A conceptual framework for the evolutionary selection of biologically ‘essential’ elements

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Standard texts dutifully list 16 essential elements for plant growth, yet the literature indicates that the boundary between essential and nonessential nutrients for plants is not always clear. When animals and “lower” organisms are considered, the team of 16 is considerably expanded and the notion of essentiality is blurred[1]. Why are some elements more important than others to plants and to organisms in general? Here I propose three criteria by which elements might have been selected in the development of organisms: low atomic weight, at least modest abundance, and ease of assembly into complex structures. Assembly of the structural elements C, N, S, P, and O is based on valency and ionic potential. The selection of monovalent elements (bar H^+) and divalent elements (bar O^{2-}) involves a trade-off between low atomic mass and low ionic potential. The essentiality of Mo and non-essentiality of As remain a problem for this model. This conceptual framework provides a basis for re-evaluating the function of an element in the nutrition of plants, animals and “lower” organisms.

There are over 90 naturally occurring elements listed in the Periodic Table but only 16 are known to be essential for plant growth. A few additional elements have roles in specific plants e.g. Si in some grass crops, and a few others are essential for animals e.g. Se. Yet still, less than ¼ of the known elements are currently considered 'essential' for life. Why didn't life forms evolve to use more of the elements in the earth's crust? Were the other elements less abundant or less available when life started? Was there a different abundance of elements in the atmosphere or solution where life formed? What is special about the team of 16 elements?

With apologies for the insinuation, if we were to design an organism from a selection of elements we might adopt the following criteria:

1. low atomic mass. If life is going to grow skyward to compete for light, or to move across the surface, it has to battle gravity. Aquatic environments might provide some exceptions but minimising weight seems sensible.
2. relatively abundant. Given the immobility of plants, and the likely low mobility of early organisms, and the limited mobility of many of the elements themselves, a non-limiting supply would seem desirable.
3. easily assembled. Reactive elements (as opposed to group 8 elements, precious metal such as Au, Pt) but 'appropriate' bonds would be required. The concept of ionic potential is relevant to this last requirement, as might be electronegativity.

If we were to design the necessarily complex structures required for organisms, we would need elements capable of multiple bonds. Group 4 meets this requirement with tetravalent elements. As might be expected from criterion 1, C, the element of lowest atomic mass in the group, is the framework for organisms. In environments where weight is less of an issue, such as the ocean, Si successfully provides the structure for some sponges.

At the other extreme, monovalent elements can only be terminal parts of structures, so group 1 elements and H simply complete charge balance. The same is probably so for group 7. In order for a C polymer to expand (grow) there must be attachment points i.e. incomplete parts of the structure. These points are “rented” by elements of valence 1 and possibly 2, while waiting for new building units of glucose (for starch, cellulose) or amino acids (for proteins) to attach to the structure. Hence these terminal points must involve bonds of only modest strength. In contrast non-attachment points of the structure could be terminally occupied by the more strongly bonded H^+.

Between these extremes, multivalent ions such as S^{6+}, N^{5+} and N^{3-} contribute to structures, while divalent ions such as Mg and transition metals often have the role of “activators”, that is bridges between enzymes and substrates as shown in Table 9.1 of Gauch[1].

The coulombic force of attraction between charged bodies is given by the product of the charges divided by the separation distance. Therefore the ionic potential (ip) of an element is a measure of potential bond strength:

$$ip = z/r_i$$

where z is the valence and r_i is the ionic radius (nm in this letter, to be consistent with SI units) of the element in that valence state. I have used a coordination number of 6 in all cases except for H, though this probably varies within organisms. The ionic radii were compiled from the CRC Handbook[2] and, where elements were missing, from online sources [3,4] that agreed with values that were common with the Handbook. The value for reduced C (C^{4-}, as in CH_4) was problematic. In the absence of a listed value, I have used the atomic radius of 0.077 nm, which theoretically should be an underestimate of the ionic radius for the C^{4-} oxidation state. Hence the ip of 52 given for C^{4-} is theoretically an overestimate.

