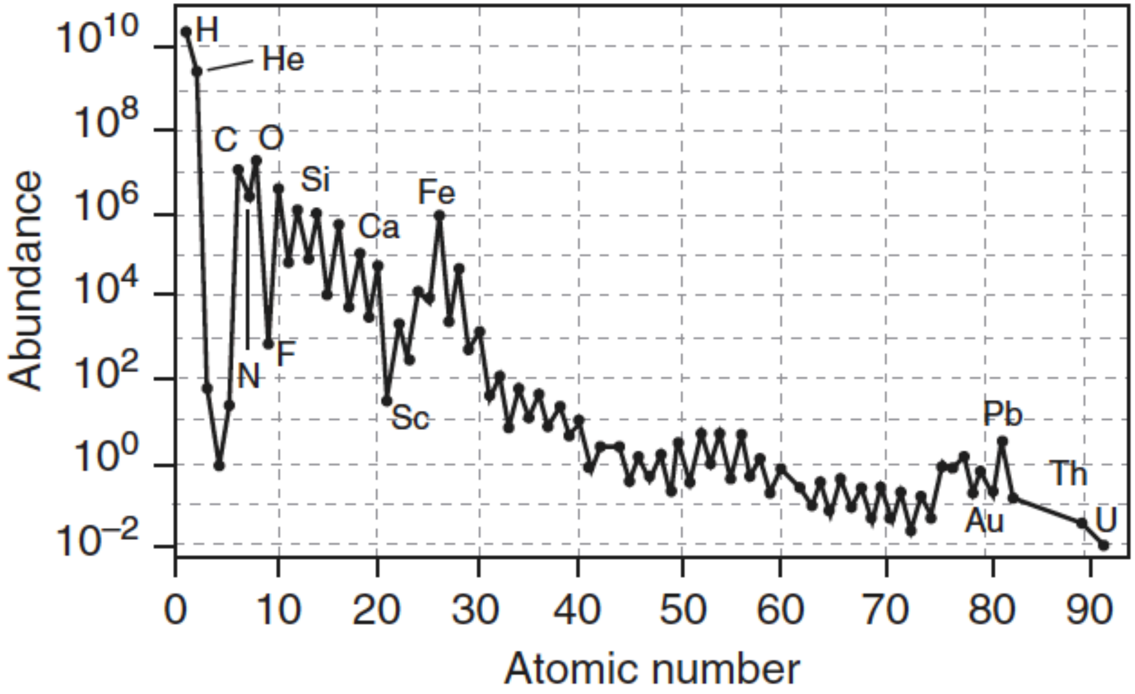
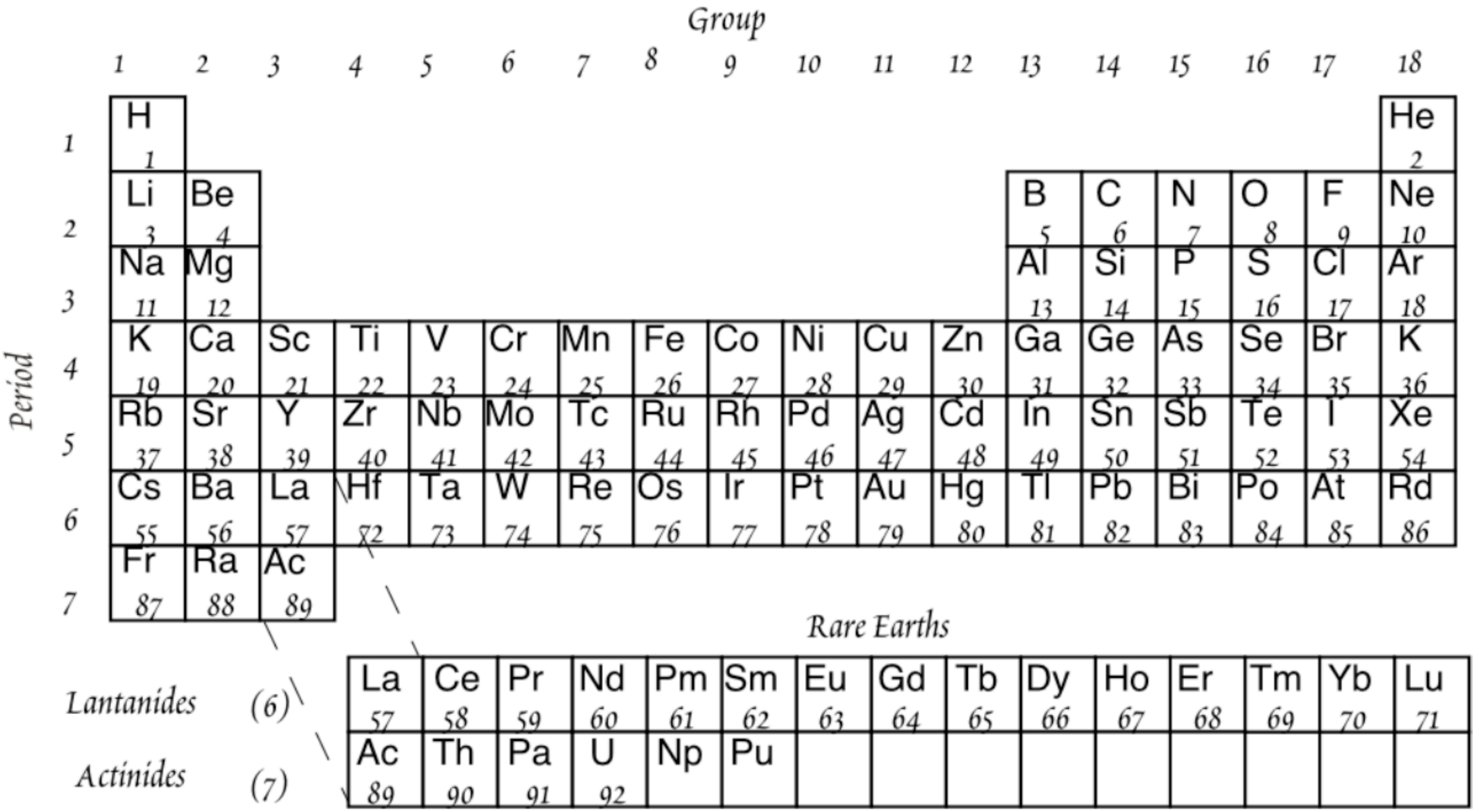
THE NATURALLY OCCURRING ELEMENTS – ORIGINS AND ABUNDANCES

The chemical elements that comprise Earth were mainly produced during the Big Bang approximately **12– 15** billion years ago.



Abundance of elements in the solar system **normalized** to Si = 10^6 on a logarithmic y-axis – this is a standard means of normalizing and plotting values for this type of data set.



	Group																	
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	K 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rd 86
7	Fr 87	Ra 88	Ac 89															

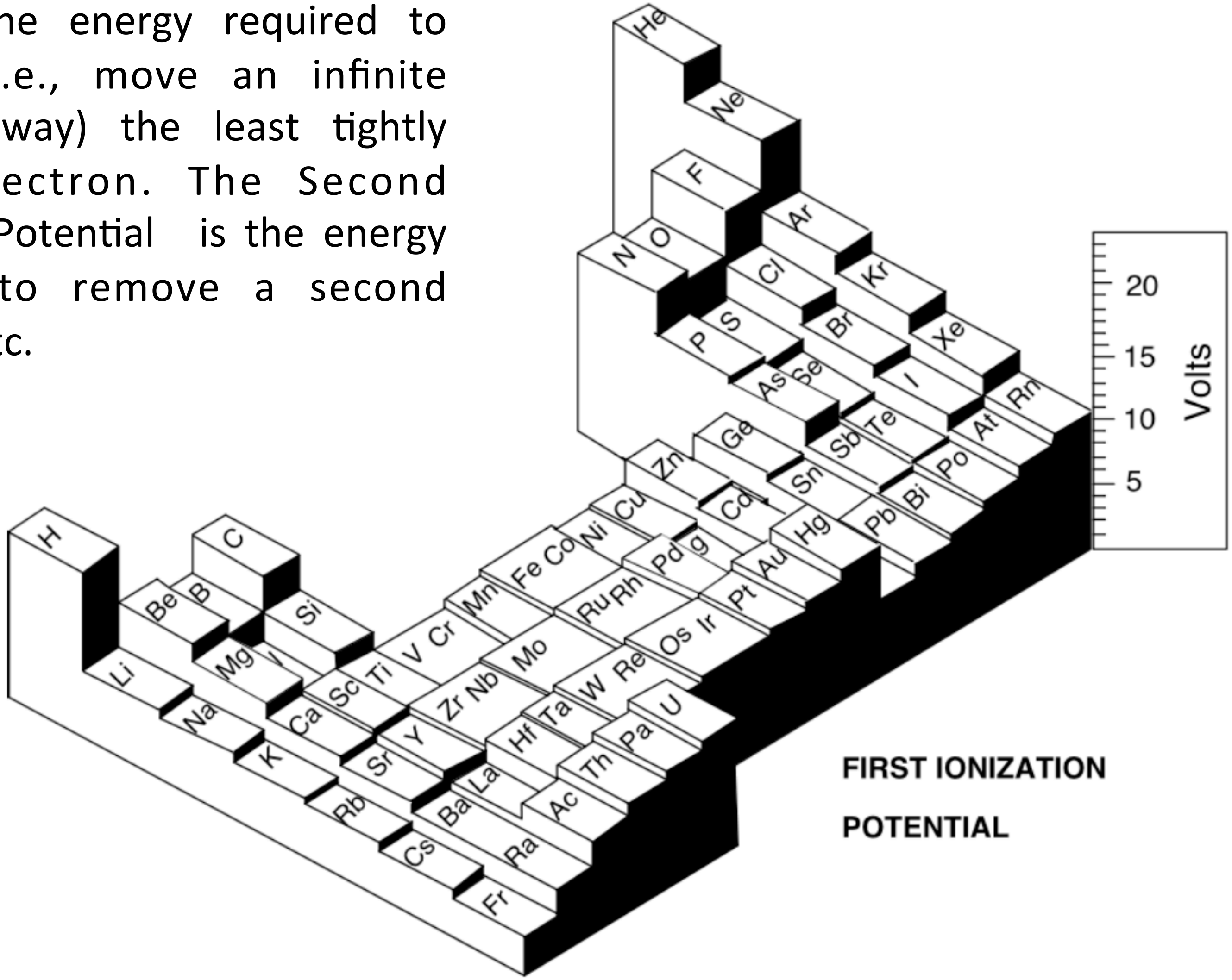
Rare Earths

Lantanides	(6)	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Actinides	(7)	Ac 89	Th 90	Pa 91	U 92	Np	Pu									

The **Periodic Table** showing symbols and atomic numbers of naturally occurring elements. Many older periodic tables number the groups as IA-VIIIA and IB-VIIB. This version shows the current **IUPAC Convention**.

