	Zn: K_D increases from 0.6 to 0.9 as Zn in Ol changes from 37 to 116 ppm
Cpx-Ol	25	peridotite, lherzolite, Skaergaard rocks	^{IV}Al,^{VI}Al,Ti,Cr,Fe,Mg,Ca,Na,Zn in Cpx	none
Cpx-Opx	20	peridotite, lherzolite	^{IV}Al,^{VI}Al,Ti,Cr,Fe,Mg,Ca,Na,Zn in Cpx	none
Grt-Ol	8	peridotite	Ca,Fe,Mg,Zn in Grt	none
Grt-Opx	8	peridotite	^{IV}Al,^{VI}Al,Ti,Cr,Fe,Mg,Ca,Zn in Opx	none
Grt-Cpx	19	peridotite, eclogite, granulite, garnet amphibolite	Ca,Mn in Grt; ^{IV}Al,^{VI}Al,Ti,Cr,Fe,Mg,Na,Zn in Cpx; P; lnK_D also regressed in 1/T	none
Bt-Ol	1	lherzolite		
Bt-Opx	1	lherzolite		
Bt-Cpx	1	lherzolite		
Cam-Ol	10	lherzolite	Al,Fe,Mg,Zn in Cam	none
Cam-Opx	8	lherzolite	^{IV}Al,^{VI}Al,Cr,Fe,Mg,Ca,Zn in Opx	none
Cam-Cpx	11	lherzolite, garnet amphibolite	^{IV}Al,^{VI}Al,Ti,Fe,Mg,Na,K,Zn in Cpx	none
Cam-Grt	6	garnet amphibolite	Al,Fe,Mg,Zn in Cam	none
Cam-Bt	25	granite, metamorphic rocks, lherzolite	Al,Ti,Fe,Mg,Zn in Bt	Zn: K_D decreases from 1.1 to 0.6 as Zn in Cam changes from 18 to 355 ppm
Mag-Ol	2	Skaergaard rocks		
Mag-Cpx	4	Skaergaard rocks		
Mag-Bt*	7	metapelites		
Ilm-Ol	2	Skaergaard rocks		
Ilm-Cpx	4	Skaergaard rocks		
Ilm-Mag	4	Skaergaard rocks		
Spl-Ol	8	lherzolite	Fe,Mg,Cr,Al,Zn in Spl	none
Spl-Opx	8	lherzolite	Fe,Mg,Cr,Al,Zn in Spl	none
Spl-Cpx	8	lherzolite	^{IV}Al,^{VI}Al,Ti,Fe,Mg in Cpx; Cr,Zn in Spl	none
Spl-Cam	6	lherzolite	Fe,Mg,Cr,Al,Zn in Spl	none

*See text.

restricted for all the mineral pairs except garnet – clinopyroxene and clinoamphibole – biotite. Additional, preferably microanalytical, data are needed to further evaluate T and X effects on partitioning. The greatest need is for data from felsic igneous and metamorphic rocks, which have lower temperatures of equilibration and higher concentrations of iron than the mantle-derived and mafic rocks that dominate the current data-set.

Despite the uncertainties in the coefficients listed in Table 2, the partitioning behavior of the minerals is sufficiently well known to draw meaningful first-order conclusions about the mass balance of zinc in common crystalline rocks. The coefficients also provide an empirical constraint on the accuracy of mineral–melt partition coefficients for zinc that have been published by other investigators.

DISCUSSION

Zinc mobilization from common crystalline rocks

Average basalt contains about 100 ppm Zn (Krauskopf 1979), and the mode of a representative sample of alkali basalt is 12% olivine, 48% clinopyroxene, 18% plagioclase, 7% opaque oxides and 14% glass (Barker 1983, p. 62). The opaque oxide is assumed to be magnetite inasmuch as magnetite is nearly ubiquitous in basalts, and ilmenite is rare (Frost & Lindsley 1991). Mass-balance calculations employing the coefficients in Table 2 reveal that magnetite is the most important carrier of zinc, with 41% of the whole rock's inventory. Clinopyroxene, olivine and matrix glass contain 25, 19 and 15%, respectively. Henderson's (1982) $D_{\mathrm{Cpx-Melt}}$ value was used to calculate the concentration of zinc in matrix glass. Mineral–melt partition coefficients for zinc are uncertain, as explained below, but the uncertainty has little effect on the outcome of this calculation.