Figure 1 shows the ip for the first 56 elements. I have shown only the commonest biological oxidation states for most elements e.g. Mo^{6+}, As^{5+}, P^{5+}, Cr^{3+}, Fe^{2+}, Mn^{2+}, Cu^{2+}. Only for C (4+, 4-), N (5+, 3-) and S (6+, 2-) have I shown 2 oxidation states. The rank order for + oxidation states is: N^{5+} (384), C^{4+} (250), S^{6+} (207), P^{5+} (131) and B^{3+} (111). Also over ip of 100 are As^{5+} (109), Mo^{6+} (101) and Si^{4+} (100). Only As and Si are regarded as non-essential among the elements with ip > 100, but Si is used by rice and sugarcane. Certainly As is bioactive as a toxin, but is it also essential? Cr^{6+} also has ip > 100 (136) though it is shown in the figure in its more common and less toxic 3+ oxidation state. Among the – oxidation states, the rank order is C^{4-} (52), N^{3-} (20), O^{2-} (14) and S^{2-} (11). Therefore the elements with the highest ionic potentials tend strongly to be the elements that form the ‘backbone’ of biological structures. The high ip is due to both their high valence and their low r_i, the latter being largely a consequence of their low atomic mass.

Why are light elements such as Li and Be not essential elements? Is it due to their lower relative abundance compared to Na, Mg, K and Ca? But if so, why is the common element Na not essential for plants? Figure 2 shows the ip for monovalent and divalent elements. The lighter elements have higher ip which then tends to plateau with increase in atomic mass. Perhaps Li (Fig 2a) forms too strong a bond or voltage gradient to ‘rent’ attachment points. Possibly the same is partly true for Na, and might represent the mechanism of specific Na toxicity if it substitutes excessively for K. K is the lightest of the monovalents on the plateau of low ip and is the dominant monovalent cation in plants. The hypothesised monovalent site "renting" role of K would explain its need at growing points (attachment points). Hence Rb could partially substitute for K (Gauch Chapter 9)[1], and Na is known to partially substitute for K in halophiles [5], subject to mass and ip limitations respectively.

Similarly Be has the highest ip among the divalent cations (Fig 2c). Mg and Ca might represent a compromise between bond strength (ip) and atomic mass i.e. a weak bond without too much mass. The arrows on Figure 2c are my suggestions for where on one hand ip might be too high and where on the other hand the elements might be too weighty. The cluster of 10 divalent cations (including Ca) are mostly essential elements, with Ti and Ge being the exceptions. Do they have a biological role or have I selected the wrong oxidation states for their bioactive state?

Among the – charged monovalents F has the highest ip (Fig 2b). As for Li, F might form a voltage gradient too strong for casual charge balance, as indicated by their standard electrode potentials. That is, their electronegativities and high ip might result in bonds or voltage gradients that are too strong for simple low energy charge balance, or 'renting' of an incomplete structural site. Cl, Br and I have similar ip but Cl is the lightest. Some partial substitution of Br for Cl is known.

The relatively high negative ip values for O and S have already been shown to be associated with their essential role in biological structures. Se is not essential for plants but is essential for animals, leaving only the heaviest element, Te, with no apparent biological role (Fig 2d).

Therefore I suggest that for monovalent and divalent ions “essentiality” is associated with either:

higher values of ip for a structural bridging (O^{2-}) or terminal role (H^+), or

is based on a compromise between low ip and low mass for a bridging (divalent cations) or charge balancing role (K^+, Cl^-).

The model suggests that a certain amount of inter-replacement can occur between non-structural elements with similar ip e.g. Ca and Mg: K, Rb and Na: Cl and Br. This is not intended to imply complete substitutability. There might be certain chemical tasks that are element specific, and other tasks for which substitution is possible simply on the basis of similar ip. Similarly it would be foolish to suggest that ip is the sole basis for substitutability, as there is evidence to the contrary, with Mg being replacable by Co but not by Mn for photosynthetic phosphorylation (Gauch p226)[1].

Another puzzle is the essential nature of Mo. As can be seen in Figure 1, the hexavalent oxidation state provides a large ip, and hence Mo sits on a peak in the cycle of ip versus atomic number, suggestive of a structural role in organisms. Yet Mo is not part of the structure of organisms but rather is needed both for N_2 fixation and for assimilatory NO_3 reduction.

