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PRELIMINARY FRACTIONATION PATTERNS OF ORE METALS THROUGH EARTH HISTORY

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Abstract

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A systematic method of comparing fractionation patterns of ore metals to those of common rock-forming elements is developed using the coherent electronic framework provided by the Periodic Table through its progressive filling of transition metal d- and f-orbitals. Four generalized fractionation processes in Earth history are addressed: (1) nebular condensation and accretion; (2) core–mantle interaction; (3) continental crustal growth; and (4) ore formation in supracrustal environments. Through each of these simplified processes, preliminary fractionation patterns of ore metals within Periods appear to vary smoothly with atomic number. Fractionation trends for each of these four processes can be ascribed respectively to: (1) differential condensation volatility; (2) multiple stages of core formation with partial separation of highly siderophile metals into the core; (3) enrichment of the continental crust in ore metals and incompatible elements by ascent of mantle-derived magmas; and (4) efficient multistage magmatic and hydrochemical ore-forming processes within the crust. Fractionation trends of ore metals are contiguous and collinear with those of rock-forming metals in the same Period, implying common geochemical controls. The systematic variation of enrichment and depletion factors across groups of elements within the same Period are termed chemical fractionation spectra.

1. Introduction

It is widely accepted that ore deposition in the Earth's crust occurs through fractionation processes involving selective mobilization, migration and redeposition of primordial elements. Magmatic and aqueous fluids serve as necessary solvents and through their mobility are the agents of mass transport. Abundance patterns of ore metals then are potentially of great utility in interpreting the geochemical history of the Earth, particularly in studying interaction of chemical subsystems under constraints imposed by simple mass balances.

One such application which has received attention is the interaction of the core and mantle. Following work by Goldschmidt (1954), Ringwood (1979) and Mason (1982) siderophile metal abundances have again been used in constraining Earth accretion and differentiation models by providing possible bounds on the extent of equilibration of the core and mantle (Newson and Palme, 1984; Wanke et al., 1984). However, there has not as yet been a synthesis of the early history of ore metals prior to their incorporation in the continental crust.

As varied as transition metal chemistry is, it is worth expanding upon these studies by: (1)

incorporating a much broader range of ore metals; (2) finding an effective systematic method of comparing elemental fractionations; (3) relating ore metal fractionation to well-understood processes affecting rock-forming elements; and (4) seeking evidence of the behavior of ore metals over the entire history of the Earth.

The purpose of effort then is to broaden the inquiry of ore genesis to include the early metallogenic history and progressive fractionation of the metals in the Earth using new data and interpretations on four processes: (1) nebular condensation and accretion; (2) continued differentiation of the Earth into the core and primitive mantle; (3) growth and evolution of the continental crust from the mantle; and, finally, (4) ore deposition in supracrustal environments.

While there is certainly no unanimity of opinion about the bulk composition of the Earth, mantle and crust, it may be possible to estimate the general effects of fractionation in a simplified, yet hopefully meaningful way by combining available compositional models. Obviously, data necessary to describe large-scale fractionations in the Earth are difficult to obtain because inaccessibility of the Earth's interior severely limits direct sampling. Heterogeneity of samples of the mantle which are available as well as metasomatic effects also introduce uncertainties in interpreting the geochemical significance of individual samples. Possible errors in the data used for this synthesis are without question quite large, and are very difficult to estimate. Therefore the fractionation patterns and interpretations offered here should be viewed with great caution and taken only as preliminary models.

2. Method of calculating fractionation factors

For each one of the four main transport processes to the addressed spanning nebular condensation to ore deposition, fractionation factors $(f_1, \ldots, f_4)$ may be defined for each element as the ratio of average metal concentration in a specific bulk material, e.g. the continental crust to the concentration in the preceding material, e.g. the primitive mantle yielding, in this example, f_3. Factors for the four fractionation processes are developed in sequence.

3. Results

3.1. Nebular and accretionary fractionation

Clearly the most critical state in describing the chemical evolution of the Earth is its bulk composition. Therefore the first stage of fractionation addressed is nebular condensation and accretion of the Earth from planetary components. A number of distinct compositional models exists for the composition of the bulk Earth as no single meteorite class can be successfully invoked as the sole accretionary material. The C1 carbonaceous chondrites, which appear to reflect solar system elemental abundances (Anders and Ebihara, 1982), are too volatile rich, but offer valuable indications of the nature of primitive nebular condensates and undifferentiated planetary components. A mixture of components is required. A bulk Earth composition (Anders, 1977) is used here, which is based upon a calculated equilibrium solar gas condensation sequence which assumes that the Earth experienced the same nebular fractionation processes as the chondrites, and is consistent with refractory early condensates (Ca, Al-rich inclusions from the Allende C3 chondrite), metal phase, Mg-silicates and volatiles condensed differentially upon cooling.

Nebular fractionation factors (f_1), which are given by elemental abundance ratios of bulk Earth (Anders, 1977) to solar system values (Taylor and McLennan, 1985), are shown in Table I. Fractionation relative to carbonaceous chondrites is then deduced by using data on the extensively analyzed Orgueil C1 carbonaceous chondrite multiplied by a factor of 1.5 to allow for loss of volatiles, water and carbonaceous

TABLE I

Fractionation factors for each of the four major processes affecting metal distribution in the Earth

	f_1 Nebular condensation and accretion (1)	f_2 Core–mantle differentiation (2)	$f_3^{l, (lower)}$ Growth of continetal crust from mantle (lower crust) (3)	$f_3^{U (upper)}$ (upper crust) (4)	f_4 Ore deposition from L or U crust (5)	f_4/f_3^U Ore/ upper (U) crustal factor (6)
Period 3:						
Mg	0.92	1.7	0.17	0.06		
Al	1.4	1.3	3.8	3.7		
Si	0.90	1.5	1.2	1.4		
Period 4:						
K	0.20	1.4	12	121	–	
Ca	1.4	1.3	2.4	1.4	1.8 (L)	1.3
Sc	1.4	1.4	2.1	0.65	–	
Ti	1.6	1.3	4.4	2.2	3 (L)	1.4
V	1.2	0.8	3.5	0.73	4 (L)	5.5
Cr	1.2	0.63	0.078	0.012	9 (L)[1]	
Mn	0.20	1.7	1.6	0.59	6 (L)	10
Fe	1.3	0.16	1.4	0.59	8 (L)	14
Co	1.2	0.11	0.33	0.10	17 (L)[1]	
Ni	1.2	0.10	0.064	0.0095	24 (L)[1]	
Cu	0.34	0.49	3.2	0.88	122 (L)	138
Zn	0.20	0.52	1.7	1.5	188 (L)	125
Ga	0.36	0.69	4.7	4.5		
Ge	0.29	0.10	1.2	1.2		
Period 5:						
Rb	0.17	1.3	7.1	150		
Sr	1.5	0.52	8.3	13		
Y	1.5	1.0	5.6	6.5		
Zr	3.6	0.42	8.4	23		
Nb	2.7	0.56	11	45		
Mo	2.1	0.02	14	25	960 (U)	38
Pd	1.2	0.0040	0.26	0.13	3,400 (L)[1,2]	
Ag	0.24	0.037	31	17	700 (L)	41
Cd	0.021	1.24	3.8	3.8	45,000 (U)[2]	
In	0.023	(6.9?)	2.7	2.7	54,000 (U)[2]	
Sn	0.28	–	–	–	236 (U)	
Sb	0.27	0.09	35	35	25,000 (U)[2]	
Period 6:						
Cs	0.21	0.15	11	400		
Ba	1.5	1.1	27	98	180 (U)	1.8
La	1.3	1.1	21	58		
Ta	1.6	0.88	23	86	91 (U)	1.1
W	2.8	0.1	29	83	280 (U)	2.4
Re	1.4	0.10	2	2		
Ir	1.5	0.003	0.05	0.007	6,500 (L)[1,2]	
Au	1.3	0.0018	6.5	3.4	400 (L)	118
Tl	0.023	1.22	38	125		
Pb			33	167	1,500 (U)	9
Bi	0.022	2.7	4	13	14,000 (U)[2]	

