

IONIC POTENTIAL CORRELATIONS WITH CHEMICAL PROCESSES OF RARE EARTHS IN THE SEA

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ABSTRACT

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Linear relationships are deduced between Ionic Potential (IP, charge/radius) of rare earth elements and their enthalpies of hydration, concentrations in some marine phases and their residence times in seawater. These relationships strongly suggest the dependence of the chemical behaviour of rare earth elements on their IP values in seawater. Empirical relations are found among various parameters considered.

INTRODUCTION

Ionic Potential (IP), defined as charge-to-radius ratio, is a measure of the geochemical mobility of the ion concerned. A.E. Fersman (1937), defined an energy constant (EK) for a cation during a geochemical process as

$$EK_{\text{cation}} = \frac{w^2}{2r} 0.75 (r + 0.20)$$

where w and r are charge and radius of the cation, respectively. The above equation is written in terms of IP as

$$EK_{\text{cation}} = \frac{0.75 (\text{IP})w}{2} (r + 0.20)$$

Earlier attempts found the relation between IP and geochemical distribution of elements (Chang Chen-Ping et al., 1979, and references therein) but, excepting one, none of these were aimed at rare earths. Recently, Whitfield and Turner (1983) linearly related an IP function to the seawater–crustal rock partition coefficients of these elements. All elements of this group exhibit excellent similarity in chemical behaviour; their ionic size variation is an important fractionation parameter in their partition between geological entities. The present paper attempts to reveal the strong IP dependence of rare earths in their geochemical processes.

DATA SOURCES AND COMPUTATIONS

Sources of the data are listed in Table I. The data have been used either directly or after performing necessary calculations.

TABLE I

Sources of data for rare earth parameters

Parameter	Source
1. Single ion enthalpies of hydration, ΔH^0 (kcal mol ⁻¹)	Burgess (1978)
2. Seawater and crustal rock concentrations	Turner et al. (1980)
3. Concentrations in ferromanganese nodules (ppm)	Elderfield et al. (1981)
4. Sedimentation rates ($\mu\text{g cm}^{-2} 10^{-3}$ years)	Piper (1974)
5. Oceanic residence times (years)	Elderfield and Greaves (1982)
6. Ionic radii of 3+ rare earth cations (Å^0)	Rösler and Lange (1972)

RESULTS AND DISCUSSION

ΔH^0 , a single ion enthalpy of hydration (Burgess, 1978), is the energy change during the formation of solvated cation from its ionic state in the gaseous phase, decreases with an increase in log IP (Fig. 1). This negative linear relation has a correlation coefficient (r) of 0.87 (Fig. 1 and Table II) which is significant at the 0.001 level. This reflects the increasing hydration

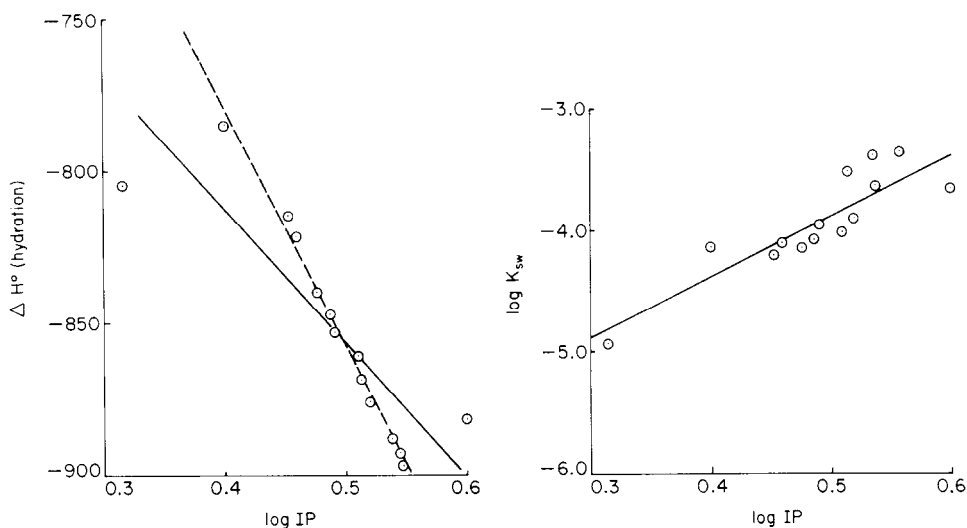


Fig. 1. log IP relations with ΔH^0 (hydration) of rare earths (Burgess, 1978). (—) all elements, (---) all elements except Ce and Er.