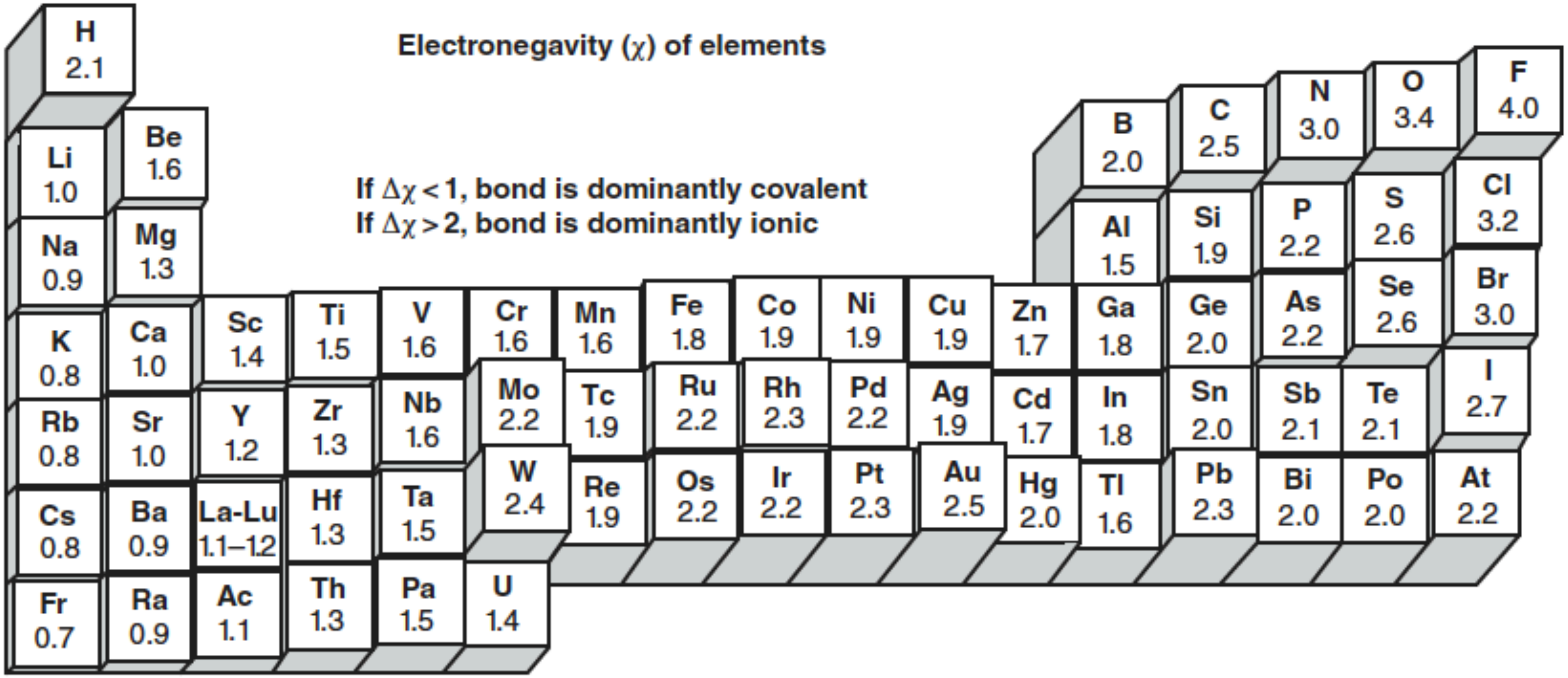
Let's now consider several concepts that are useful in describing the behaviour of atoms and elements: **ionization potential** , **electron affinity** , and **electronegativity**.

The **First Ionization Potential** of an atom is the energy required to remove (i.e., move an infinite distance away) the least tightly bound electron. The Second Ionization Potential is the energy required to remove a second electron, etc.



The **electron affinity** is the energy given up in reactions such as:

$$F + e^- \rightarrow F^-$$



Electronegavity (χ) of elements

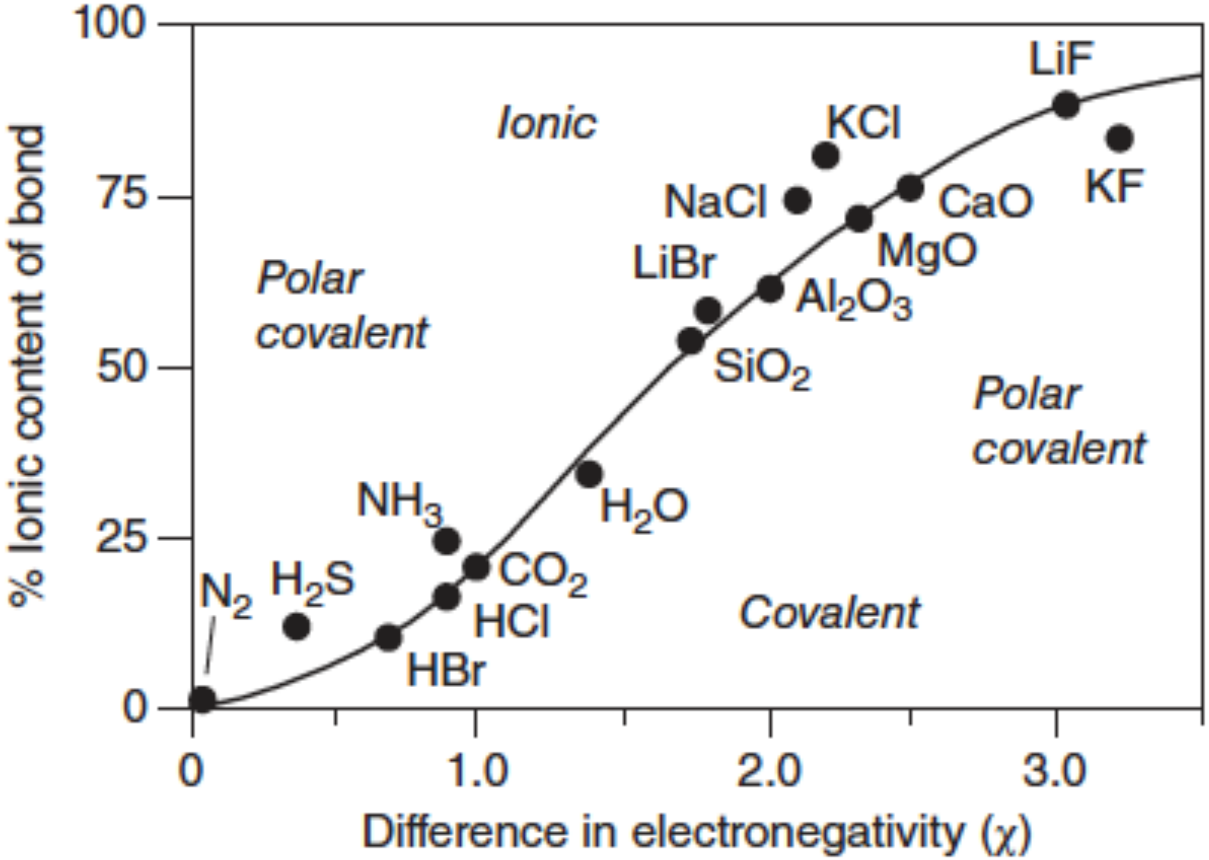
If $\Delta\chi < 1$, bond is dominantly covalent
If $\Delta\chi > 2$, bond is dominantly ionic

H 2.1																
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.4	F 4.0
Na 0.9	Mg 1.3											Al 1.5	Si 1.9	P 2.2	S 2.6	Cl 3.2
K 0.8	Ca 1.0	Sc 1.4	Ti 1.5	V 1.6	Cr 1.6	Mn 1.6	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	Se 2.6	Br 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.6	Mo 2.2	Tc 1.9	Ru 2.2	Rh 2.3	Pd 2.2	Ag 1.9	Cd 1.7	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7
Cs 0.8	Ba 0.9	La-Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.3	Au 2.5	Hg 2.0	Tl 1.6	Pb 2.3	Bi 2.0	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.5	U 1.4											

Electronegativity of elements based on Linus Pauling's early 20th-century research.

Electronegativity is another parameter that is often used to characterize the behaviour of the elements. It is a relative, unites quantity determined from the differences in bond energy between an A-B molecule and the mean energies of A-A and B-B molecules.

Electronegativity quantifies the tendency of an element to attract a shared electron when bonded to another element.



Plot of relationship between difference in electronegativity of two atoms in a bond and the percent ionic character of the bond. Note that no bond is 100% ionic; however, diatomic gases (e.g. N_2, Cl_2, O_2) and the C–C bonds in diamond are 100% covalent.. Based on early and middle 20th-century work of Linus Pauling and more recent research by Lu et al. (2006).

In general, first ionization potential, electron affinity, and electronegativity, **increase from left to right** across the periodic table, and to a less degree **from bottom to top**.

This reflects the shielding of outer electrons, particularly those in s orbitals, by inner electrons, particularly those in p orbitals, from the charge of the nucleus. Thus the outer 3s electron of neutral sodium is effectively shielded from the nucleus and is quite easily removed. On the other hand, the 2p orbitals of oxygen are not very effectively shielded, and it readily accepts 2 additional electrons. With the addition of these 2 electrons, the 2p orbital is filled and the 3s orbital effectively shielded, so there is no tendency to add a third electron. With the outer p (and s) orbitals filled, a particularly stable configuration is reached. Thus Ne has little tendency to either add or give up an electron.

The number of electrons that an element will either give up or accept is known as its **valence** . For elements in the 'wings' of the periodic table (i.e., all except the transition metals), valence is easily determined simply by counting how far the element is horizontally displaced from Group 18 in the periodic table. For Group 18, this is 0, so these elements, the noble gases, have 0 valence. For group 1 it is 1, so these elements have valence of +1; for group 17 it is -1, so these elements have valence of -1, etc. Valence of the transition metals is not so simply determined, and these elements can have more than 1 valence state. Most, however, have valence of 2 or 3, though some, such as U, can have valences as high as 6.

A final characteristic that is important in controlling chemical properties is **ionic radius**.

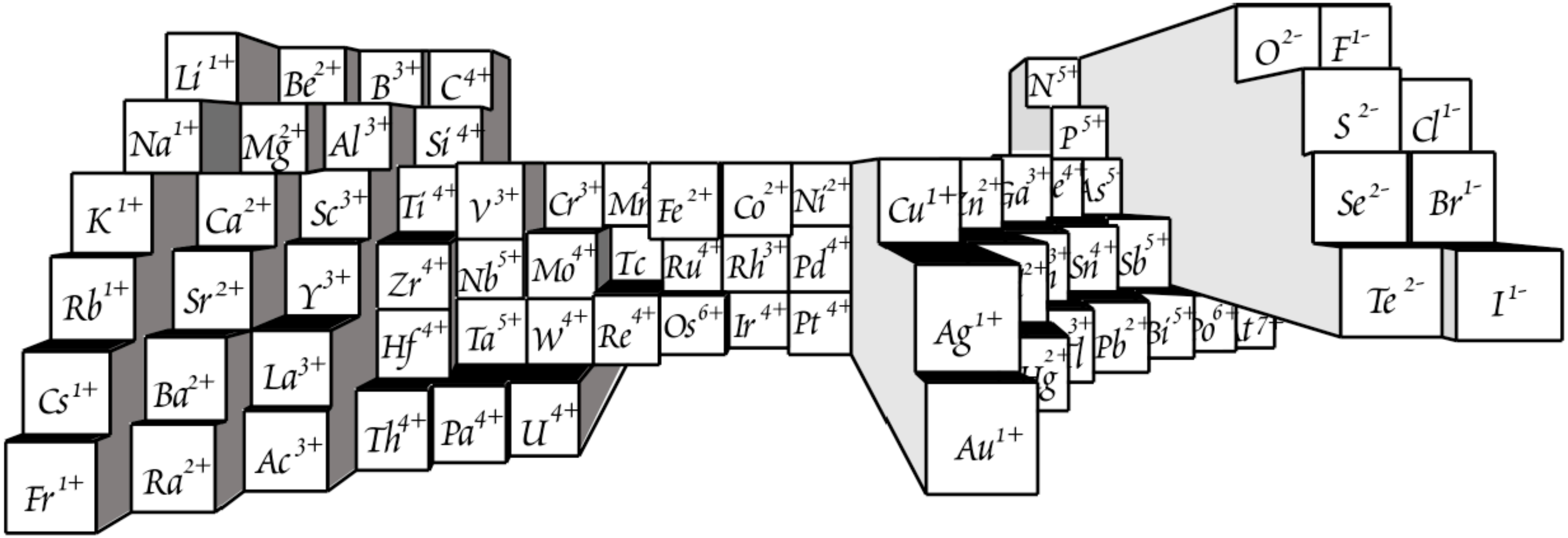
This is deduced from bond length when the atom is bonded to one or more other atoms.