The factors are multiplicative in that the volatile-free C1 abundance of an element (column 3) may be multiplied successively by each of the factors to arrive at the minimum normalized mining grade. Column 6 gives the f_4/f_3^U ratio expressing the relative effects of localized ore-forming processes and fractionation from crustal growth in accessible environments. Ore-forming fractionation factors > 1000 are for metals which occur in dispersed form in other ore minerals and are therefore recovered generally as by-products. These high fractionation factors, shown with [2], should be viewed only as being apparent factors. Values in columns 1–6 are calculated using the data listed in references given in Fig. 7.
[1]Metal is not concentrated in continental crust; f_4 is not comparable to factors for other metals (see Fig. 9).
[2]Apparent ore-forming fractionation factor for a dispersed metal produced as a by-product of mining a principal ore metal.

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compounds (Anders and Ebihara, 1982; Taylor and McLennan, 1985).

The resulting fractionation factors have been arranged according to Groups of the Periodic Table in order to recognize coherent cosmochemical and geochemical elemental behavior for groups of elements using the method of Anders (1977). In addition, in this study important advantage is made of systematic variation of chemical properties within Periods as d- or f-orbitals are progressively filled as atomic number increases.

A well-known nebular fractionation pattern (Ganapathy and Anders, 1974; Anders, 1977) is shown in Fig. 1. The early high-temperature phase of accretion was apparently dominated by incorporation of an early refractory condensate, a somewhat lower-temperature metallic condensate, and a still lower-temperature Mg-silicate condensate, with the entire aggregate having C1 abundance ratios (fractionation factors $\doteqdot$ 1.0). Moderate depletion is indicated for elements condensing subsequently only when temperatures had decreased into the range 1300–600 K (K, Rb, Cs, Mn, Cu, Ag, etc.). Major depletion is shown for highly volatile species condensing only below 600 K in Periods 5 and 6 (Cd, In, Tl, Hg, Bi).

3.2. Core–mantle differentiation

Fractionation by segregation of the mantle and core (f_2) is based upon interpreting ultramafic spinel-lherzolite xenoliths as representing the composition of the upper mantle. Used here are ultramafic nodules from San Carlos, Arizona, which have been studied previously (Frey, 1978; Jagoutz et al., 1979; Wanke et al., 1984). Proposed primitive mantle abundances are deduced by weighted averaging of estimates of elemental values in present mantle and crust in which the crust is 0.59% of the total mass of the mantle and crust. Values of this fractionation factor are given by elemental abundance ratios of primitive mantle (Wanke et al., 1984) to bulk Earth values (Taylor and McLennan,

1985) and are summarized in Fig. 2 and Table I.

Under the assumption that the core equilibrated with the mantle, mass balances using the present masses of the core ($1.9 \cdot 10^{27}$ g) and mantle ($4.05 \cdot 10^{27}$ g) indicate maximum values of mantle enrichment factors should be 1.47 (mass of Earth/mass of mantle) for *completely* immobile elements retained in the mantle as growth of the core occurred (i.e. assuming zero concentration in the core). This prediction is borne out by fractionation factors for many lithophile elements, e.g. Al (1.3), Si (1.5), K (1.4), Ca (1.3), Rb (1.3), Mg (1.7) and Mn (1.7), as shown in Table I (column 2). The only non-siderophile, non-chalcophile exception is Cs (0.15).

Depletion of siderophile metals in the mantle, specifically the stronger depletion of the highly siderophile elements Au (0.0018), Ir (0.003) and Pd (0.004) in relation to the weaker depletion of the moderately siderophile elements Mo (0.02), W (0.1), Co (0.11) and Ni (0.10), suggests that core formation did not continue after ~85–90% of the Earth had accreted (Newsome and Plame, 1984). However, a core growth curve based upon Pb isotopes shows evidence of extraction of Pb from the mantle and influx into the core, implying that 85% of the core formed as a continuous process in the early period (50–200 Ma after 4.55 Ga ago (Allègre et al., 1982). Complicating these interpretations is mantle heterogeneity.

