

Ionic Potential as a Controller of Seawater Composition

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Attempts have been made to study whether linear relations exist between ionic potentials (IP) and factors determining their fate in seawater. Various elements have been studied according to the geochemical classification. Lithophilic (L) elements depend on IP inversely but L2, L3, siderophilic and chalcophilic elements exhibit positive linear relationships with respect to seawater-crustal rock partition coefficients. The mean oceanic residence times of L1 elements show negative relationship. It is evident from the results that the residence times of elements in the sea are controlled by their IP.

Ionic potential (IP), charge-to-radius ratio of an ion, can be used as a solid state chemical parameter to study the mobility of an ion in the earth crust since it is a measure of the reactivity of the ion. In order to elucidate its significance, in determining the fate of elements in oceans, it is necessary to study the linear dependence of various reactions involved on IP. Ishibashi¹, and Banin and Navrot² found that the relations of IP with crustal rock-seawater and seawater-crustal rock partition coefficients, respectively, are complex. However, Chang Chen-Ping *et al.*³, and Whitfield and Turner⁴ used IP functions to derive linear relationships with $\log \bar{t}_y$ (log residence times of elements in seawater) and $\log K_{sw}$ (log seawater-crustal rock partition coefficients) respectively.

The present study aims to find some generalised relations, unlike the complex non-linear ones^{1,2}, between $\log IP$ (using individual IP values as such rather than IP functions^{3,4}) and other parameters. These parameters include $\log K_{sw}$, $\log P_y$ (log phytoplankton concentration factors), $\log K_{Mc}$ (stability constants for the interaction between metals and organically coated particulate matter) and $\log \bar{t}_y$ and are treated on the basis of geochemical classification⁵. The observed relations shall explain how a set of chemically similar elements depend on IP for the processes occurring in the sea.

IP is calculated obtaining ionic radii from Rösler and Lange⁶ with respect to the stable oxidation state of the dissolved element in seawater. $\log K_{sw}$ is calculated from the data of Turner *et al.*⁷ and $\log P_y$ is taken from Bowen⁸. The generalised regression equation of Balistrieri *et al.*⁹ (for an average surface site concentration of 1 mole.kg⁻¹)

$$\log K_{Mc} = 1.61 \log K_1^* + 13.56$$

given for the metal-organically coated particulate matter interaction, is used in the computation of $\log K_{Mc}$ values. The $\log K_1^*$ value (first hydrolysis constant)

is based on that reported by Turner *et al.*¹⁰ for zero ionic strength and corrected to an ionic strength of 0.72. The $\log \bar{t}_y$ value is evaluated from the sedimentation rates of Li¹¹.

All parameters investigated are plotted against $\log IP$ (Figs 1 to 4) keeping in view their geochemical classification. As per this classification, lithophilic (L) and chalcophilic (C) elements have strong affinity for oxygen and sulphur, respectively, whereas siderophilic

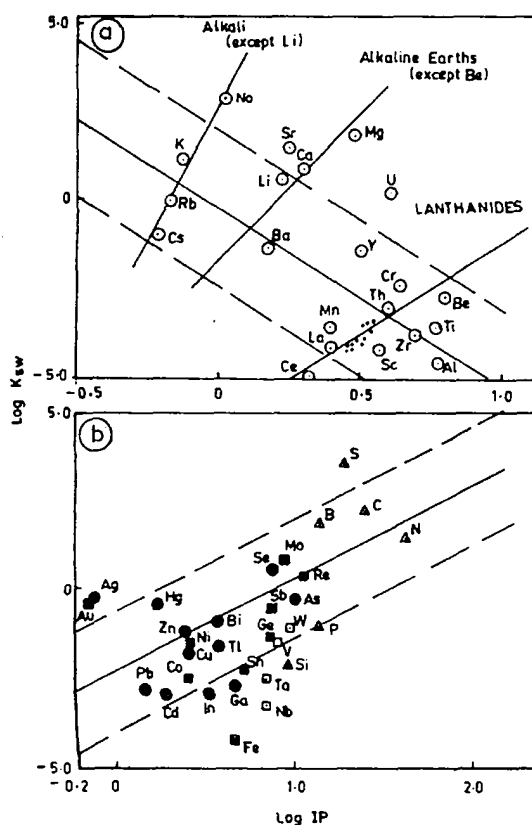


Fig. 1—(a) Relation between $\log IP$ and $\log K_{sw}$ for L1 elements. (b) $\log IP$ versus $\log K_{sw}$ for L2 (\square), L3 (Δ), siderophilic (\blacksquare) and chalcophilic (\bullet) elements

(S) elements have weak affinity for both. Lithophilic elements are subdivided into L1, L2 and L3 classes depending on their cationic, metal oxyanionic or cationic and nonmetal anionic behaviour, respectively⁵. In fact, elements with IP below 4 behave chemically as strong cations, those with IP between 4 and 12 as amphoteric ions and those with IP above 12 as oxyanion forming ions.