The elements of high ip tend to be enriched in biological structures compared with their abundance in crustal rocks [6]. The shape of the Banin- Navrot plots for biological/crustal enrichment could be a reflection of the conditions under which organisms evolved, as the authors[6] speculated, but given the increased abundance of free O_2 sometime over the last 4 billion years since the first organisms, the shape could additionally contain a reflection of a second phase of evolution during which a degree of protection from oxidative processes was required. Energy for organisms could initially be derived from reduced compounds but eventually other energy systems developed. For example, elements in the first enrichment peak and following descent of the Banin-Navrot plot for plants are associated with photosynthesis. Similarly, the assimilation of N_2 and NO_3 as opposed to the absorption of reduced N ions creates additional metabolic requirements on organisms, which includes protection from O_2 in the case of nitrogenase. Since Mo is required for the assimilation of neutral (N_2) and oxidised forms of N (NO_3) I speculate that Mo became an essential element after reduced forms of N became less abundant i.e. sole NH_4 supply could make Mo non-essential. Elements required for photosynthesis as an energy source and elements required for assimilatory NO_3 reduction might not have been among the initial group of essential elements.

Minerals in rocks and soil have Si as their primary structural element, again indicating that tetravalent elements are ideal for forming complex structures. Soil is the interface between geochemical and biochemical processes. Its composition reflects both its origin in rocks and the input of dead organisms. The composition of some sedimentary rocks (limestone, coal) can themselves reflect the activity of organisms. This interface is conceptualised in Figure 3. While rocks are based on Si, Fe(III) and Al structures, organisms are generally based on C, N, P structures. Both have the divalent elements S, Fe(II), O, Ca and Mg in common. My hypothesis/contention is that complex structures emerged based on elements with high ip and low atomic mass compared with rocks. These elements are currently, and possibly were, of modest relative abundance in the crust: P 0.1% 6th, S 0.05% 11th, C 0.03%, 19th and N in trace amounts only, though abundant in the atmosphere (78%, 1st). Crystallisation of minerals from cooling magma probably forced an increase in the relative concentration of these elements into the solution and gaseous phases. This is essentially the reciprocal of the Goldschmidt model for crystallisation from magma [7]. Bridging (other than O^{2-}) and terminal charge balancing (other than H^+) elements associated with C structures were provided by elements that were a compromise between the need for low ip and low atomic mass.

This analysis suggests that the team of 16 isn't necessarily exclusive. The concept of ionic potential suggests that substitutions can take place at least to some degree, and that therefore there are degrees of essentiality. C, H, N, P, S and O are critical for the biological structure, hence their role is immutable; some ions could be amenable to a degree of substitution (K by Rb and Na), while some elements (such as Si in grass crops and V in N-fixing Azotobacter) can sometimes fill a role. Given the example[8] that the uptake of cationic nutrients by mycorrhizal beech was largely influenced by ip it could be expected that various organisms have evolved roles for a wide range of elements, some "essential" and some opportunistic. Experimental substitution of ions for those of similar ip might therefore help to explain:

1. why some elements are non-essential but appear to have a role in at least some plants e.g. Si in grass crops
2. whether the stimulatory effects of non-essential elements is due to partial replacement of deficient essential elements e.g. Na for K.
3. the mechanism of toxicities e.g. Cd displacing Ca, and the reverse, the partial alleviation of toxicities e.g. Mg for MnII.

4. the triggering of genes by elements i.e. genetic by environmental interactions e.g. Arabidopsis under Al exposure [9].

References

1. Gauch, H.G. *Inorganic Plant Nutrition*. (Dowden, Hutchinson and Ross, Stroudsburg, 1972)

2. *CRC Handbook of Chemistry and Physics* Editor-in-Chief: D.R. Lide. (CRC Press, Boca Raton, 1994).

3. Barbalace, K. Periodic Table of Elements – Sorted by Ionic Radius. http://EnvironmentalChemistry.com/yogi/periodic/ionicradius.html (2009)

4. Wikipedia. Ionic radius. http://en.wikipedia.org/wiki/Ionic_radius.html (2009)

5. Brady, N.C. and Weil, R.R. *The Nature and Properties of Soils*. (Prentice Hall, New Jersey, 1996).

6. Banin, A. Navrot, J. Origin of life: clues from relations between chemical compositions of living organisms and natural environments. *Science* **189**, 550-551 (1975).