Nevertheless, interpretation of the siderophile abundance pattern seems best explained in terms of multiple stages of accretion and core formation (Arculus and Delano, 1981; Wanke, 1981; Wanke et al., 1984) with early accretion of most of the metals as a highly reduced, high-temperature nebular component. Segregation of siderophile metals into the core occurred simultaneously with accretion, and was followed by a later addition of ~10% of the Earth as more oxidized, volatile-rich, lower-temperature component, thereby establishing the rela-
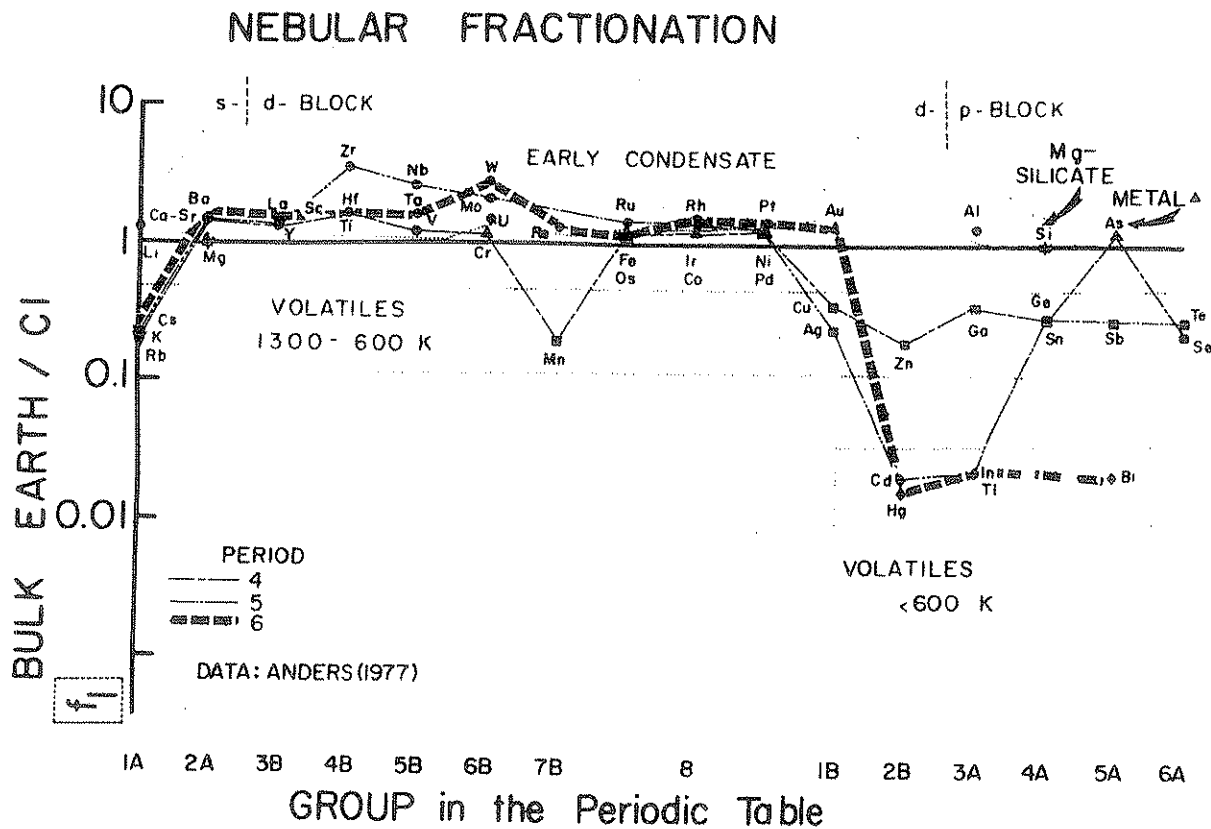
NEBULAR FRACTIONATION

Fig. 1. One of several theoretical models for the earliest fractionation involved in formation of the Earth. Effects of both nebular condensation and accretion are included in f_1. *Heavy solid horizontal line* ($f_1 = 1.0$) represents no fractionation. Very little fractionation is indicated for early condensate consisting of refractory elements [e.g., Zr, Nb and W), Mg-silicate phase and metallic Fe–Ni–Co phase (f_1-values near 1; data points are shown with *triangles*)]. These apparently condensed and accreted in approximately C1 (chondritic) proportions. Elements with moderate volatility, e.g. Cu, Ag, Zn, Ga and Sn are slightly depleted in the bulk Earth. Highly volatile elements (Cd, Hg, In, Tl, Bi) are strongly depleted. These stepped fractionation patterns result largely from the assumption that elements behave as cosmochemical groups dominated by volatility. Data are from Anders (1977) and Taylor and McLennan (1985).

tively high abundances of the moderately siderophile elements (W, Co, Ni).

3.3. Crustal growth from the mantle

Growth of the continental crust from the primitive mantle (Fig. 3) occurred over a period of geological time spanning > 3 Ga, much longer in comparison to the possibly short, several hundred million year interaction between the core and mantle (Wanke, 1981; Allègre et al., 1982; Newsom and Palme, 1984). Within continents, melting of primary basaltic crust and re-melting of existing continental rocks in the

presence of volatiles, largely water and CO_2, produces igneous rocks of granodioritic composition typical of continents.

The proposed bulk crustal composition used (Taylor and McLennan, 1985) is bounded by heat flow constraints which limit heat-producing elemental abundances (K, U, Th) and by the provision that the bulk crust must be capable of producing the upper-crustal granodiorites mentioned previously by partial melting. In addition, the proposed composition includes 75% of average Archean crustal composition and 25% andesitic model composition respectively representing the relative contributions of
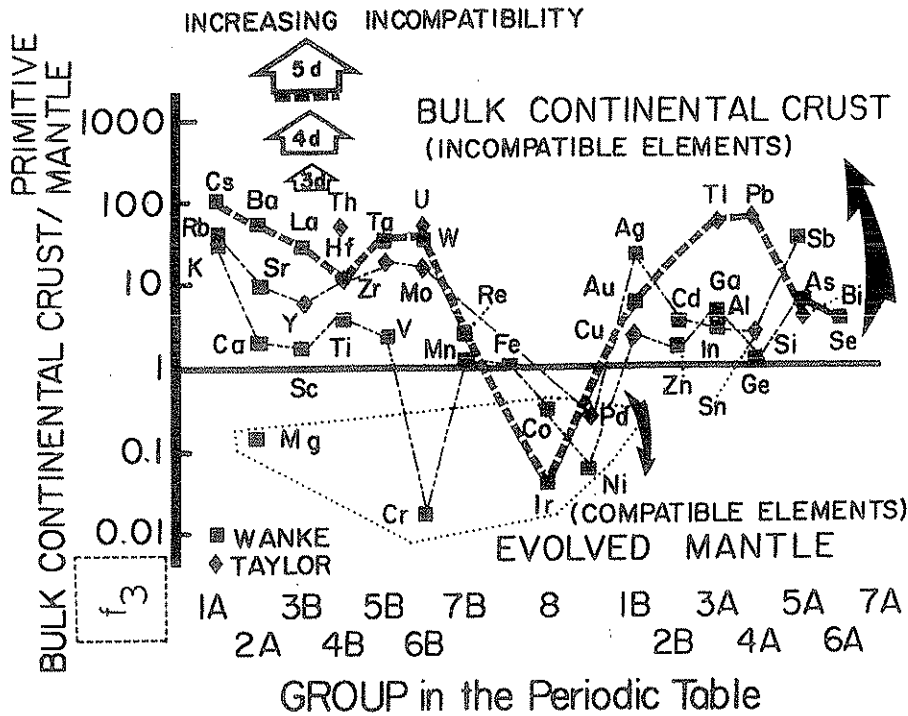
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Fig. 2. Mantle fractionation factor f_2. Mantle is depleted in moderately and strongly siderophile elements apparently entering the Earth's core. Primitive mantle data are based on analysis of ultramafic nodules (Wanke et al., 1984). For comparison, data on Fe, Co and Ni in lherzolites from the Trinity Alpine, California, peridotite (Quick, 1983) are identical, as indicated by the tips of the *arrows*. Data on bulk Earth are from Anders (1977).

the Archaen and post-Archean crustal growth processes (Taylor and McLennan, 1985).