Fig. 1a depicts negative relation between log IP and log K_{sw} with a correlation coefficient (r) of 0.58 for L1 elements (Table 1). It is evident (Fig. 1a) that L1 elements with uniform ionic charge show positive linear relation, in general, as observed by Whitfield and Turner⁴. Alkali (except Li), alkaline earths (except Be) and lanthanides yield r values of +0.99, +0.77 and +0.88, respectively. A linear decrease in quantities of alkali and alkaline earth metal ions with increase in atomic number is observed, with the exception of Li and Be, respectively. Relation of log IP with log K_{sw} is shown in Fig. 1b for L2, L3, siderophilic and chalcophilic elements. These elements exhibit positive relation with a r of 0.45 (Table 1). Though r is relatively lower than that for L1 elements, L2, L3, siderophilic and chalcophilic elements show less standard deviation (Table 1).

In addition to biochemical needs IP may also be responsible for the selective ionic uptake by phytoplankton². Bowen⁸ reported an increase in affinity of metals towards phytoplankton with increase in ionic charge. The log IP shows negative relation with land organism-crustal rock partition coefficients for L1 elements² whereas the considered L1 elements (Fig. 2) yield positive relation between log IP and phytoplankton-seawater partition coefficients, which has a r of +0.68 (Table 1). L2, L3, siderophilic and chalcophilic elements do not have any significant relation ($r = -0.17$) in this case, and even by considering all L1, L2, L3, siderophilic and

chalcophilic elements together the observed r is only +0.20 (Table 1).

It is well known⁹ that dissolved trace metals react with surface phenolic or carboxylic groups of organically coated particulate matter, which does maintain the trace levels of these ions in the ocean. The effect of IP on log K_{Me} is given in Fig. 3. The relation is directly proportional, irrespective of their geochemical classification, and has a r of +0.67 which is highly significant (Table 1). In general, elements with high log IP and log K_{Me} (Fig. 3) have low log K_{sw} values (Figs 1a and 1b) showing more adsorption tendency on to the available particulates.

From the above results the effect of IP on the regulation of seawater composition is striking. Fig. 4 reveals the negative relation between log IP and log \bar{i}_y with a r of -0.65 (Table 1) for L1 elements. As discussed earlier (Fig. 1a), IA and IIA groups (except Li and Be, respectively) and lanthanides (with uniform

Table 1—Linear Relations ($y = mx + c$) Observed for the Investigated Parameters Against Log IP (x)

Parameter	Elements	m	c	r^*	σ^{**}	s^\dagger
log K_{sw}	A [‡]	-5.02	-0.19	-0.58	2.22	VS
	B [§]	+1.85	-2.33	+0.45	1.74	S
log P_y	A [‡]	+5.50	-0.36	+0.68	2.11	S
	C ^{§§}	+0.85	+0.25	+0.20	1.71	NS
log K_{Me}	C ^{§§}	+19.91	-8.05	+0.67	5.42	VS
log \bar{i}_y	A [‡]	-5.54	+5.64	-0.65	2.24	VS
	B [§]	-1.20	+5.53	-0.26	2.16	NS

*Observed correlation coefficient.

**Standard deviation of y on x.

†Level of significance at the correlation coefficient observed:

S = significant, VS = very highly significant and NS = not significant

‡All L1 elements.

§All L2, L3, S and C elements.

§§All L1, L2, L3, S and C elements.