Average granite contains about 50 ppm Zn (Krauskopf 1979), and has as ferromagnesian phases 5% biotite, 1% clinoamphibole, 2% magnetite and 1% ilmenite (Daly *et al.* 1942). Magnetite is predicted to be the dominant host of zinc, with 67% of the whole rock's inventory. Biotite, ilmenite and clinoamphibole carry 22, 7 and 4%, respectively.

An obvious question concerns the behavior of these phases during hydrothermal alteration. Observations made on natural samples (Humphris & Thompson 1978a, Ito & Anderson 1983) and experimental products (Mottl *et al.* 1979, Seyfried & Janecky 1985) indicate that in basalts, olivine and matrix glass are readily dissolved. Pyroxene and plagioclase can persist as relict phases, but they are commonly altered as well. Magnetite is common in altered basalts; it is rarely clear, however, whether it is a relict primary phase or a product of secondary replacement.

In granitic rocks, magnetite and biotite, the two most important reservoirs of zinc, break down during propylitic, phyllic and argillic alteration (*e.g.*, Beane 1982). During potassic alteration, biotite persists but adjusts its chemical composition by reaction with the fluid. Zinc removal in this case is likely to be governed by biotite–fluid cation-exchange reactions, which result in strong partitioning of zinc into the fluid (Ilton & Eugster 1990). Magnetite also persists as a stable phase in the potassic assemblage; whether it equilibrates with the fluid is unknown.

Because magnetite is the most important host of zinc in common crystalline rocks, its persistence may severely limit the amount of zinc that is removed during alteration. Zinc mobilization from relict crystals would be controlled by the degree of equilibration with the fluid. Ilton & Eugster (1989) have shown that the equilibrium partitioning is strongly in favor of a chloride-bearing solution over magnetite. Equilibration is likely to be limited by intramineral diffusion of cations, so that the time required for zinc removal can be estimated using kinetic arguments. Magnetite grains in basalts have grain sizes of about 0.01 mm. If the crystals are approximately spherical, then zinc loss by volume diffusion will reach 50% in less than 1 year at 600°C, 3×10^3 years at 400°C and 5×10^{10} years at 200°C [equation from Crank (1975, p. 91), diffusion coefficients extrapolated from data of Freer & O'Reilly (1980)]. Cathles (1981) has shown that ore-forming hydrothermal systems associated with oceanic spreading ridges have lifetimes no longer than 10^4 yr. Thus in hydrothermal systems developed at spreading ridges, significant removal of zinc from primary magnetite by volume diffusion is feasible only above about 400°C. Equilibration with fluids may be enhanced by the oxidation–exsolution process that affects magnetite in many basalts (*e.g.*, Haggerty 1991), but the possibility remains that zinc removal during low-T alteration is limited by the persistence of unreacted, primary magnetite. The same critical T applies to zinc removal from magnetite in granite in the porphyry environment. Hydrothermal systems associated with cooling plutons can last up to 10^6 yr (Cathles 1981), but the longer time available for diffusive loss of zinc from crystals is offset by the coarser grain-size of granite.

Unlike the case for zinc, mobilization of copper from crystalline rocks depends on the susceptibility of igneous and metamorphic sulfides to dissolution or cation exchange. Petrographic observations of altered rocks have shown that primary sulfides are readily dissolved, and that they may reprecipitate in veins or as pseudomorphs (Humphris & Thompson 1978a, Harper *et al.* 1988). The ease of dissolution of copper sulfides and the more resistant nature of magnetite imply that the Cu:Zn mass ratio removed from crystalline source-rocks may decrease with progressive alteration. Initially, the metals would be released from dissolving sulfides (copper) and silicates (zinc). As copper becomes depleted in the rock, zinc would continue to be supplied to the fluid by magnetite. The extent of replacement or reaction of primary minerals, in other words the progress of alteration, is controlled by the integrated volume of fluid passing through a rock and also the temperature. The Cu:Zn mass ratio removed from crystalline rocks then is expected to decrease with time or with increasing temperature.