The bulk post-Archean continental fractionation factors (f_3), given by ratios of elemental abundances in the bulk continental crust (Taylor and McLennan, 1985) to primitive mantle (Wanke et al., 1984), show a systematic variation with enrichment in the continental crust, increasing from periods 4–6. In general, most ore metals are enriched in the continental crust by factors of 2–100, apparently indicating their behavior as incompatible elements during partial melting of the mantle through incorporation in basaltic liquids which ascend to form oceanic crust which is further modified during continental growth.

This conclusion is supported by crystal–liquid partitioning data on andesites and basalts for Period-4 metals summarized in Henderson (1982). Using these data, it is clear that partition coefficients exhibit a maximum in the central Groups (Cr, Mn, Fe, Co and Ni) of the Periodic Table, corresponding to the

minimum in Fig. 3 for the compatible elements in the mantle. Specifically, partition coefficients for incompatible metals, K to Sc, increase with atomic number from 0.01 up to Cr which has a coefficient slightly > 1.0. The compatible elements, Cr, Mn, Fe, Co and Ni have increasing partition coefficients. However, metals with atomic numbers higher than Ni, e.g. Zn and In, have partition coefficients which fall sharply to values between 0.1 and 0.001, again in the range of incompatible elements.

The maximum incompatible element enrichment factor attained for the bulk continental crust of ~ 100 is exhibited by Cs. This is consistent with derivation of the continental crust from the primitive mantle subject to mass-balance constraints which limit the maximum fractionation factor to a value of ~ 140 for elements completely extracted from the mantle.

Considering the continental crust to be vertically heterogeneous and subdivided into an upper and lower portion in the simplest of models (Taylor and McLennan, 1985) yields

Fig. 3. Bulk continental crust fractionation f_3 from the primitive mantle. Most metals are enriched in the crust relative to the mantle by factors varying systematically with Period, but not exceeding 160, a maximum limit imposed by mass balances through the relative masses of the crust and mantle. Incompatible elements are extracted from the mantle by partial melting, and ascend in basaltic magmas into the crust. The only elements apparently not extracted from the mantle are those accommodated as constituents in mantle minerals such as olivine, pyroxene and spinel (Fe, Ni, Co). Data are from Wanke et al. (1984) and Taylor and McLennan (1985).

fractionation factors which are shown in Fig. 4. Direct sampling of the upper crust makes estimates of its overall composition more accurate than those inferred for the lower continental crust. The proposed lower-crustal composition calculated by Taylor and McLennan (1985) was obtained from their total crustal composition by subtracting the upper-crustal values, subject to a mass-balance constraint in which the upper crust is 25% of the mass of the total crust. Use of these compositional estimates indicates that Period-4 metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) are fractionated into the lower crust along with the siderophile elements (Ir, Au, Ag, Pd) from Periods 5 and 6. The remainder of the ore metals (U, Th, Mo, Ta, W, Pb, Bi) are clearly fractionated into the upper crust and represent material derived by intracrustal partial melting of more primitive lower continental crust or

melting of still older continental crust. The composition of the continental crust used here is from (Taylor and McLennan, 1985) and is inferred from the uniformity of sedimentary rock compositions which reflect a wide sampling of the exposed crust and a variety of crustal processes. Shown are results using post-Archean continental crustal values, which differ from Archean values mainly in that the latter are richer in Cr, Fe and Ni.

3.4. Ore-forming processes

The systematics relating metallogenic history to crustal evolution have been described by Hutchinson (1981) and Meyer (1985). Growth of the continental crust is known to have been episodic and most rapid ~2.5–3 Ga ago (McCulloch and Wasserburg, 1978; Taylor and
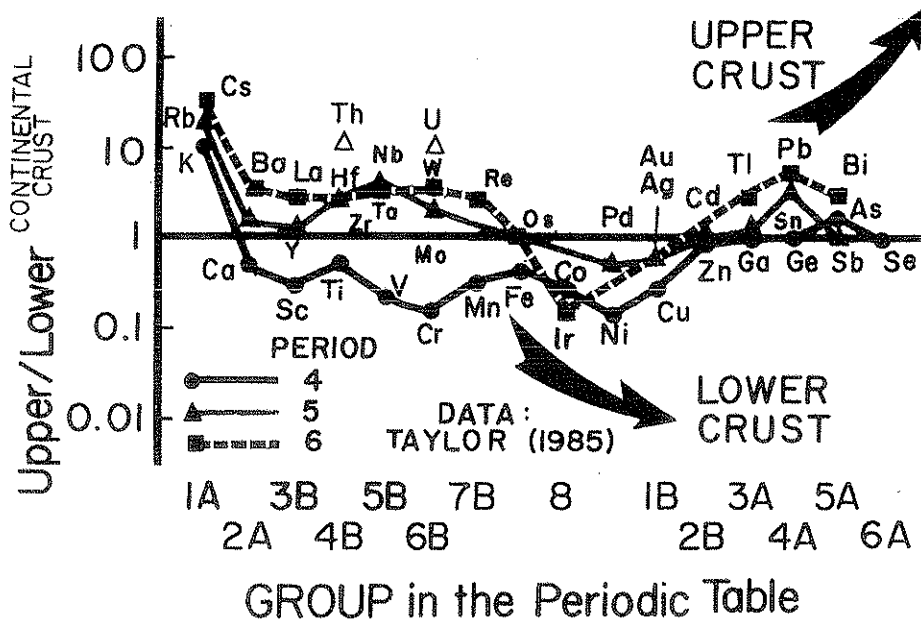
Fig. 4. Fractionation between the upper and lower continental crust. The upper crust may be derived from the lower crust by magmatic processes. The effect is to separate groups of ore metals in accord with Periods by factors < 10. Data are from Taylor and McLennan (1985).

McLennan, 1985). This crustal event is manifest in the evolution of the structural and chemical characteristics of metallic ore deposits formed in supracrustal environments (Hutchinson, 1981; Sawkins, 1983; Meyer, 1985). Before this rapid growth phase and stabilization of continental cratons, various types of metallic ore deposits formed in which Ni-, Au- and Fe-rich stratiform segregations accumulated in linear submarine rift systems where mafic and ultramafic lavas erupted on the sea floor following their ascent from the mantle. With more rapid continental growth, deposits containing Cu and Zn formed in differentiated submarine volcanic piles resulting from the remelting of older, perhaps more primitive volcanic crust. Once the continents were largely formed by 2.5 Ga ago, sedimentary deposits of Fe formed on the margins of continents in stable rifted basins as submarine hydrothermal accumulations. At the same time within stable cratonal masses, ore deposits of Cr, Ni and Pt formed by differentiation within large layered mafic intrusions. Sedimentary deposits formed where enormous quantities of Cu, Zn, Pb and Ag were precipitated from hot aqueous fluids circulating in rift basins. Finally, during the recent 200-Ma-old episode of sea-floor spreading and plate tectonics, a varied array of deposits have fixed Cu, Mo, Cr, Zn, Pb, Ag, Au, U, Sn and W in the continental crust.