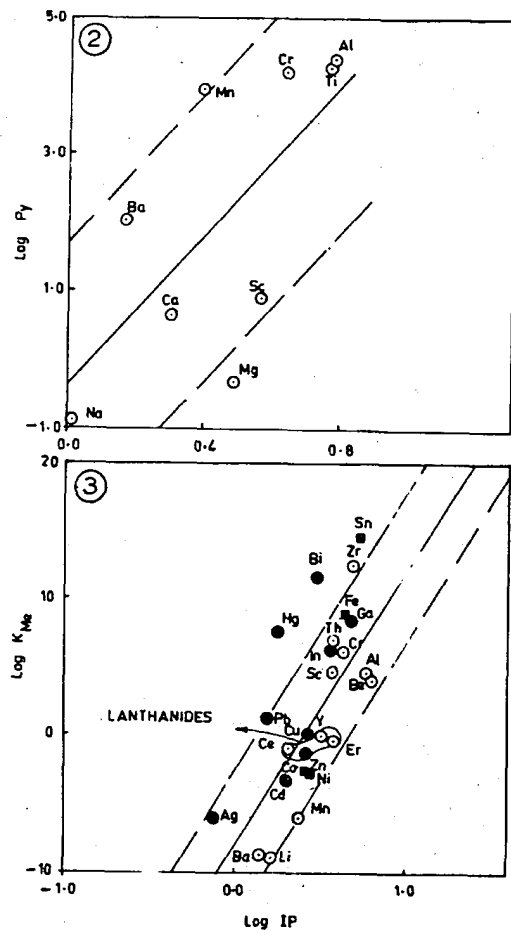


Fig. 2—Relation between log IP and log P_y for L1 elements

Fig. 3—Log IP versus log K_{Me} for L1 (○), L2 (□), L3 (Δ), siderophilic (■) and chalcophilic (●) elements

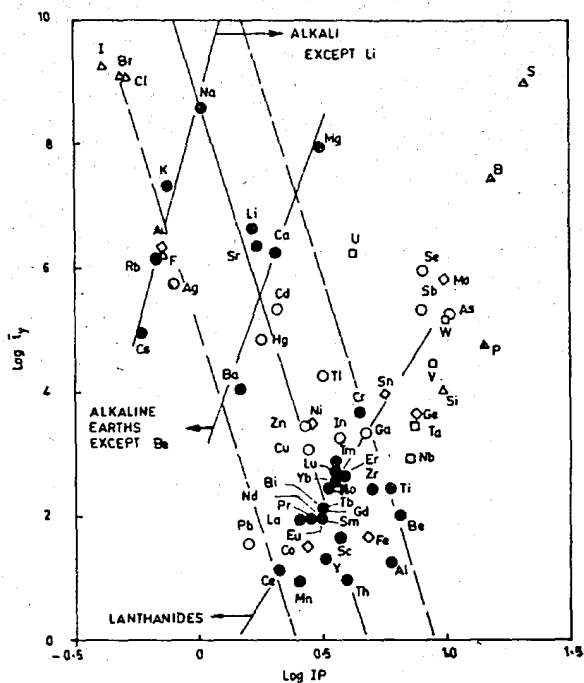


Fig. 4—Log IP relation with $\log \bar{I}_y$ for L1 (●), L2 (□), L3 (Δ), siderophilic (◊) and chalcophilic (○) elements. Main regression line is only for L1 elements

charge and decreasing radii) exhibit positive relationships (Fig. 4) with r of +0.96, +0.92, and +0.93, respectively. Li and Be have higher IP with respect to the other elements in their groups, but have low $\log \bar{I}_y$ values which may be due to their increased covalent character. In addition, the possibility of achieving +4 coordination number and the similar behaviour to Al may explain the low $\log \bar{I}_y$ values of Be. Obviously, L1 elements with low values of $\log K_{sw}$ and with high $\log IP$ and $\log K_{Mc}$ values have low residence times in seawater (Fig. 4). But the relation between $\log \bar{I}_y$ and $\log P_y$ is ambiguous due to less data points available (Fig. 2). L2, L3, S and C elements

investigated yielded scattered points for the plot of $\log IP$ against $\log \bar{I}_y$ (Fig. 4 and Table 1) and, in general, with $IP > 7$ many elements show high $\log \bar{I}_y$ due to oxyanion formation. Interestingly, these elements with high $\log IP$ and $\log K_{Mc}$ values do not have low $\log \bar{I}_y$ values (Fig. 4) but have low $\log K_{sw}$ values (Fig. 1b) with few exceptions. Actually, elements with $\log IP$ in range 0.6 to 1 would be expected to have low residence times in the sea, since they form amphoteric oxides and/or hydroxides⁶ which is not the case owing to many deviations (Fig. 4).

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