Positively charged atoms, or cation , have smaller ionic radii than do negatively charged atoms, or anions .

Also, ionic radius decreases as charge increases. This decrease is due both to loss of electrons and to shrinking of the orbits of the remaining electrons. The latter occurs because the charge of the nucleus is shared by fewer electrons and hence has a greater attractive force on each.

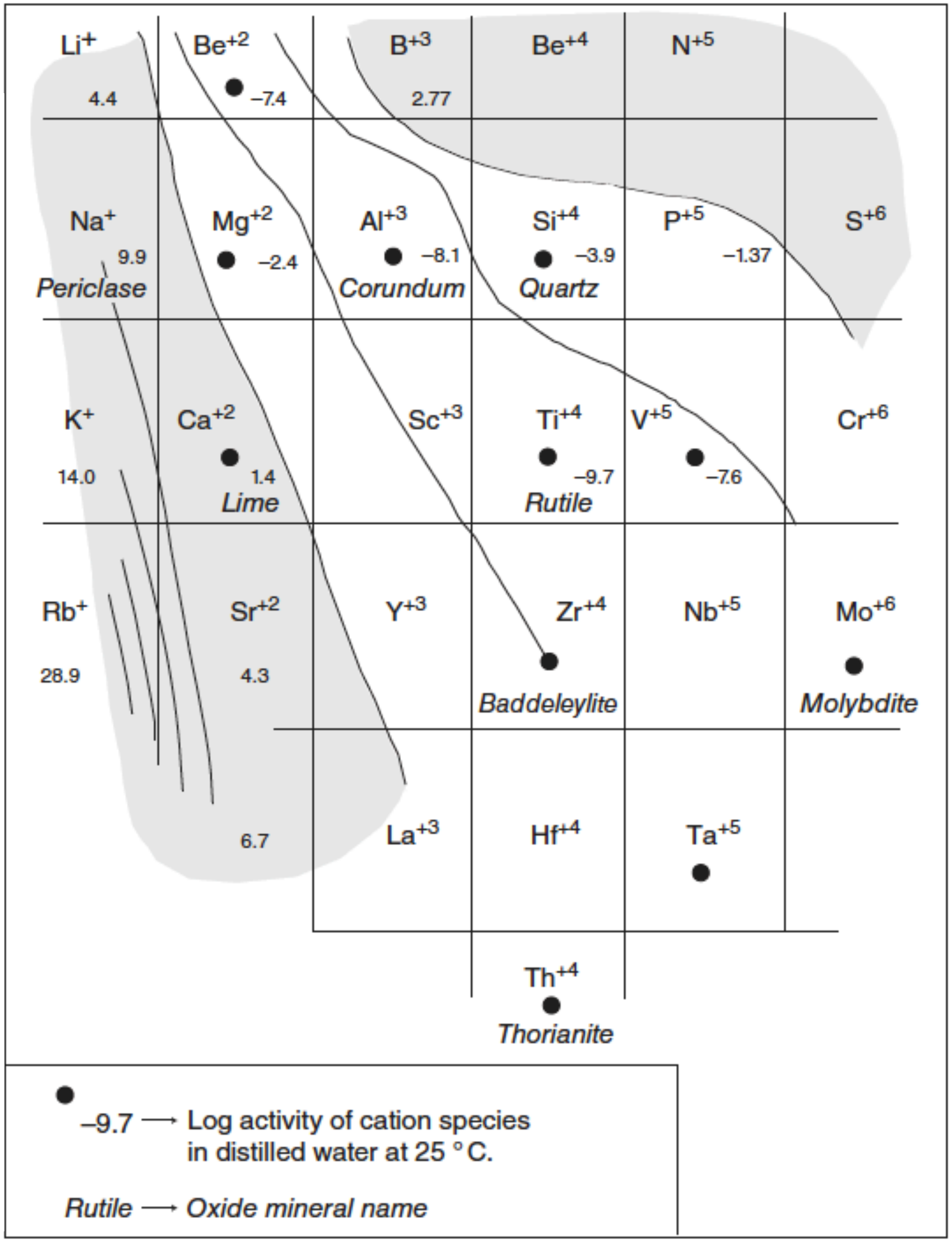
In addition, ionic radius increases downward in each group in the periodic table, both because of addition of electrons to outer shells and because these outer electrons are increasingly shielded from the nuclear charge by the inner ones.

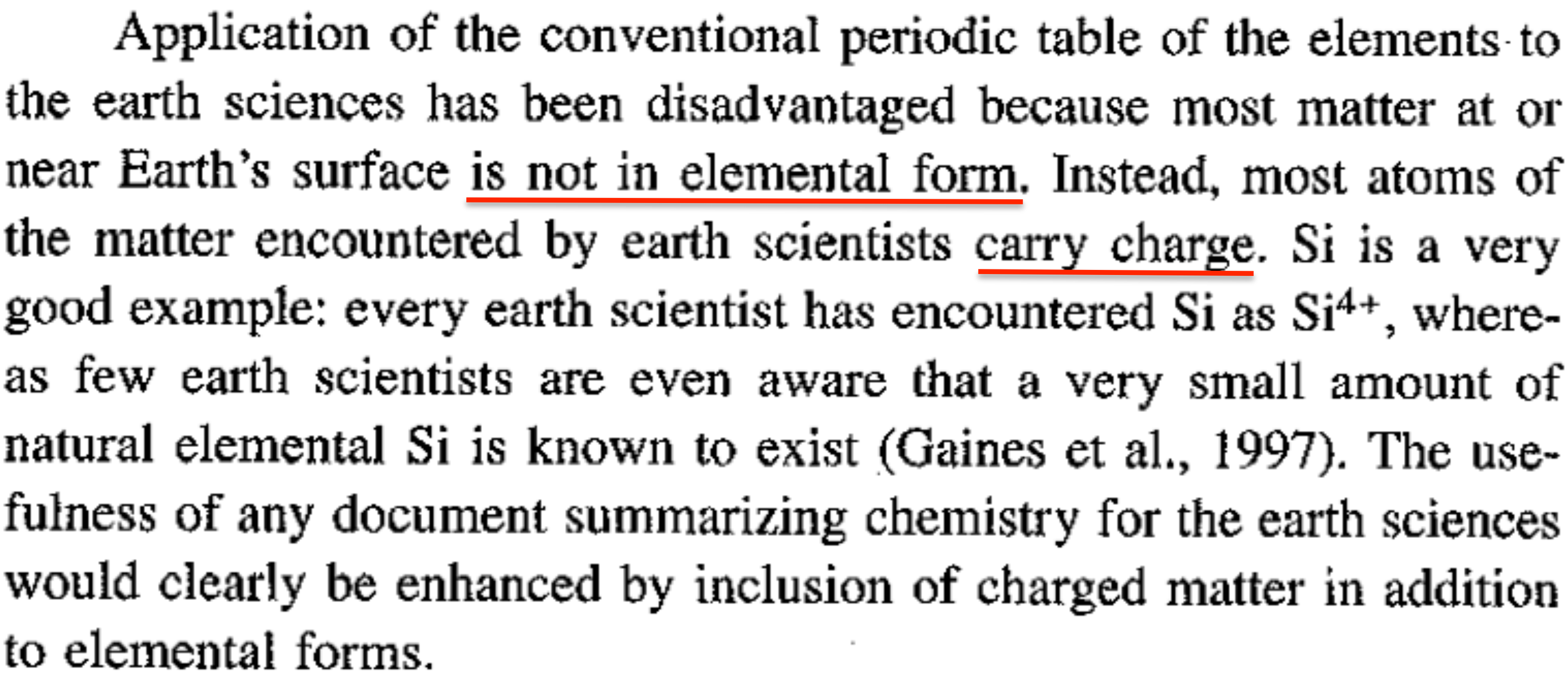
Ionic radius is important in **determining important geochemical properties** such substitution in solids, solubility, and diffusion rates. Large ions need to be surrounded, or coordinated , by a greater number of oppositely charged ions than do smaller ones.


Li1+
Be2+
B3+
C4+
Na1+
Mg2+
Al3+
Si4+
K1+
Ca2+
Sc3+
Ti4+
V3+
Cr3+
Fe2+
Co2+
Ni2+
Cu1+
Ga3+
N5+
P5+
O2-
F1-
S2-
Cl1-
Se2-
Br1-
Rb1+
Sr2+
Y3+
Zr4+
Nb5+
Mo4+
Tc
Ru4+
Rh3+
Pd4+
Ag1+
Sn4+
Sb5+
Te2-
I1-
Cs1+
Ba2+
La3+
Hf4+
Ta5+
W4+
Re4+
Os6+
Ir4+
Pt4+
Au1+
Pb2+
Bi5+
Fr1+
Ra2+
Ac3+
Th4+
Pa4+
U4+

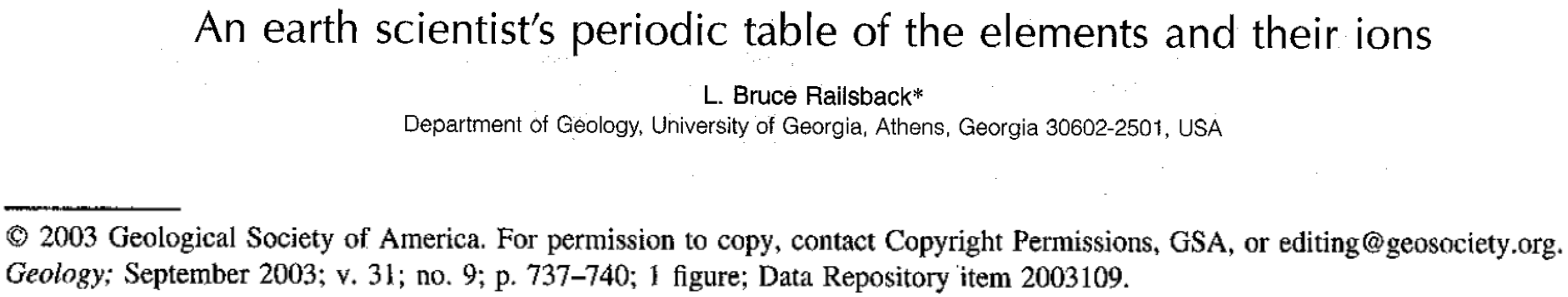
Ionic Radii

Solubilities of ions as a function of ionic charge, from Inset 4 of *An Earth Scientist's Periodic Table of the Elements and Their Ions* (Railsback, 2003). Oxides of the elements are used as reference (e.g. lime, periclase, etc.). Note that low-charge base cations/alkali metals and cations of the alkaline Earth metals are relatively soluble, as are high-charge cations such as S^{+6} and N^{+5}, which form polytatomic anions (SO_4^{-2}, NO_3^-). Cations with +3 and +4 charges (e.g. Al^{+3}, Ti^{+4}, Zr^{+4}) are insoluble in most surficial environments, with activities in H_2O at 25 °C of ~10^{-8} to 10^{-10}. (Railsback 2003.)