These complex and evolving multistage ore-forming fractionation processes have operated locally as varied and efficient outgrowths of crustal fractionation. The overall enrichments necessary to attain ore-grade concentrations can be described simplistically by the fractionation factor (f_4). Here, these factors are based upon a normalized minimum mining metal grade defined in such a way as to minimize variable technological components in the factor such as increase in production costs with mining depth. Nevertheless, the definition of ore as mineable concentrations makes it impossible to totally eliminate economic considerations. Alternative definitions which might simply use

a certain metal concentration instead, would not have relevance in the context of mining. Consequently, a minimum value of US $ 15/t[*1] of in situ ore is used in conjunction with average 1984 metal prices (Dayton, 1985). For example, an ore containing 1.10 wt.% Cu selling for $ 0.68 lb.$^{-1}$[*2] has an in situ value of $ 15.00. Undoubtedly there is a temporal effect on enrichment factors defined using metal prices, but the factors so defined are internally consistent with a possible exception that certain metals, e.g. Cr, are used in specific metallurgical applications. For example, because chemical processing is not feasible in the preparation of refractory furnace linings made of chromite, such materials require a very high mining grade.

Ore-forming processes (Fig. 5) have enriched the crust by fractionation factors (f_4) that increase with atomic number from ~ 2 to 200 for the Period-4 metals, Ti to Zn, which are mined as primary ore minerals such as ilmenite ($FeTiO_3$), hematite (Fe_2O_3) and sphalerite (ZnS). Increasing, though erratic fractionation factors of 100 to several thousand for Period-5 and -6 metals, Mo to Sb and Ta to Bi, respectively, are higher in general than factors of Period-4 metals.

The maximum fractionation factor for any metal in Periods 5 or 6 that is mined as a primary ore constituent is 1500 for Pb. However, certain metals in Periods 5 and 6 (Ir, Pd, Cd, In, Bi and Sb) are often recovered instead as by-products of mining other more abundant metals which, in contrast to these rare elements dispersed in other minerals, form independent ore compounds such as Au, MoS_2, Ag_2S, SnO_2 and PbS. The fractionation factors for these dispersed elements should then be considered only as apparent fractionation factors, as they represent approximate enrichment values were these elements to be mined as principal ore constituents and not simply recovered as by-

*1 t = 1 metric tonne = 10^3 kg.
*2 1 lb. = 1 (U.S.) pound = 0.4536 kg.

products. These apparent fractionation factors exceed 1500, and fall in the range of $3.4 \cdot 10^3$ (Pd) to 10^5 (Cd, In, Sb, Ir, Bi).

With this cautionary note it is possible to interpret the general increase in values of f_4 with atomic number, which is apparent in Fig. 5. These trends, if in fact real, appear to be unlike the fractionation patterns f_1, f_2 and f_3 which each exhibit major disruptions, either maxima or minima within Periods over certain Groups of the Periodic Table. These were explained earlier as differential chemical effects due respectively to variable condensation volatility (Fig. 1), core formation over multiple growth phases (Fig. 2) and crystal–liquid fractionation in the mantle (Fig. 3).

The general increase in ore-forming fractionation factors with atomic number can be rationalized in part by considering that crustal abundances of Co, Ni, Cu and Zn are lower than that of Ti, V, Cr, Mn and Fe, implying that the former elements must be enriched relatively effectively to reach minimum ore grades, the mean price of each group being roughly equal. However, this relationship between abundance, metal price and fractionation factor may involve other factors as well.

Another, more systematic and fundamental effect which relates to the distribution of ore minerals as a function of atomic number (Fig. 5) comes from thermodynamic arguments. It is well known that thermodynamic properties of inorganic compounds such as standard state enthalpy of formation from the elements vary systematically (Lagowski, 1973; Parish, 1977) across Periods of the Periodic Table (Fig. 6). Very stable (low enthalpy) oxide ore phases with a variety of possible valences (2, 3 and 4) dominate Period (4) (Ti to Fe) but beyond, from Co to Zn, sulfides predominate with only subordinate oxides, SnO_2 being one such compound. Above intermediate atomic numbers native metals (Cu, Au, Ag and Hg) occur in Groups where sulfide and oxide enthalpies of formation from the elements increase to values
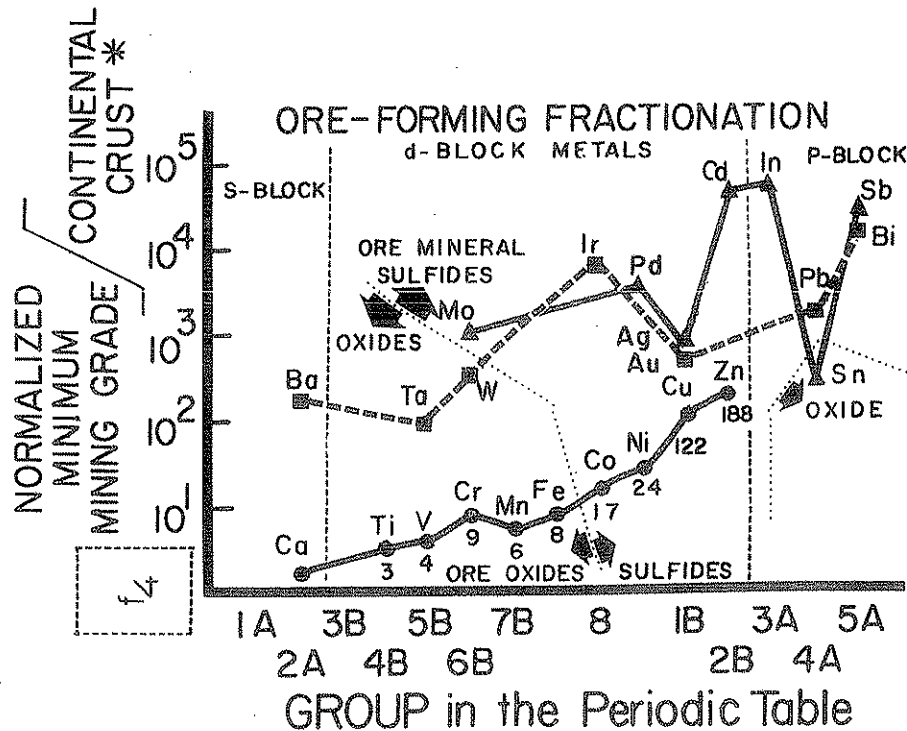
Fig. 5. Final ore-forming fractionation f_4 expressed as the ratio of normalized minimum mining metal grades to continental crustal abundances. In general fractionation factors increase with atomic number. Period-5 and -6 metals have fractionation factors almost two orders of magnitude greater than Period-4 metals (Sc to Zn). These normalized fractionation factors differ from the ones presented in past work (Clarke concentration numbers) in that those shown here take into account the immediate crustal (upper or lower) source of metals (Table I, colums 3–5; Fig. 4) and are normalized to a common production cost. Metal values are discussed in text. Data are from Taylor and McLennan (1985). See text for discussion of apparent fractionation factors of dispersed elements, e.g. Cd and In. Notice that ore minerals are predominantly oxides on the left and sulfides on the right with a few native metals (Au, Cu, Ag, Hg) in the middle. This pattern occurs also in Fig. 6.