There have been few analytical studies of the source rocks for known mineral deposits against which to check this prediction. The available data do, however, provide supporting evidence. The results of whole-rock analyses of footwall rocks at the Matagami, Quebec massive sulfide deposits (MacGeehan 1978) show that copper was depleted more rapidly than zinc with progressive silicification. If the degree of silicification is an index of the integrated volume of through-going fluid (MacGeehan

1978), then the data agree with the predicted temporal trend toward lower Cu:Zn. The wallrocks for massive sulfide deposits at the Troodos and Josephine ophiolites were analyzed by Richardson *et al.* (1987), Schiffman & Smith (1988) and Zierenberg *et al.* (1988). The data display kinked patterns on Cu *versus* Zn plots, which imply removal of the metals at high Cu:Zn mass ratios from partially leached rocks, and at lower Cu:Zn ratios from more strongly leached rocks. The difference in ratios suggests a different mechanism of release for one or both of the metals, and is in agreement with the predicted removal of copper from sulfides and zinc from silicates on one hand, and near-exhaustion of copper and removal of zinc from magnetite on the other hand. The transition from one mechanism of release to another may be caused by the attainment of some critical fluid:rock ratio or critical temperature. Overall, some 90% of the copper and 50% of the zinc were removed from the rocks (Richardson *et al.* 1987).

The extraction of base metals from primary minerals in source rocks is only the first step in the complex process by which metals are mobilized, transported and precipitated at a site of deposition. The evidence presented here suggests that the extraction process can fractionate copper from zinc. There is evidence that subsequent steps in the process also may lead to fractionation of the base metals from one another. For example, dissolved copper and zinc have been found to adsorb onto fine-grained phases formed during alteration of basalt glass (Seyfried & Janecky 1985) or, in some cases, to reprecipitate as sulfides (Humphris & Thompson 1978b). Metal fixation by either process is unlikely to reduce the concentrations of dissolved copper and zinc by an equal amount; thus metal ratios in the hydrothermal fluids would be affected. Sverjensky (1986) has given a more general demonstration that fluid–aquifer reactions exert a strong control on the base metal contents of hydrothermal fluids and, ultimately, on the metal ratios observed in ore deposits.

An important consequence of these processes is that the metal contents observed in ore deposits are not reliable indicators of the metal contents of the source rocks. Although many investigators have identified the source rocks for specific deposits by matching metal ratios of the ores and the rocks (see discussion in Franklin *et al.* 1981), the practice neglects metal fractionation occurring at the source as well as in aquifers, and should be used with caution.

Evaluation of mineral–melt partition coefficients for zinc

The coefficients in Table 2 also can be used to evaluate mineral–melt partition coefficients determined for zinc by other investigators. If phenocrysts and matrix glass in a volcanic rock display equilibrium partitioning of zinc, then phenocrysts of different minerals should themselves display equilibrium partitioning. Thus, for example, the quotient of $D_{\mathrm{Opx–Melt}}$ and $D_{\mathrm{Ol–Melt}}$ determined from analyses of phenocrysts and glass in a volcanic rock would be expected to match the $D_{\mathrm{Opx–Ol}}$ value in Table 2, barring any P–T–X effects.

Mineral-pair partition coefficients from this study and those derived from mineral–melt coefficients are compared in Table 4. Mineral–melt coefficients were obtained from analyses of high-silica rhyolite (Mahood & Hildreth 1983) and trachyandesite (Luhr *et al.* 1984), and from the compilations of partition coefficients of Steinberg *et al.* (1979) and Henderson (1982). The use of compilations in this comparison introduces the possibility that the mineral–melt coefficients may themselves be inconsistent. For example, the quotient of $D_{\mathrm{Opx–Melt}}$ determined in a rhyolite and $D_{\mathrm{Ol–Melt}}$ determined in a basalt will not give the equilibrium $D_{\mathrm{Opx–Ol}}$ value if mineral–melt partitioning varies with melt composition. Henderson (1982) accounted for possible compositional effects by giving

TABLE 4. COMPARISON OF D VALUES FROM THIS STUDY WITH VALUES CALCULATED USING MINERAL-MATRIX PARTITIONING DATA FROM VOLCANIC ROCKS*.