Application of the conventional periodic table of the elements to the earth sciences has been disadvantaged because most matter at or near Earth's surface is not in elemental form. Instead, most atoms of the matter encountered by earth scientists carry charge. Si is a very good example: every earth scientist has encountered Si as Si^{4+}, whereas few earth scientists are even aware that a very small amount of natural elemental Si is known to exist (Gaines et al., 1997). The usefulness of any document summarizing chemistry for the earth sciences would clearly be enhanced by inclusion of charged matter in addition to elemental forms.

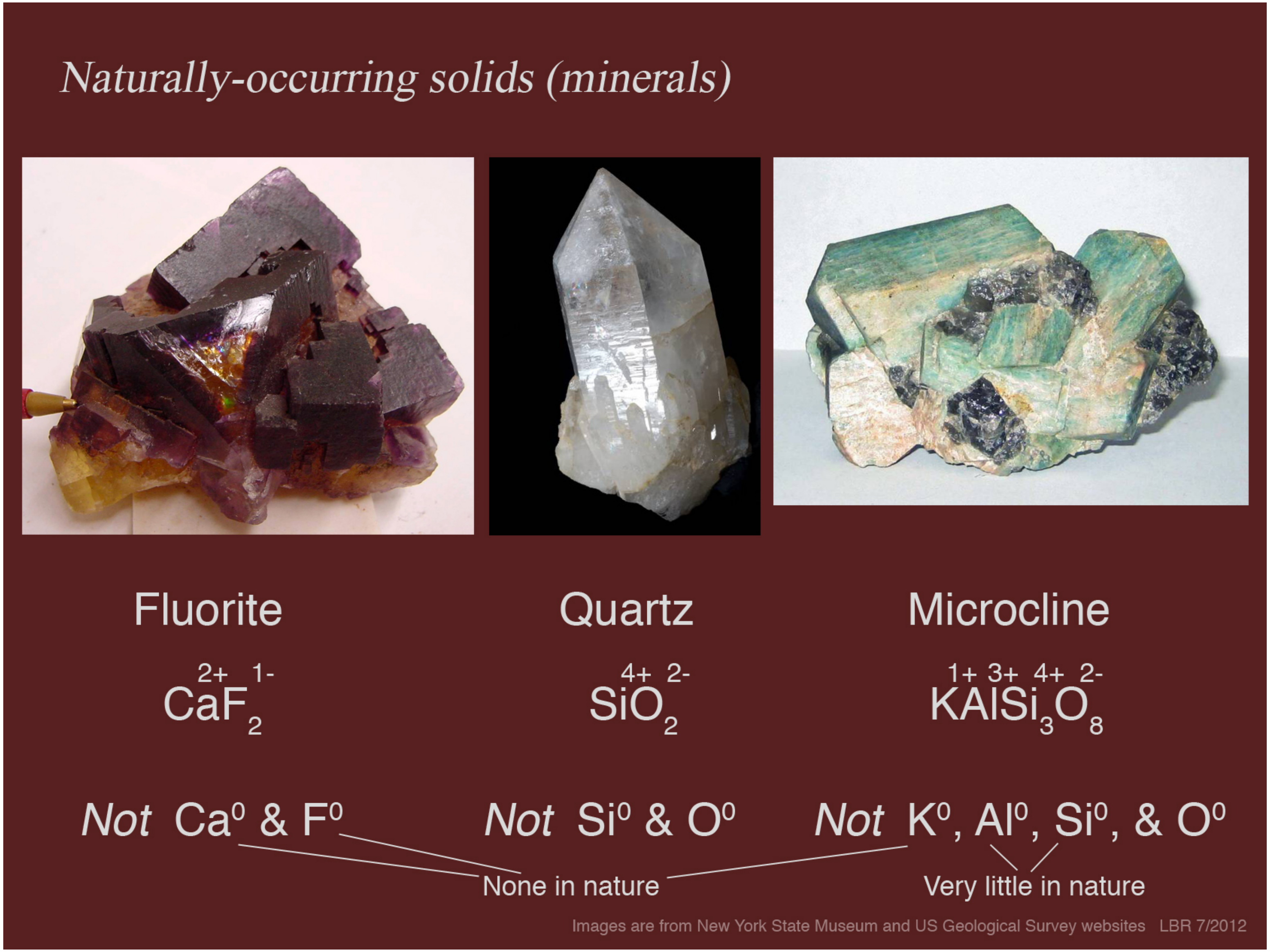


An earth scientist's periodic table of the elements and their ions

L. Bruce Railsback*
Department of Geology, University of Georgia, Athens, Georgia 30602-2501, USA

Geology; September 2003; v. 31; no. 9; p. 737–740; 1 figure; Data Repository item 2003109.

With that view in mind, this paper presents an *Earth Scientist's Periodic Table of the Elements and Their Ions*[1]. In this table, natural groupings and trends in geochemistry, marine chemistry, and nutrient chemistry become apparent, allowing a more general synthesis of the chemistry of the earth sciences. The result is an integrated view of geochemistry applicable from the mantle to soil to seawater. One fundamental concept in rationalizing these geochemical patterns is the difference in bonding exhibited by hard and soft cations, which favor O^{2-} and S^{2-}, respectively. The other is the extent to which charge of cations is sufficiently focused (i.e., ionic potential is sufficiently high) to provide strong bonds to O^{2-} without causing repulsion between those cations. Thus bonding and coordination with oxygen, Earth's most abundant element in the mantle and crust (McDonough and Sun, 1995), dictate many of the trends discussed in the following sections.



Naturally-occurring solids (minerals)

Fluorite

$\overset{2+}{\mathrm{Ca}}\overset{1-}{\mathrm{F}}_2$

Quartz

$\overset{4+}{\mathrm{Si}}\overset{2-}{\mathrm{O}}_2$

Microcline

$\overset{1+}{\mathrm{K}}\overset{3+}{\mathrm{Al}}\overset{4+}{\mathrm{Si}}_3\overset{2-}{\mathrm{O}}_8$

Not Ca^0 & F^0

Not Si^0 & O^0

Not K^0, Al^0, Si^0, & O^0

None in nature

Very little in nature

Images are from New York State Museum and US Geological Survey websites LBR 7/2012

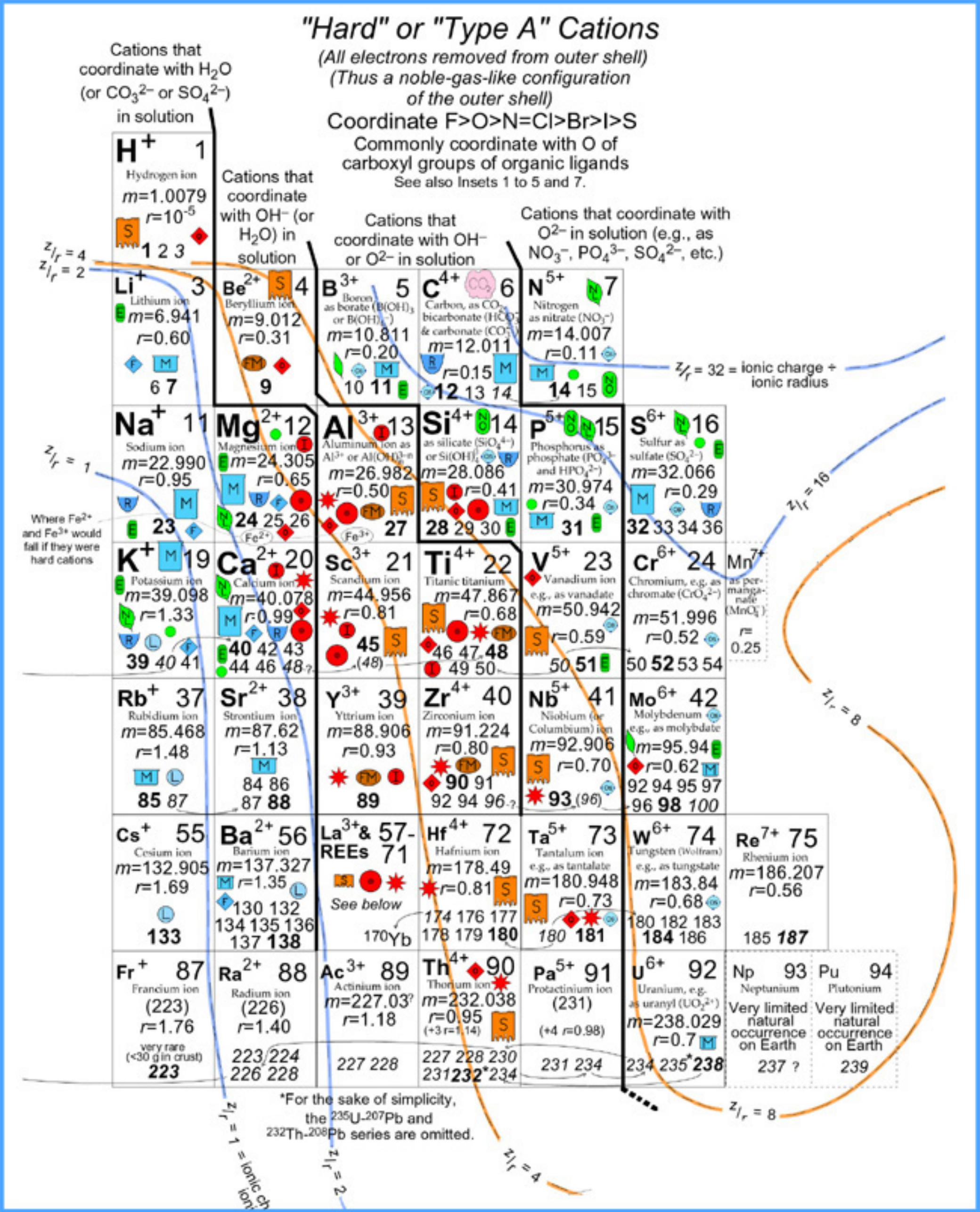
These are three common minerals, and . . . .understanding the role of their constituent elements has nothing to do with the elemental uncharged form of those elements.

1. Organization of chemical entities by charge:

H^+					
Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	
Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}
K^+	Ca^{2+}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}
Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}	Nb^{5+}	Mo^{6+}
Cs^+	Ba^{2+}	La^{3+}	Hf^{4+}	Ta^{5+}	W^{6+}
Fr^+	Ra^{2+}	Ac^{3+}	Th^{4+}	Pa^{5+}	U^{6+}

Earth Scientists would want a table more like this. Note the charges shown on all the symbols: at Na^+, we would emphasize that we're thinking about sodium *ions*, either in albite, or dissolved in seawater, or in some other natural context. There is no elemental sodium in nature, so we don't need to show that.