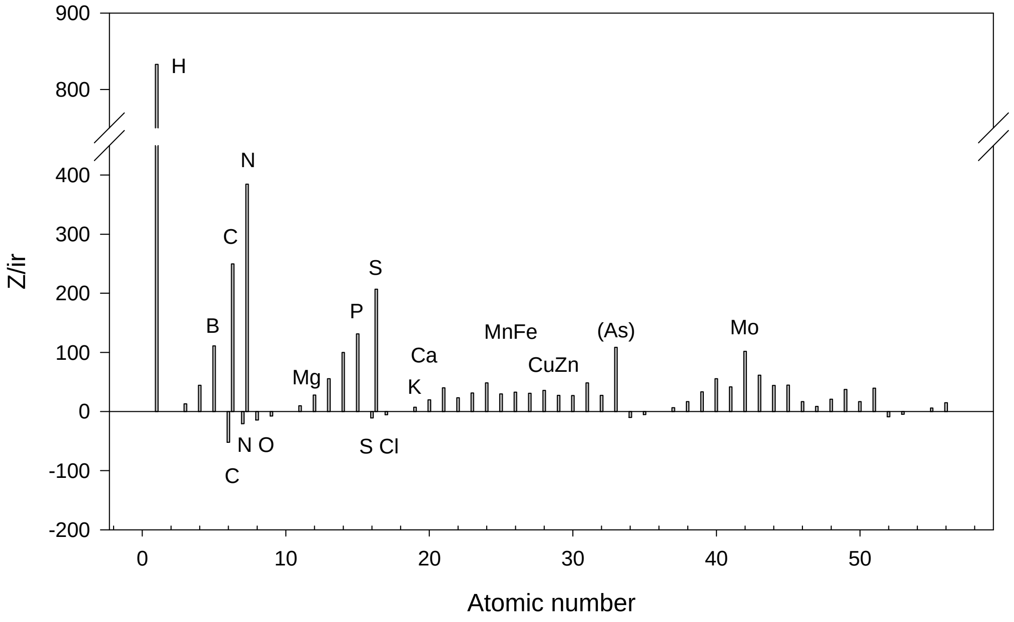
7. Railsback, L.B. An earth scientist's periodic table of the elements and their ions. *Geology* **31**, 737-740 (2003).

8. Tyler, G. Ionic charge, radius, and potential control root/soil concentration ratios of fifty cationic elements in the organic horizon of beech (Fagus sylvatica) forest podzol. *Science of the Total Environ*. **329**, 231-239 (2004).

9. Goodwin, S.B. and Sutter, T.R. Microarray analysis of Arabidopsis genome response to aluminum stress. *Biologia Plantarum* **53**, 85-99 (2009).