Fig. 2. Relation of log IP with $\log K_{sw}$.

TABLE II

Linear regression analyses ($y = mx + c$) between log IP and other parameters of REE

Parameter	m	c	r^a	σ_y^b	s^c
ΔH^0 (hydration)	-442	-637	-0.87	35.21	0.001
$\log K_{sw}$	+5.10	-6.43	+0.88	0.41	0.001
\log (sedimentation rate)	-7.56	+3.29	-0.83	0.71	0.010
$\log [M]_{\text{nodule}}$	-5.10	+3.90	-0.80	0.52	0.010
$\log \bar{t}_y$	+1.42	+2.43	+0.74	0.16	0.010

^a Observed correlation coefficient.^b Standard deviation of y on x .^c Level of significance for the observed correlations.

of rare earth cations with increase in atomic number as noted by Topp (1965). Relative to the comparatively low concentrations of heavier lanthanides in the earth's crust, the relatively high $-\Delta O^{2-}$ (Tardy and Garrels, 1976) values needed might contribute to their minor contents in seawater rather than the lighter ones. Tardy and Garrels (1976) defined ΔO^{2-} as a negative value of the free energy of reaction for the formation of an aqueous cation from its respective oxide.

In seawater almost all cations are complexed by inorganic and organic ligands to a large extent. Rare earth ions are no exception and their complexing ability increases from La to Lu (Topp, 1965). Martin et al. (1976) found an increase in the ratio of soluble rare earth elements versus detrital rare earth elements with decreasing ionic radii. Consequently, Fig. 2 shows a fairly positive relation for log IP with $\log K_{sw}$, the seawater-crustal rock partition coefficients, with an r value of 0.88 (Table II) which is significant at the 0.001 level. Seawater-crustal rock partition coefficients increase with the decrease in ΔH^0 (hydration) values. This related equation is

$$K_{sw} = 10^{-[(\Delta H^0 \text{ (hydration)/86.5}) - 13.784]}$$

In Fig. 3 log IP is plotted against rare-earth sedimentation rates (Piper, 1974) and their concentrations in a ferromanganese nodule (Elderfield et al., 1981) to find its impact on the elemental deposition at the deep sea floor (Fig. 3, curves a and b, respectively). These curves yield r values of -0.83 and -0.80 , respectively, and are significant at the 0.01 level (Table II). The compounds of the earlier members of the series have higher coordination numbers than compounds of the latter members (Burgess, 1978) and can be captured by particles in seawater by ion capture, though the polarising power increases with increase in atomic number (Turner and Whitfield, 1979). In addition, lighter lanthanides may substitute for sodium in mineral lattices or calcium in calcite minerals. Interestingly, although Ce deviates from the regression lines of Figs. 1 and 2, it is closer to the line