approaching zero. Therefore the distribution of metal oxides, sulfides and native elements in this thermodynamic plot (Fig. 6) is consistent with ore metal mineral types distributed as shown in Fig. 5. This implies that observed ore-forming fractionation factors are in general correlative with mineral enthalpies. Such a correlation may be due essentially to the large contribution of enthalpy to Gibbs free energy and hence mineral solubility in transport fluids, either aqueous or silicate magma which can be viewed as solvents affecting fractionation. Furthermore an anomaly in the generalization about apparent monotonicity of f_4 shown in Fig. 5, that is the metal, Sn, can be explained too by the low enthalpy of formation of SnO_2 as seen in Fig. 6.

4. Conclusions

For purposes of comparing ore-forming fractionation with the other transport processes a summary of all fractionation factors is presented (Table I) and shown graphically (Fig. 7) beginning with volatile-free C1 chondrites as representative of solar system elemental abundances. Over the sequence of events shown, many minor and trace elements are fractionated much more extensively than major elements. The relatively weak fractionation of major elements Fe, Si, Al, Ca and Mg is due largely to the fact that these elements in addition to oxygen constitute the bulk of the Earth and enrichments are therefore severely limited by material-balance considerations. Conse-
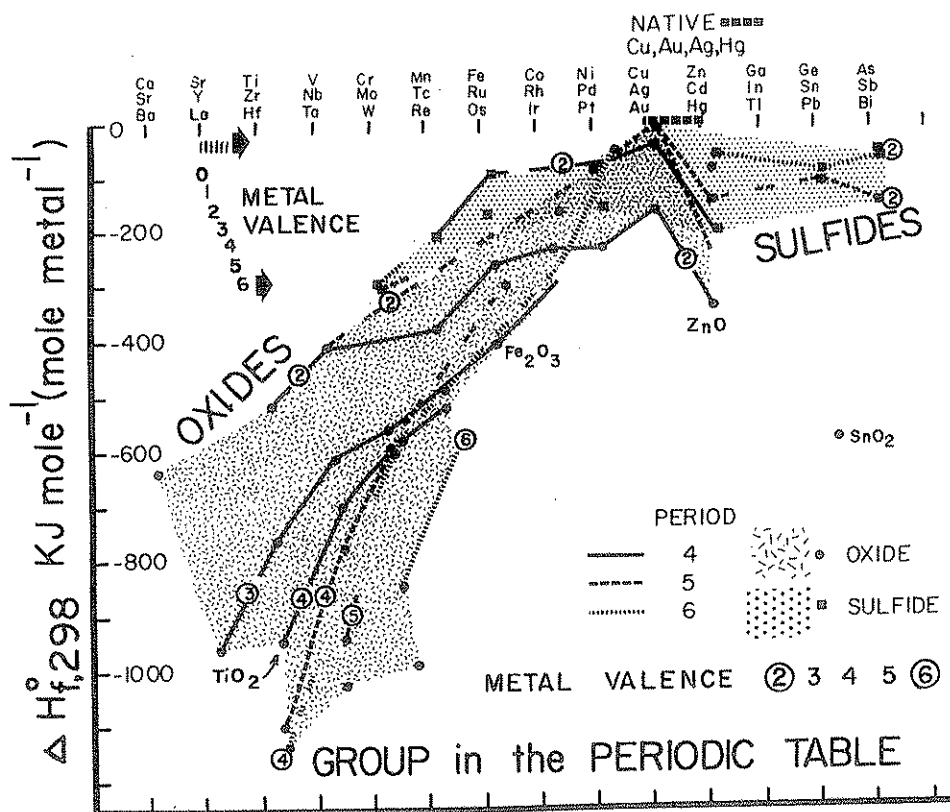
Fig. 6. Standard state enthalpy of formation per mole of metal for metal oxides, sulfides and native elements arranged in accord with the Groups of the Periodic Table. Valence of metal in compounds is *circled*. Each compound is plotted in accord with the valence of the metal: 0, 1, 2, 3, 4, 5, 6. The Period in the Periodic Table of the metal is indicated with *solid line* (Period 4), *long-dashed line* (Period 5) and *short-dashed line* (Period 6).

quently, at each stage of the fractionation process (Fig. 7), the abundances of the major elements display a high degree of negative covariation.

During growth of the continental crust (f_3), almost all ore metals are fractionated out of the mantle into this principal repository of ores near the surface of the Earth. Here, ore-forming processes (f_4) further enhance the concentration of metals from this primary state. Ore-forming enrichment factors of > 1000 are interpreted to be due either to the initial depletion of highly volatile elements (Cd, In, Bi) in the Earth during its nebular condensation or accretion or to segregation of highly siderophile elements (Au, Ir, Pd) into the Earth's metallic core reflected in inverse correlations of f_4 with f_2 (Fig. 8). For example, Au which was probably frac-

tionated out of the mantle into the core (Ringwood, 1979), has a low f_2 of 0.0018. With this depletion from the mantle, extremely high crustal and ore-forming enrichments are required to concentrate Au in the crust to mineable levels. Similar inverse correlations shown in Fig. 8 are manifestations of mass balances of primordial elements conserved throughout redistributive processes.