Figure legends

1. The ionic potential (valence/ionic radius in nm) of the first 56 elements of the periodic table.
2. The relationship between ionic potential, ip, and atomic number for a) monovalent cations, b) monovalent anions, c) divalent cations and d) divalent anions.
3. The biochemical: geochemical interface of the major elements.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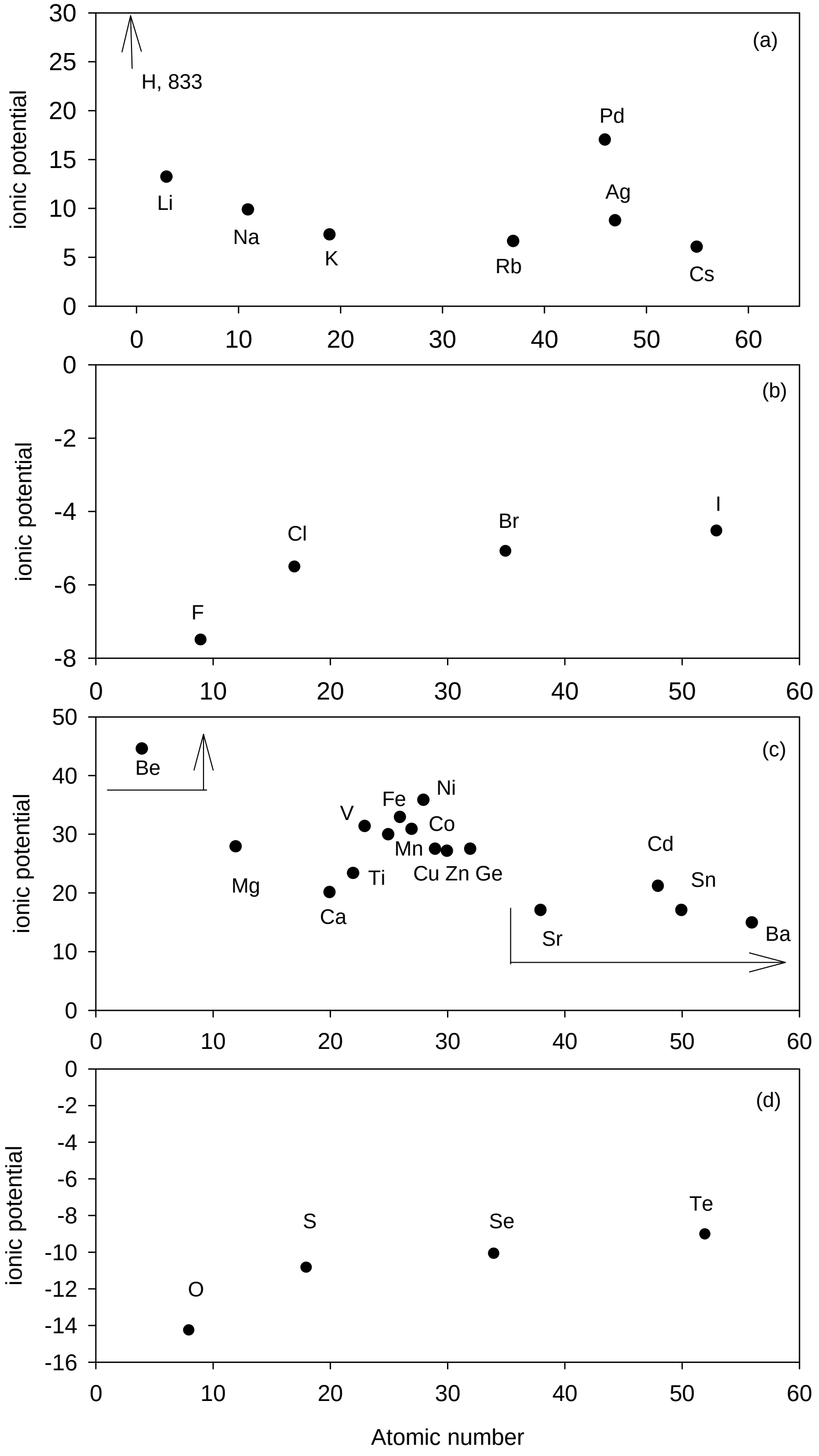
(a)
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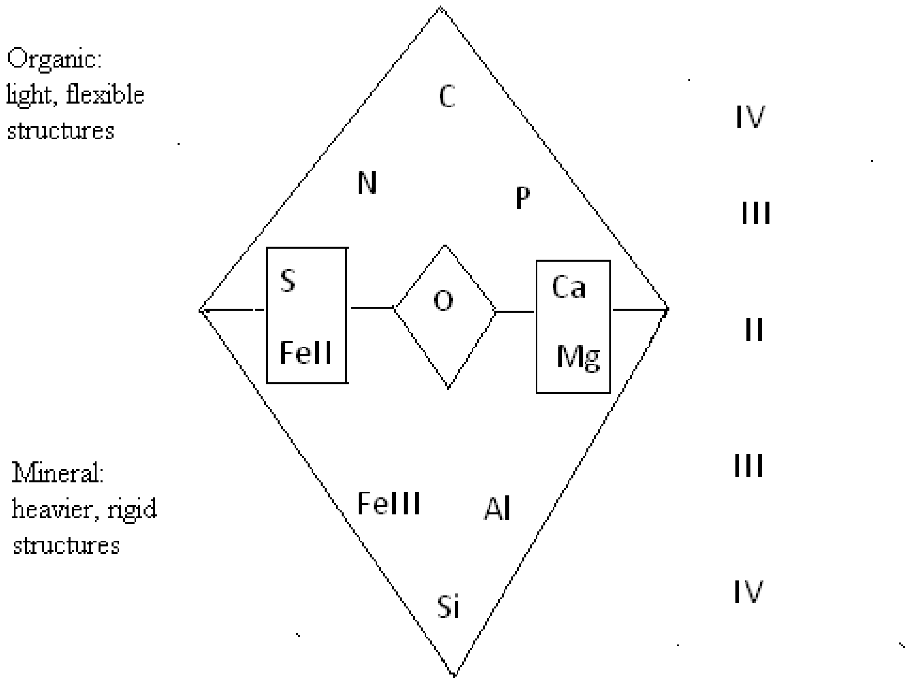
Organic:
light, flexible
structures
C
IV
N
P
III
S
FeII
O
Ca
Mg
II
Mineral:
heavier, rigid
structures
FeIII
Al
III
Si
IV