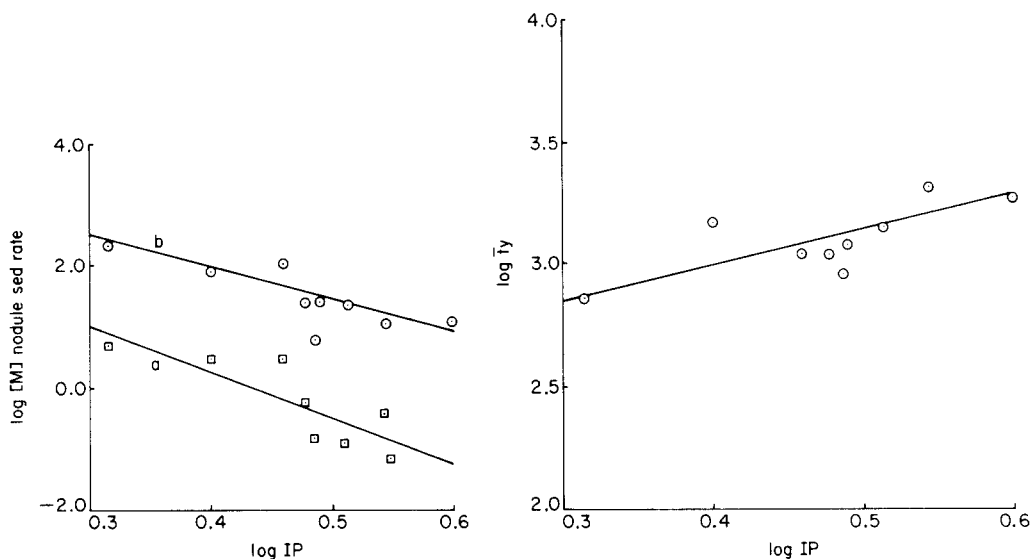


Fig. 3. Relation of log IP with sedimentation rates of Piper (1974; \square , curve a) and log $[M]_{\text{nodule}}$ of Elderfield et al. (1981; \circ , curve b).

Fig. 4. log IP relation with $\log \bar{t}_y$.

in Fig. 3 corresponding to the presence of higher concentrations of Ce^{3+} than Ce^{4+} in deep depositional environments.

Weathered ions from crustal rocks are being carried to the sea and are mainly concentrated in seawater and sediment phases. Elderfield et al. (1981) have shown approximately the same concentrations of lanthanides in ferromanganese nodules and sediments, excepting Ce. On this basis the mass equation between various major geological bodies for lanthanides may be written as

$$[M]_{\text{crust}} = [M]_{\text{sw}} + [M]_{\text{nod./sed.}}$$

and the distribution coefficient, in general, is

$$\frac{[M]_{\text{sw}} [M]_{\text{nod./sed.}}}{[M]_{\text{crust}}} = 10^{-2.59}$$

Also, the sedimentation pattern can be predicted by hydration enthalpies, since the latter are the criterion for stabilization of cations in aqueous solution, as is explicable from the equation

$$\text{Sedimentation rate} = 10^{[(\Delta H^{\circ}(\text{hydration})/58.37) + 14.191]}$$

Finally, log IP is examined against the residence times of rare earths ($\log \bar{t}_y$) in seawater. The most recent values of Elderfield and Greaves (1982) are considered. Figure 4 depicts the observed relation which has an

r value of + 0.74 and is significant at the 0.01 level. In this case also Ce falls close to the line. The residence time of elements in seawater is a function of both seawater—crustal rock partition coefficient and sedimentation rates. High $\log K_{sw}$ should result in a high $\log \bar{t}_y$ whereas a high log sedimentation rate results in low $\log \bar{t}_y$ values. The deduced equations relating these parameters illustrate these facts and are found to be

$$\frac{\log \bar{t}_y}{(\log K_{sw} + 15.18)} = 0.28$$

and

$$\log \bar{t}_y = -0.19 (\log (\text{sed. rate}) - 16.26)$$

A point worth mentioning is that although $\log K_{sw}$ and $\log \bar{t}_y$ show direct proportionality with $\log IP$ for rare earth elements, this is not the case for Lithophilic 1 elements (that have strong oxygen affinity with pure cationic behaviour) altogether, wherein they are negatively related (Kumar, 1983). However, the rare earths trend is similar to that of the alkali and alkaline earths, in this respect, and so a generalisation may be made that Lithophilic 1 elements with the same charge exhibit linear positive correlations for $\log IP$ with $\log K_{sw}$ and $\log \bar{t}_y$ (Kumar, 1983).

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