Mineral Pair	D Values				
	This Study	1	2	3	4
Opx-Ol	0.62(0.08)	1.7			
Cpx-Ol	0.32(0.25)	0.5	0.58**	0.7-1.4	
Mag-Cpx	7.2(1.3)	10		1.1-5.5	2.0
Mag-Bt	5.0(1.3)		0.5-0.7†	2.6-2.8	
Cam-Bt	0.69(0.22)		0.35†		
Cam-Cpx	1.5(0.5)				0.78
Ilm-Cpx	1.5(0.1)			1.1	

Note: $D_{A\text{-}B}$=(wt% Zn in A)/(wt% Zn in B).

*Sources of data are 1=Steinberg *et al.* (1979), 2=Henderson (1982), 3=Mahood & Hildreth (1983), 4=Luhr *et al.* (1984).

**Data from basalts and andesites.

†Data from dacites and rhyolites.

separate coefficients for basaltic to andesitic and dacitic to rhyolitic rocks.

Coefficients derived from mineral–melt data and those determined in this study agree to within 25% at best and a factor of ten at worst. In some cases, the discrepancies may be due to the effects of large extrapolations of P–T–*X*. There is a hint that $D_{\mathrm{Cpx-Ol}}$ may increase with increasing iron content. There is also a hint that $D_{\mathrm{Mag-Cpx}}$ may decrease with increasing zinc or decreasing temperature.

The discrepancy for other mineral pairs does not seem to correlate with P, T or mineral composition, which suggests that the variations result from disequilibrium in some samples or analytical errors. The large uncertainties in the partitioning behavior of magnetite and biotite (Table 4) hamper the modeling of the behavior of zinc in felsic magmatic systems, where exsolution of vapor produces ore-forming fluids. The difficulty arises from the fact that either mineral can appear early in the crystallization sequence (*e.g.*, Maaløe & Wyllie 1975); the amount of zinc that they sequester must be known in order to accurately determine zinc concentrations in the residual magma and in the exsolving aqueous phases (Candela 1989). To illustrate the potential importance of order of crystallization, consider the effect of 1% fractionation (by volume) of magnetite from a magma. The range of $D_{\mathrm{Mag-Melt}}$ values quoted in the literature is 5–40. The zinc concentration in the residual magma would be 92% of its original value for the low-*D* case and 45% for the high-*D* case. It is clear that a small amount of crystallization of magnetite prior to fluid saturation has the capacity to greatly reduce the amount of zinc available to magmatic fluids. In order to properly assess the effect, the mineral–melt partitioning behavior of zinc must be determined more accurately.

CONCLUSIONS

Mass-balance calculations based on empirically derived mineral-pair partition coefficients suggest that magnetite is the major reservoir of zinc in common basalts and that clinopyroxene, olivine and matrix glass also are significant reservoirs. In common granites, magnetite is the major reservoir, and biotite also is an important reservoir. During hydrothermal alteration of crystalline rocks, removal of zinc may be limited by the degree to which magnetite dissolves in or reacts with the hydrothermal fluids. There is a greater tendency for magnetite to be dissolved during alteration of granitic rocks than basaltic rocks. The two lithologies may thus be equally fertile sources of zinc despite the fact that granites contain half as much zinc as basalts.

Copper, which in crystalline rocks is contained mainly in sulfide minerals, appears to be mobilized more readily than zinc during the alteration process. The Cu:Zn mass ratio removed from crystalline rocks may therefore decrease with progressive alteration. Inasmuch as metals may be fractionated from one another (1) during extraction from their source rocks, (2) during transport to depositional sites, and (3) during ore precipitation, the metal ratios observed in ore deposits are unlikely to be reliable indicators of the compositions of the source rocks.

There are inconsistencies in the mineral – melt partition coefficients that have been published for zinc, and between mineral – melt coefficients and the mineral – mineral coefficients determined in this work. Despite the uncertainty in the partitioning behavior, however, it is clear that early crystallization of magnetite or biotite may substantially reduce the efficiency of removal of zinc from magmas by exsolving fluids. A worthwhile goal for future studies would be to accurately determine magnetite – melt and biotite – melt partition coefficients so that the effect can be properly evaluated.

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