In red, elements have been moved from the right side of the conventional table in order to make this new table organized by charge. If charge is going to increase regularly from Na^+ to Mg^{2+} and then to Al^{3+} and Si^{4+}, we need to move Al and Si and P and S over from the right. Also the actinides have to be moved up to follow radium, because they too increase by one unit of charge across the table.



An Earth Scientist's Periodic Table of the Elements and Their Ions

Bruce Railsback

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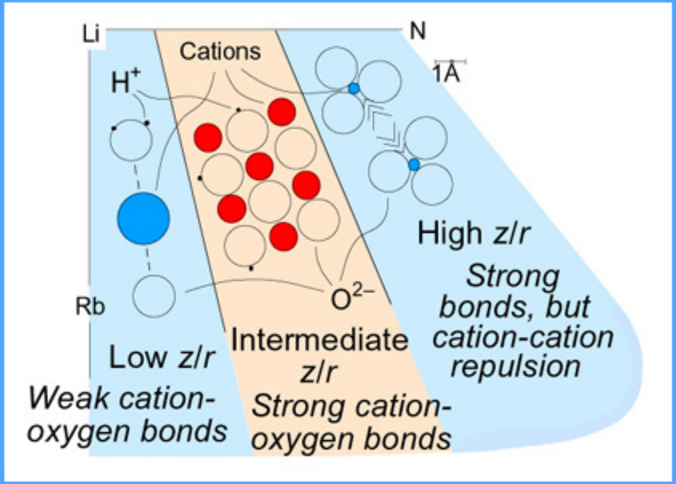
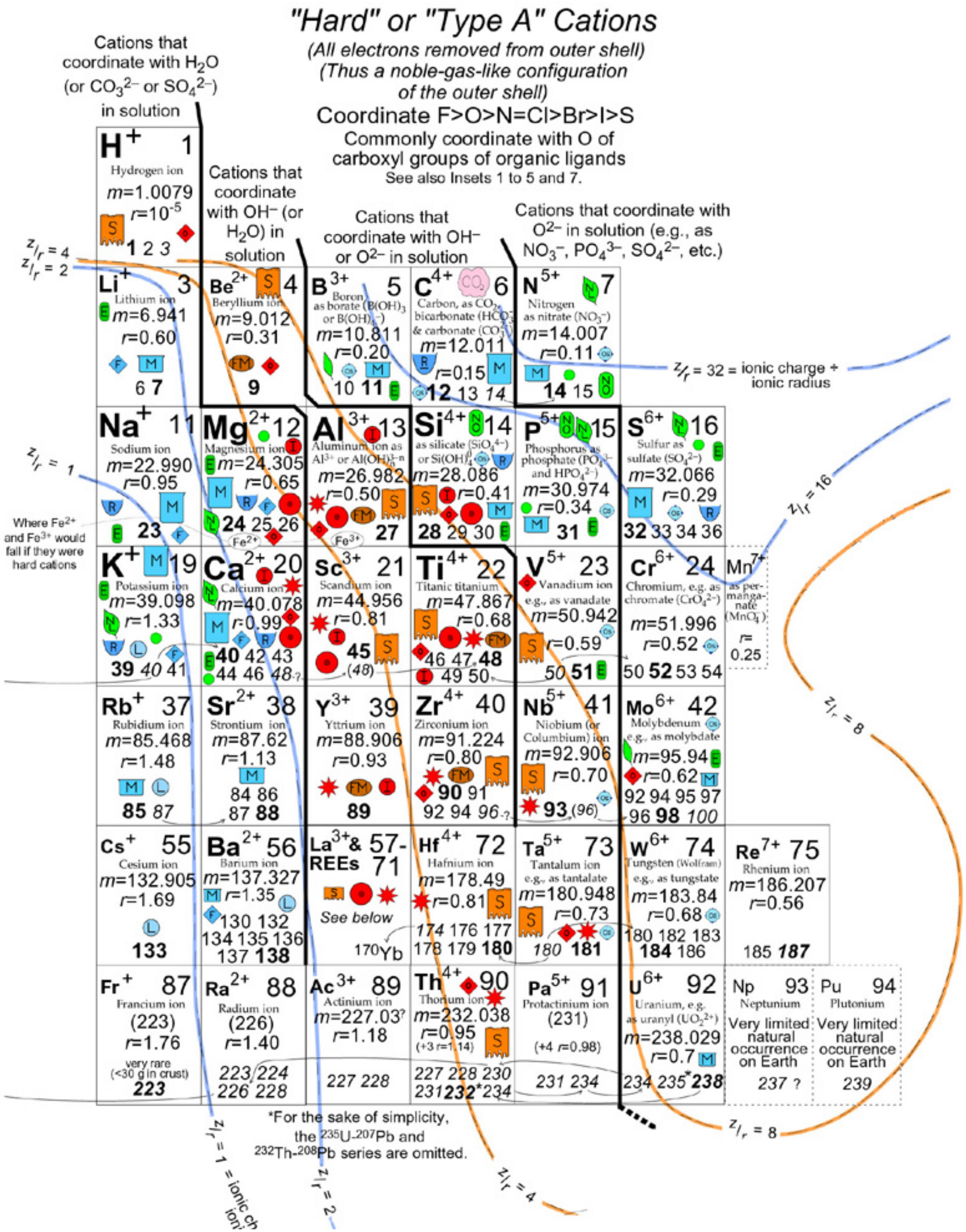




The new table has contours that are visible here as blue and brown lines. These are contours of **ionic potential**.

Ionic potential is a parameter to characterize how tightly focused the charge of an ion is, or how dense that charge is.

The simplest and most commonly used formulation is shown here. For the example of Ca^{2+}, we come to a low value of ionic potential that we associate with a diffuse charge. In contrast, with N^{5+}, the higher charge and smaller radius give a large value of ionic potential, and we envision N^{5+} as a tightly focused beacon of positive charge.

Ionic Potential = "density of charge"

= charge of ion ÷ radius of ion

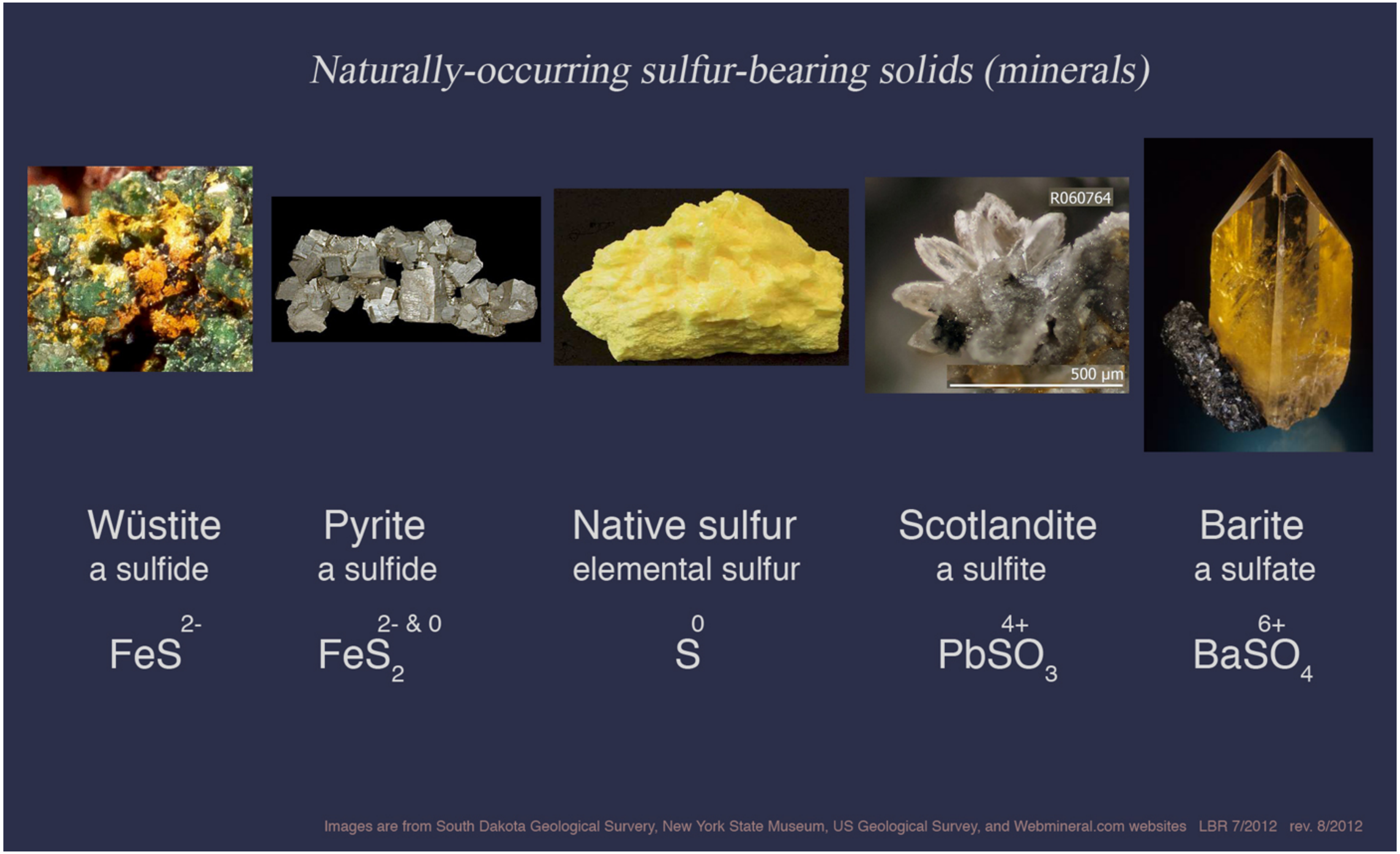
= z / r

For Ca^{2+}: z = 2 r = 1.0Å z/r = 2

For N^{5+}: z = 5 r = 0.11Å z/r = 45

Chemical entities are arranged according to charge in the *Earth Scientist's Periodic Table of the Elements and Their Ions* (Fig. 1)[2]. Thus, B, C, and N, which are conventionally on the right side of the periodic table, appear on the left in the left-to-right horizontal sequence Li^{+}, Be^{2+}, B^{3+}, C^{4+}, and N^{5+}. Al, Si, P, and S similarly appear on the left and within the left-to-right horizontal sequence Na^{+}, Mg^{2+}, Al^{3+}, Si^{4+}, P^{5+}, and S^{6+}. A more striking result of organizing the table according to charge is that many elements appear multiple times, because different natural conditions cause those elements to assume different charges. Many elements (e.g., P and U) thus appear twice, a few appear three times (e.g., V, Fe, C, and N), and a few appear four times (most notably S, as S^{2-}, S^{0}, S^{4+}, and S^{6+}).