Comparison of f_4 with f_3 (Fig. 9) separates ore metals into two groups: those transported mainly by felsic magmas generated within the continental crust ($f_3 > 1$), e.g. Zn, Mo, W, Ba, in contrast to metals carried by more mafic magmas apparently originating directly from the mantle ($f_3 < 1$), e.g. Cr, Ni, Co, Ir, Pd. While Au is a highly siderophile metal entering the core (Fig. 9), the little Au remaining in the
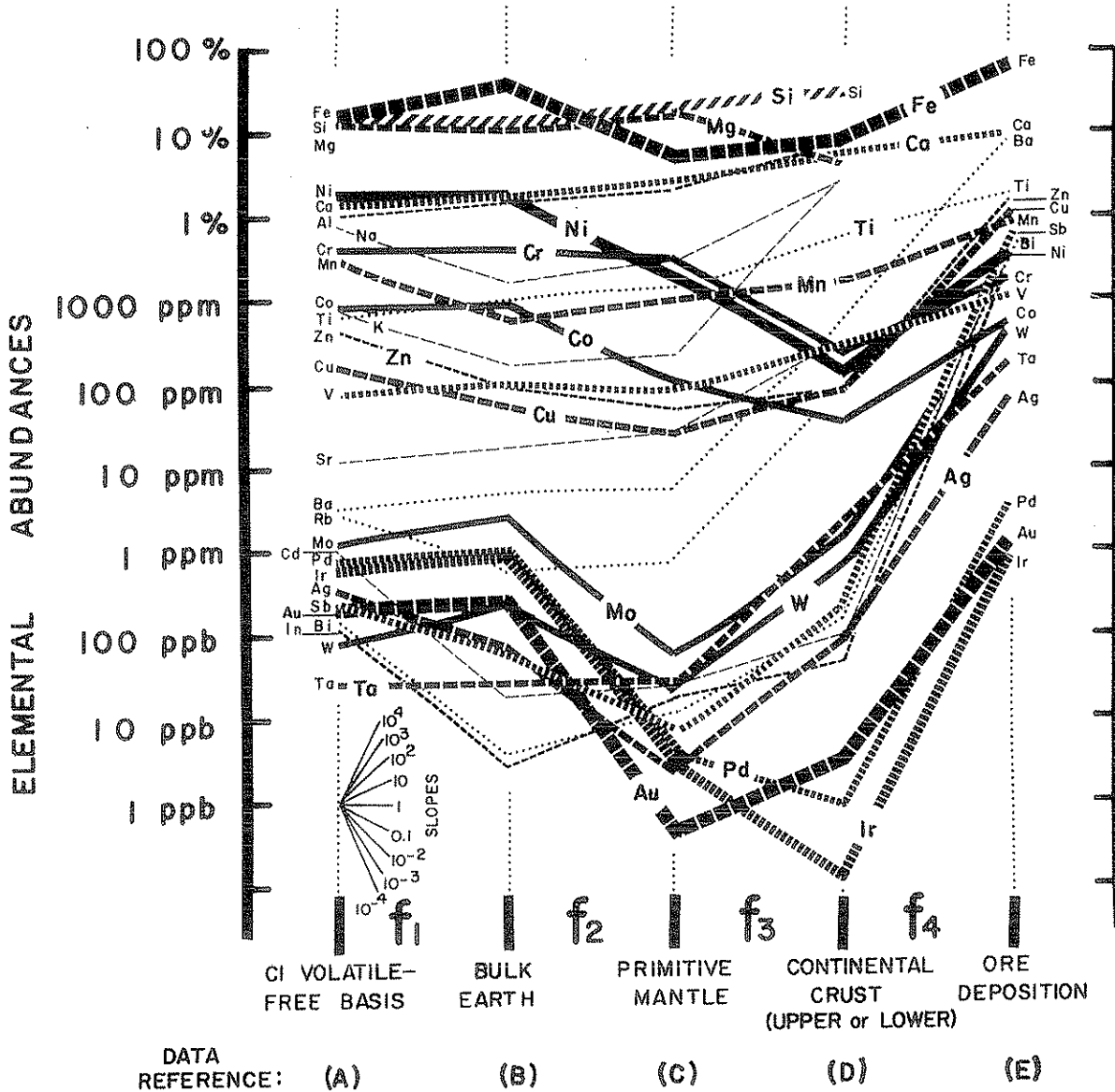
Fig. 7. Elemental abundance patterns through the four fractionations discussed in the text. Fractionation factors of > 1 (enrichments) appear as lines with positive slopes. Factors of < 1 (depletions) appear as lines with negative slopes. The magnitudes of the slopes are proportional to the fractionation factors (see *inert*). Notice the steep positive slopes for ore deposition. Elemental abundances at each chemical stage, for example for continental crustal growth, can be calculated by a chain multiplication beginning with C1 carbonaceous chondrite compositions corrected for loss of volatiles (equal to the product $C1 \times 1.5 \times f_1 \times f_2 \times f_3$). Major elements are only slightly fractionated, while minor and trace elements are strongly fractionated. Data references are shown at bottom: $A =$ Taylor and McLennan (1985); $B =$ Anders (1977); $C =$ Wanke et al. (1984); $D =$ Taylor and McLennan (1985); and $E =$ Dayton (1985). Abundances shown in column for ore deposition sum to > 100 wt.% as all types of ore metals are represented, not simply an analysis of a single rock.

primitive mantle has apparently been largely fractionated into the continental crust.

In summary, tentative fractionation patterns of elements within Periods of the Periodic Table appear to vary smoothly with atomic number, with Period-5 and -6 elements fractionated
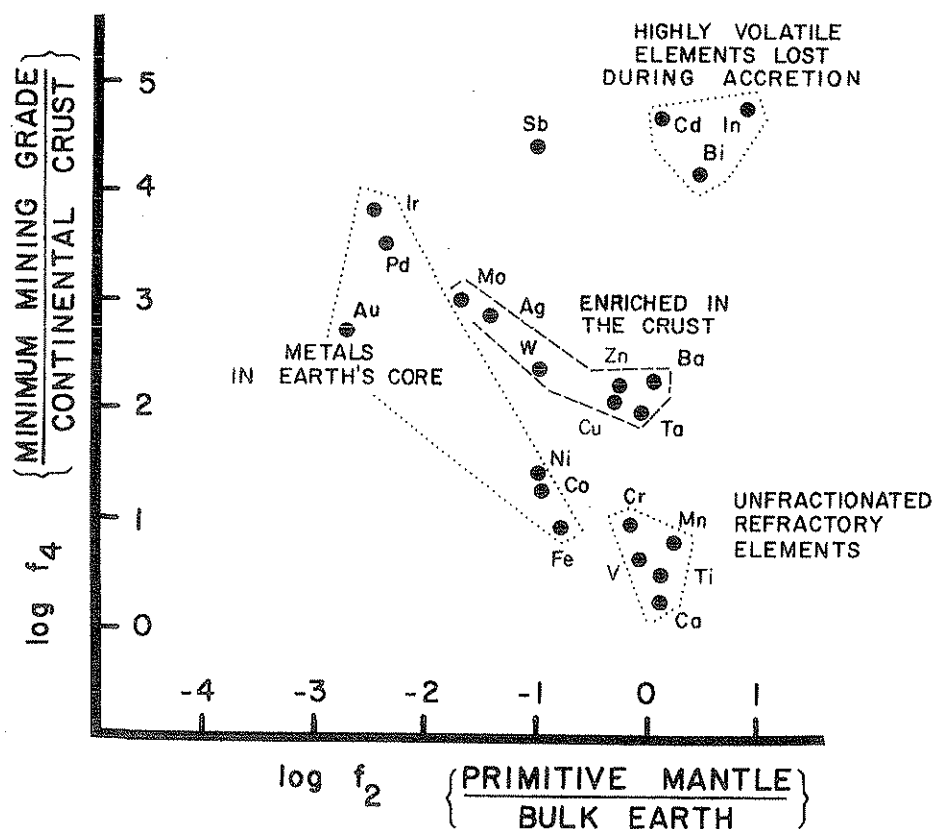
Fig. 8. Ore-forming fractionation (f_4) in relation to mantle fractionation (f_2) processes. Metals which are strongly depleted in the primitive mantle with very high ore-forming fractionation factors (Au, Pd, Ir) have been apparently removed from the mantle during core formation (Fig. 2), requiring extraordinarily high enrichments in the differentiated crust to attain mineable levels. Similarly, the volatile elements Cd, In and Bi were apparently depleted in the Earth during its accretion (Fig. 1). Metals, including Mo, Ag and Cu requiring only moderate enrichment in the crust to become ores have intermediate values of f_4 between 90 and 960. Metals relatively unaffected by core–mantle differentiation (Ti, V, Mn, Ca) require much less enrichment in the crust. Values of upper (U) or lower (L) continental crust used are given in Fig. 4 and Table I, columns 3-5.