The table is broken from left to right to separate noble gases, hard or type A cations (those with no outer-shell electrons), intermediate to soft or type B cations (those with at least some outer-shell cations), elemental (uncharged) forms, anions, and the noble gases again (Fig. 1). The significance of the division of cations is that hard cations bond strongly to F^- and O^{2-} but not to S^{2-}, whereas the soft cations bond strongly to S^{2-} and the larger halides, Br^- and I^- (Stumm and Morgan, 1996) (Fig. 1, Inset 8). These patterns are exemplified in nature by the absence of sulfide minerals of Ca^{2+} and of the other hard cations, but the existence of oxides and sulfates of those cations (Fig. 1). The nat-

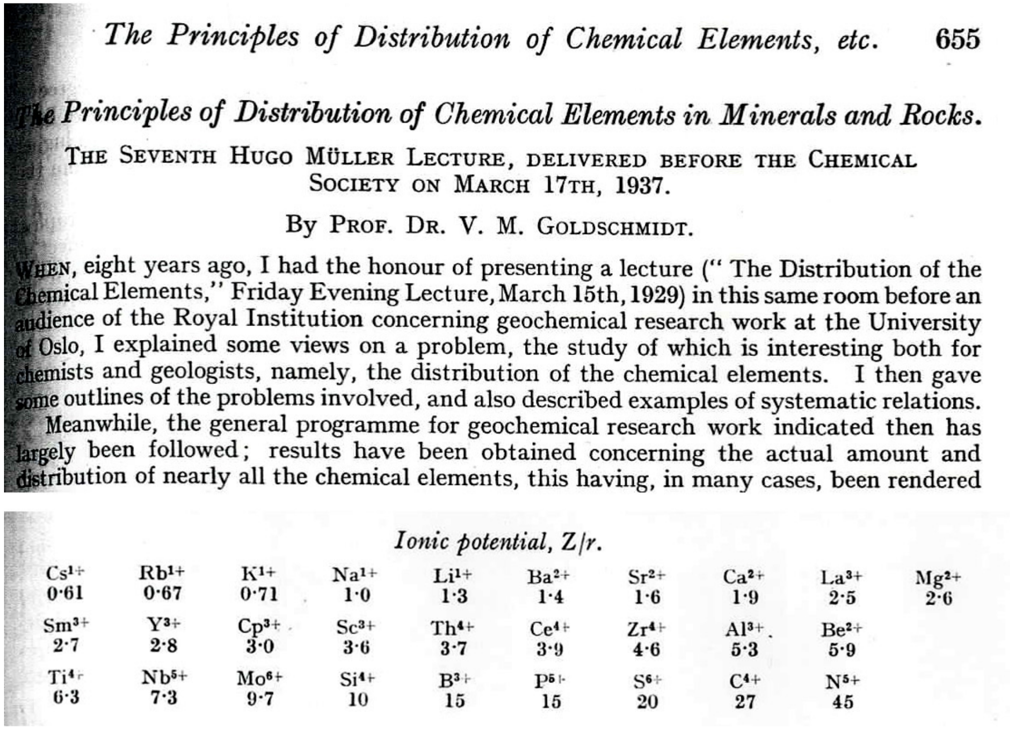


Naturally-occurring sulfur-bearing solids (minerals)

Wüstite	Pyrite	Native sulfur	Scotlandite	Barite
a sulfide	a sulfide	elemental sulfur	a sulfite	a sulfate
$Fe\overset{2-}{S}$	$Fe\overset{2-\ \&\ 0}{S}_2$	$\overset{0}{S}$	$Pb\overset{4+}{S}O_3$	$Ba\overset{6+}{S}O_4$

Images are from South Dakota Geological Survery, New York State Museum, US Geological Survey, and Webmineral.com websites LBR 7/2012 rev. 8/2012

Three of the four are common minerals; scotlandite is not (and sulfite minerals in general are rare) - but the four demonstrate the range of forms of sulfur in nature.



The Principles of Distribution of Chemical Elements in Minerals and Rocks.

THE SEVENTH HUGO MÜLLER LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON MARCH 17TH, 1937.

By PROF. DR. V. M. GOLDSCHMIDT.

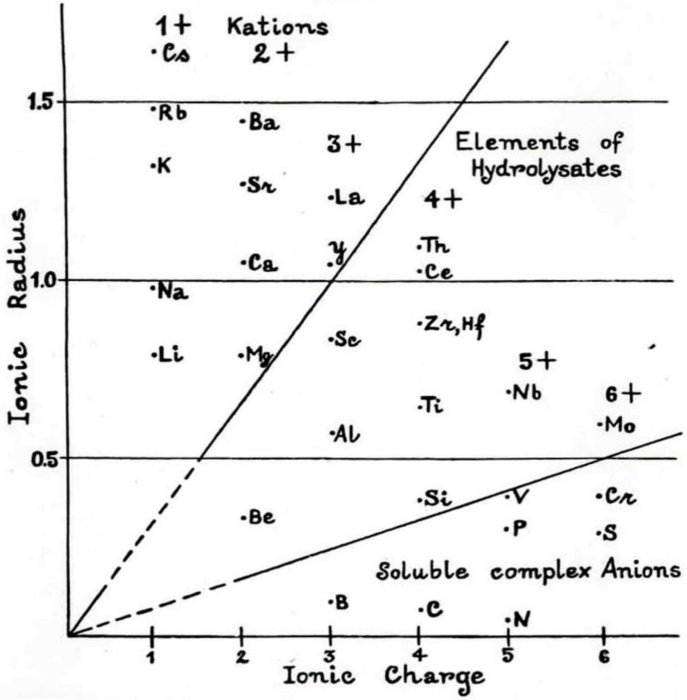
WHEN, eight years ago, I had the honour of presenting a lecture ("The Distribution of the Chemical Elements," Friday Evening Lecture, March 15th, 1929) in this same room before an audience of the Royal Institution concerning geochemical research work at the University of Oslo, I explained some views on a problem, the study of which is interesting both for chemists and geologists, namely, the distribution of the chemical elements. I then gave some outlines of the problems involved, and also described examples of systematic relations.

Meanwhile, the general programme for geochemical research work indicated then has largely been followed; results have been obtained concerning the actual amount and distribution of nearly all the chemical elements, this having, in many cases, been rendered

Ionic potential, Z/r.

Cs^{1+} 0·61	Rb^{1+} 0·67	K^{1+} 0·71	Na^{1+} 1·0	Li^{1+} 1·3	Ba^{2+} 1·4	Sr^{2+} 1·6	Ca^{2+} 1·9	La^{3+} 2·5	Mg^{2+} 2·6
Sm^{3+} 2·7	Y^{3+} 2·8	Cp^{3+} 3·0	Sc^{3+} 3·6	Th^{4+} 3·7	Ce^{4+} 3·9	Zr^{4+} 4·6	Al^{3+} 5·3	Be^{2+} 5·9	
Ti^{4+} 6·3	Nb^{5+} 7·3	Mo^{6+} 9·7	Si^{4+} 10	B^{3+} 15	P^{5+} 15	S^{6+} 20	C^{4+} 27	N^{5+} 45	

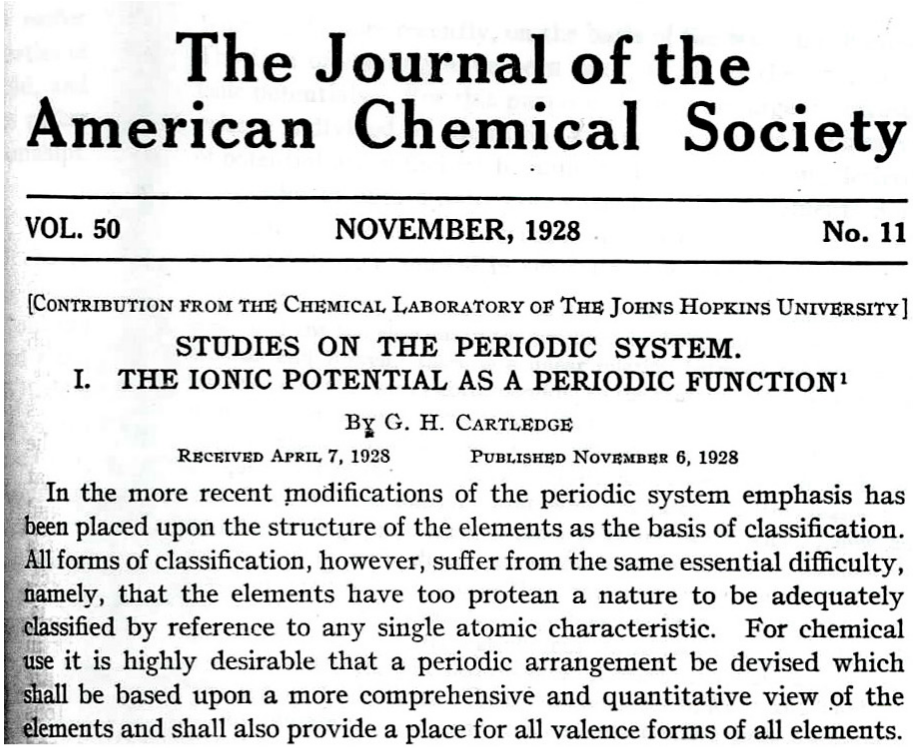
FIG. 2.



Ionic potential is a concept that geochemists trace back to **Victor Goldschmidt's work** in the 1930s. Goldschmidt produced the classic diagram on the right, still used in many textbooks. On that diagram, lines radiating from the origin are lines of equal ionic potential, and the two lines shown divide ions into a field of soluble ions, ions that are insoluble and make hydroxides, and ions soluble in oxyanions (e.g., S^{6+} in sulfate).

However, note that Goldschmidt fell into the trap of only putting one element one place: he has Fe as insoluble Fe^{3+}, but didn't also show Fe^{2+}, which is much more soluble.

Goldschmidt, however, was not the first to consider ionic potential . . . .



The Journal of the American Chemical Society

VOL. 50 NOVEMBER, 1928 No. 11

[Contribution from the Chemical Laboratory of The Johns Hopkins University]

STUDIES ON THE PERIODIC SYSTEM.
I. THE IONIC POTENTIAL AS A PERIODIC FUNCTION[1]

By G. H. Cartledge

Received April 7, 1928 Published November 6, 1928

In the more recent modifications of the periodic system emphasis has been placed upon the structure of the elements as the basis of classification. All forms of classification, however, suffer from the same essential difficulty, namely, that the elements have too protean a nature to be adequately classified by reference to any single atomic characteristic. For chemical use it is highly desirable that a periodic arrangement be devised which shall be based upon a more comprehensive and quantitative view of the elements and shall also provide a place for all valence forms of all elements.

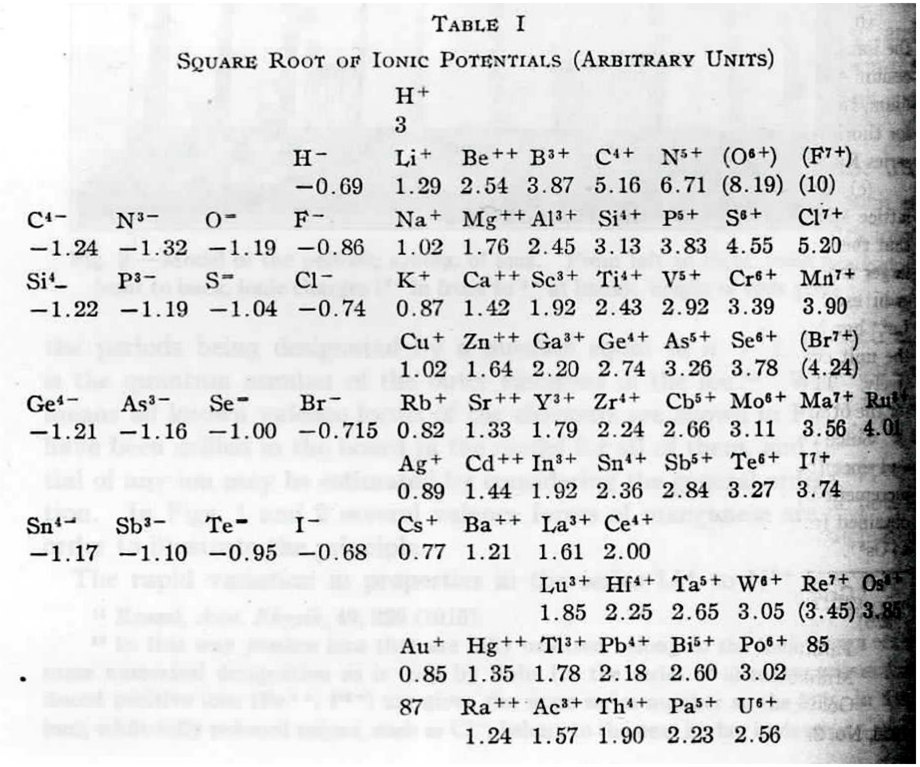


Table I

Square Root of Ionic Potentials (Arbitrary Units)

				H^+							
				3							
			H^-	Li^+	Be^{++}	B^{3+}	C^{4+}	N^{5+}	(O^{6+})	(F^{7+})	
			−0.69	1.29	2.54	3.87	5.16	6.71	(8.19)	(10)	
C^{4-}	N^{3-}	$O^{=}$	F^-	Na^+	Mg^{++}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}	
−1.24	−1.32	−1.19	−0.86	1.02	1.76	2.45	3.13	3.83	4.55	5.20	
Si^{4-}	P^{3-}	$S^{=}$	Cl^-	K^+	Ca^{++}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}	
−1.22	−1.19	−1.04	−0.74	0.87	1.42	1.92	2.43	2.92	3.39	3.90	
				Cu^+	Zn^{++}	Ga^{3+}	Ge^{4+}	As^{5+}	Se^{6+}	(Br^{7+})	
				1.02	1.64	2.20	2.74	3.26	3.78	(4.24)	
Ge^{4-}	As^{3-}	$Se^{=}$	Br^-	Rb^+	Sr^{++}	Y^{3+}	Zr^{4+}	Cb^{5+}	Mo^{6+}	Ma^{7+}	Ru
−1.21	−1.16	−1.00	−0.715	0.82	1.33	1.79	2.24	2.66	3.11	3.56	4.01
				Ag^+	Cd^{++}	In^{3+}	Sn^{4+}	Sb^{5+}	Te^{6+}	I^{7+}	
				0.89	1.44	1.92	2.36	2.84	3.27	3.74	
Sn^{4-}	Sb^{3-}	$Te^{=}$	I^-	Cs^+	Ba^{++}	La^{3+}	Ce^{4+}				
−1.17	−1.10	−0.95	−0.68	0.77	1.21	1.61	2.00				
						Lu^{3+}	Hf^{4+}	Ta^{5+}	W^{6+}	Re^{7+}	Os
						1.85	2.25	2.65	3.05	(3.45)	3.85
				Au^+	Hg^{++}	Tl^{3+}	Pb^{4+}	Bi^{5+}	Po^{6+}	85	
				0.85	1.35	1.78	2.18	2.60	3.02		
				87	Ra^{++}	Ac^{3+}	Th^{4+}	Pa^{5+}	U^{6+}		
					1.24	1.57	1.90	2.23	2.56		

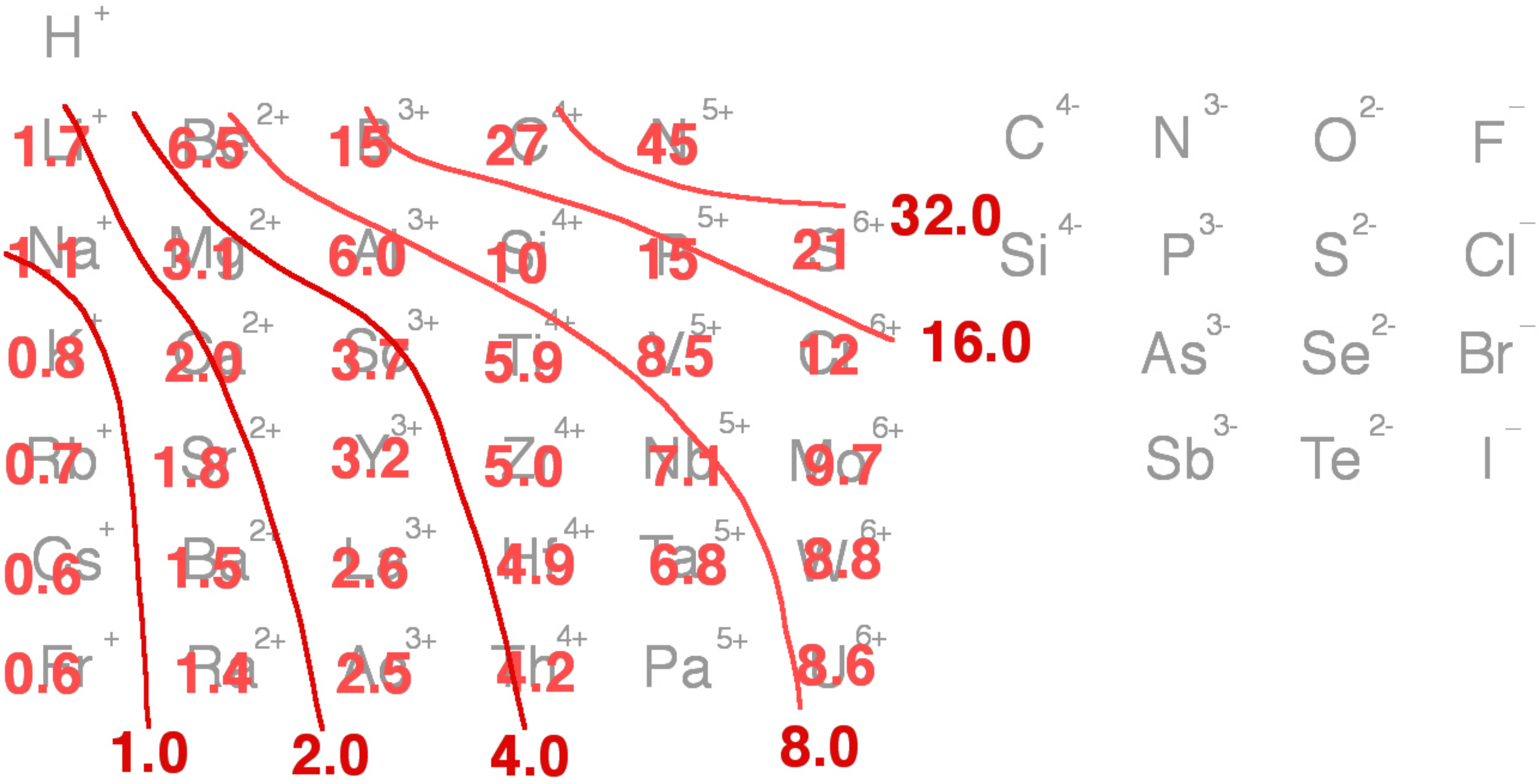
The idea of ionic potential **goes back at least a decade earlier** to this paper. Cartledge in fact made the periodic table at right that considered ions and showed some elements twice. In that respect, his table is one predecessor of the table shown previously. Returning to the new table with this concept of ionic potential . . .

3. Contouring of ionic potential (ionic charge ÷ ionic radius)

H^{+}									
Li^{+} $\frac{1}{0.60}=1.7$	Be^{2+} $\frac{2}{0.31}=6.5$	B^{3+} $\frac{3}{0.20}=15$	C^{4+} $\frac{4}{0.15}=27$	N^{5+} $\frac{5}{0.11}=45$		C^{4-}	N^{3-}	O^{2-}	F^{-}
Na^{+} $\frac{1}{0.95}=1.1$	Mg^{2+} $\frac{2}{0.65}=3.1$	Al^{3+} $\frac{3}{0.50}=6.0$	Si^{4+} $\frac{4}{0.41}=10$	P^{5+} $\frac{5}{0.34}=15$	S^{6+} $\frac{6}{0.29}=21$	Si^{4-}	P^{3-}	S^{2-}	Cl^{-}
K^{+} $\frac{1}{1.33}=0.8$	Ca^{2+} $\frac{2}{0.99}=2.0$	Sc^{3+} $\frac{3}{0.81}=3.7$	Ti^{4+} $\frac{4}{0.68}=5.9$	V^{5+} $\frac{5}{0.59}=8.5$	Cr^{6+} $\frac{6}{0.52}=12$		As^{3-}	Se^{2-}	Br^{-}
Rb^{+} $\frac{1}{1.48}=0.7$	Sr^{2+} $\frac{2}{1.13}=1.8$	Y^{3+} $\frac{3}{0.93}=3.2$	Zr^{4+} $\frac{4}{0.80}=5.0$	Nb^{5+} $\frac{5}{0.70}=7.1$	Mo^{6+} $\frac{6}{0.62}=9.7$		Sb^{3-}	Te^{2-}	I^{-}
Cs^{+} $\frac{1}{1.69}=0.6$	Ba^{2+} $\frac{2}{1.35}=1.5$	La^{3+} $\frac{3}{1.15}=2.6$	Hf^{4+} $\frac{4}{0.81}=4.9$	Ta^{5+} $\frac{5}{0.73}=6.8$	W^{6+} $\frac{6}{0.68}=8.8$				
Fr^{+} $\frac{1}{1.76}=0.6$	Ra^{2+} $\frac{2}{1.40}=1.4$	Ac^{3+} $\frac{3}{1.18}=2.5$	Th^{4+} $\frac{4}{0.95}=4.2$	Pa^{5+}	U^{6+} $\frac{6}{0.7}=8.6$				