(enriched or depleted) more than metals in Period 4. In general mass balances limit the maximum extent of fractionation in accord with the masses (size and density) of zones of depletion and enrichment within the Earth. Because of the relatively small size of ore deposits in comparison to the large reservoirs such as magmatic chambers from which metals have been extracted, ore-forming enrichment factors can exceed those of crustal growth by as much as two orders of magnitude (Table I, column 6).

Utilizing the coherent electronic framework provided by the Periodic Table through its progressive filling of transition metal d- and f-

orbitals, a systematic method of comparing preliminary fractionation patterns of common rock-forming elements to those of the less abundant trace ore metals is provided, and in so doing, supplies evidence of their common cogenetic geochemical behavior during terrestrial processes.

However, by no means are these results offered as being completely definitive, but are put forth rather as tentative though provocative results which are based upon development of a systematic method in critical need of much new analytical data. Interpretation of anomalies in the smooth fractionation trends may
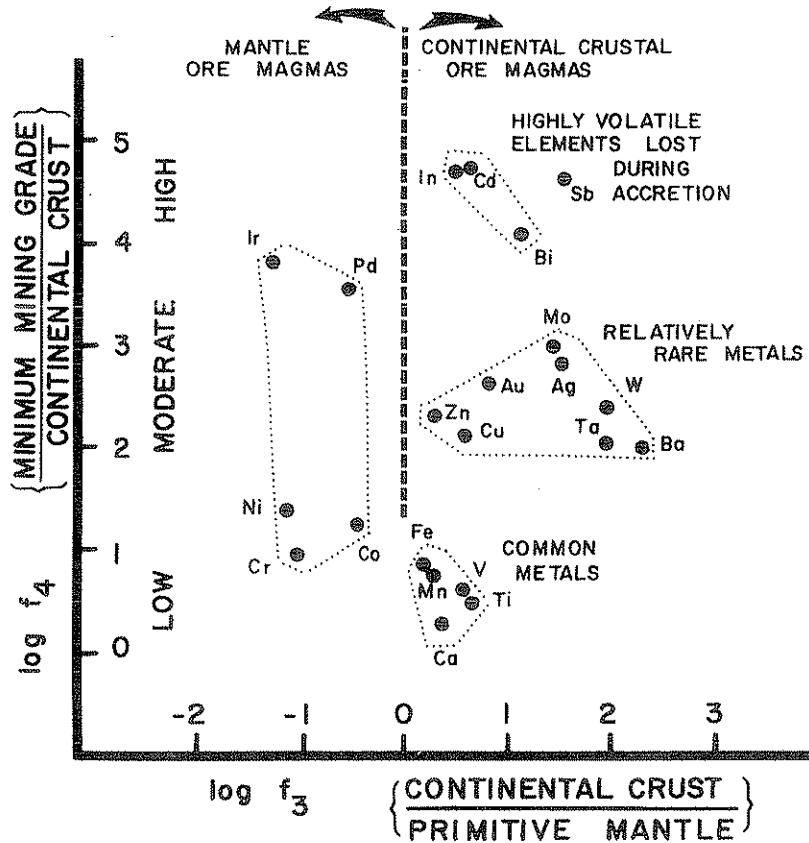
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Fig. 9. Ore-forming fractionation factor (f_4) as a function of crustal fractionation factor (f_3). Separation of metals into two groups is apparent: one from felsic magmas generated in the crust ($\log f_3 > 0$) and the other from mafic magmas originating directly from the mantle ($\log f_3 < 0$) (Cr, Ni, Co, Ir, Pd). Ore-forming fractionation factors of > 1000 for elements (Ir, Pd, Bi, Sb, In, Cd) which occur as dispersed elements in other ore minerals are referred to as "apparent" fractionation factors. Dispersed elements are produced as by-products of mining ore metals. See Table I for composition of upper (U) or lower (L) continental crust used.

provide new insights into terrestrial processes, or may indicate substantial errors in abundance data. Comprehensive rock analyses of transition metals are required, and these should span complete Periods.

The fractionation patterns within Periods are best referred to as chemical fractionation spectra, inasmuch as enrichment or depletion factors for each successive element are ordered in accord with the monotonic electronic structure of the elements. Work in progress on metasomatic processes in chemical weathering shows clearly that hydrochemical fractionation spectra for Period-4 and -5 transition metals are

continuous, well-behaved functions of mineral solubilities.

In this respect, ore deposits provide an almost unique opportunity to examine the thermodynamic controls on enrichment of these otherwise rare elements. Rather than occurring as dispersed species in solid solution in rock-forming minerals, ore metals in mineable hydrothermal deposits become concentrated to the point of attainment of the aqueous solubility product of ore sulfides, oxides, or native metals. Fractionation factors required for ore-grade concentration apparently increase with atomic number for all three transition metal series. These trends, though imperfectly known, are

consistent with decreasing stability inferred from increasing enthalpy trends.

Overall, most ore-forming processes are extensions of fractionation originating in the mantle, with ore metals behaving as incompatible elements released by partial melting, and ultimately becoming part of the continental crust through magmatic activity. Throughout the simplified chain of fractionation processes described, the importance of continental crust formation stands out as a major factor in the progressive enrichment of all ore metals except Ni, Co, Ir, Pt and Cr. Supracrustal tectonic and surficial environments then provide varied opportunities for further multistage enrichment by magmatic and hydrochemical activity, which is essential to attainment of ore-grade concentrations.

It is therefore clear that we should be careful in making inferences about the mineral potential of other inner planets based upon metallogenic processes recognized on Earth. The success of planetary exploration may largely depend upon recognizing evidence of near-surface environments where multistage enrichment processes have occurred. Sampling should be done where it is possible to maximize the data required to infer fractionation trends. For example, positions near the edge of volcanic fields could provide opportunities to obtain a variety of critical samples, such as xenolith nodules, lavas and substrate materials.

Acknowledgements

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