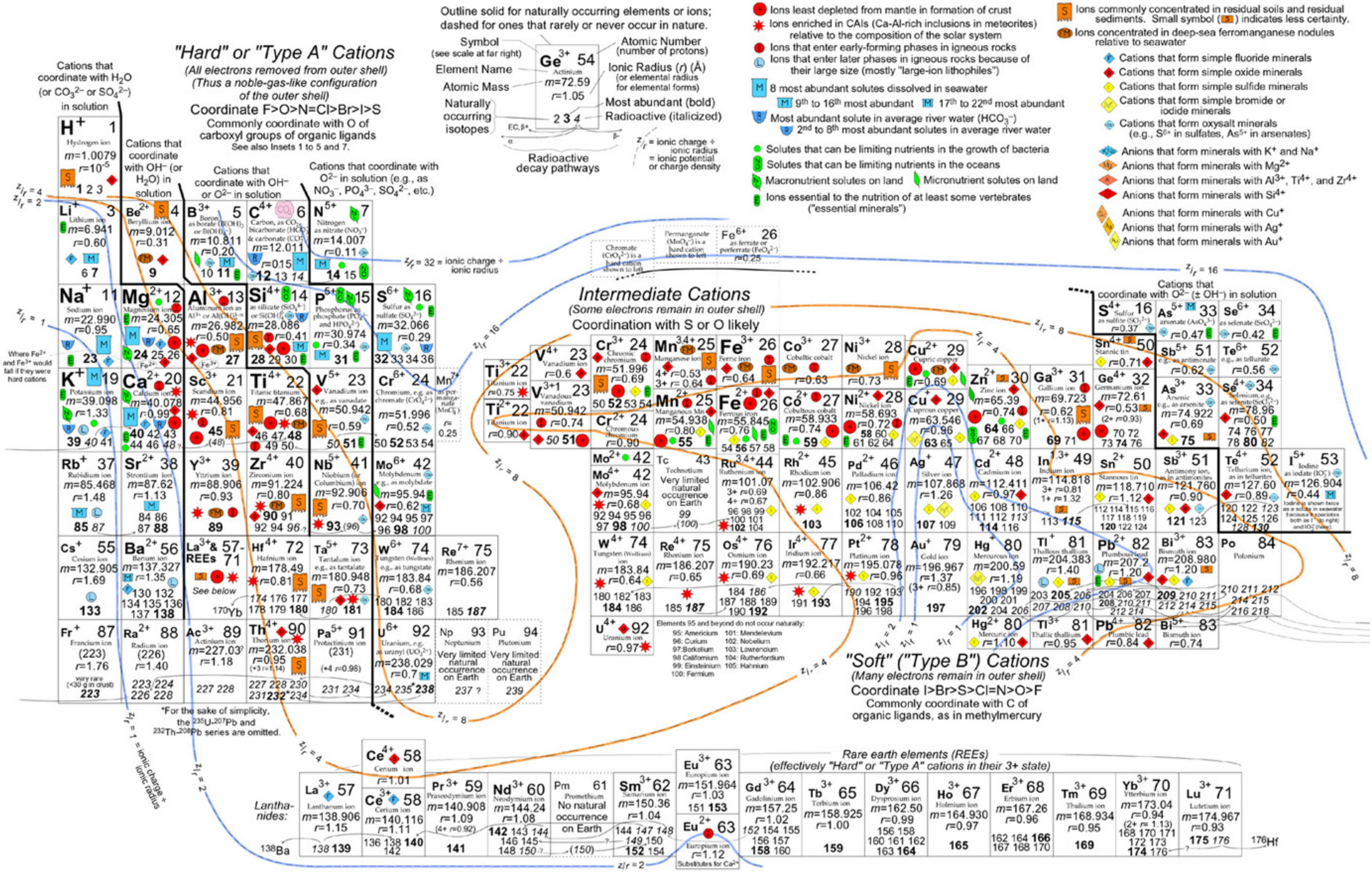
We can take our new format of the periodic table, with the ions shown here in gray, and calculate **ionic potential** for each ion. Again, Ca^{2+} is a good example: a charge of 2 and a radius of one angstrom yields an ionic potential of 2. Now we can contour the results . . . .

3. Contouring of ionic potential (ionic charge ÷ ionic radius)

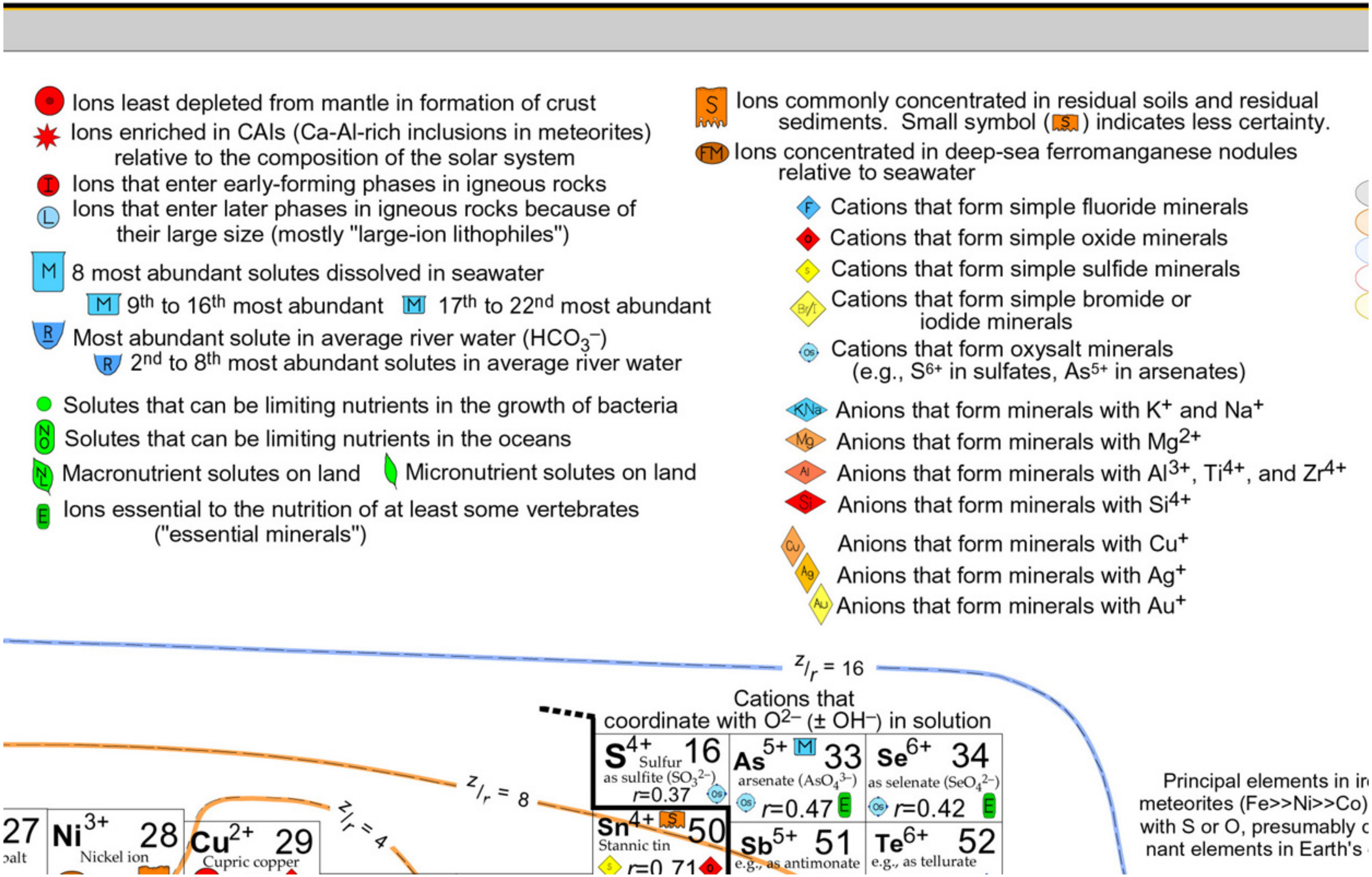


Contouring the values of ionic potential gives this pattern. Note the sharp increase toward the upper right. As we go to the right across this part of the table, charge (the numerator) increases and radius (the denominator) decreases, so we get a **tremendous increase** in ionic potential.

All that remains is to put the contours on our new table . . .

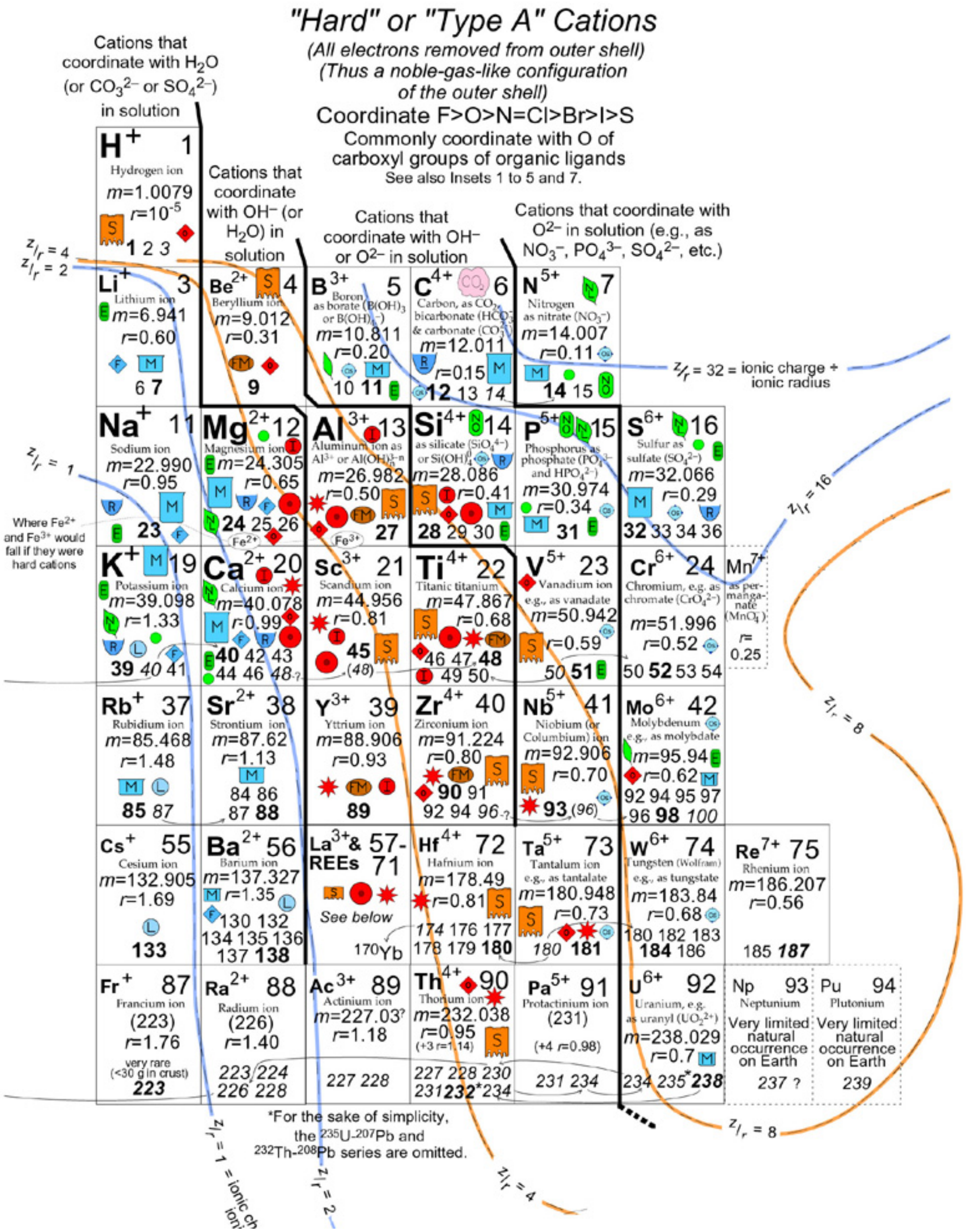


We can bring those contours on the table.



The legend shows that all of the colorful symbols on the table denote **natural occurrences** of the ions. In the part shown here, **red symbols** have to do with ions that go into solid phases at high temperatures. **Brown symbols** show ions that stay in solids at low temperatures, in weathering, or go into solids at low temperature, and are incorporated into deep-sea ferromanganese nodules. Thus reds and browns will marks ions that reside well in solids.

Blues and **greens**, on the other hand, are for symbols having to do with ions that go into solution readily. **Blue symbols** show the most abundant ions in river water and sea water. **Greens** show ions that can be limiting or critical nutrients. That relates to solubility, because a nutrient must be sufficiently soluble to be taken from soil water into roots or transported through a cell membrane in an organism. There's also a blue symbol for ions that enter minerals in igneous rocks relatively late, and thus at lower temperature, and thus also pertains to ions with less affinity for solid phases than those with red symbols.



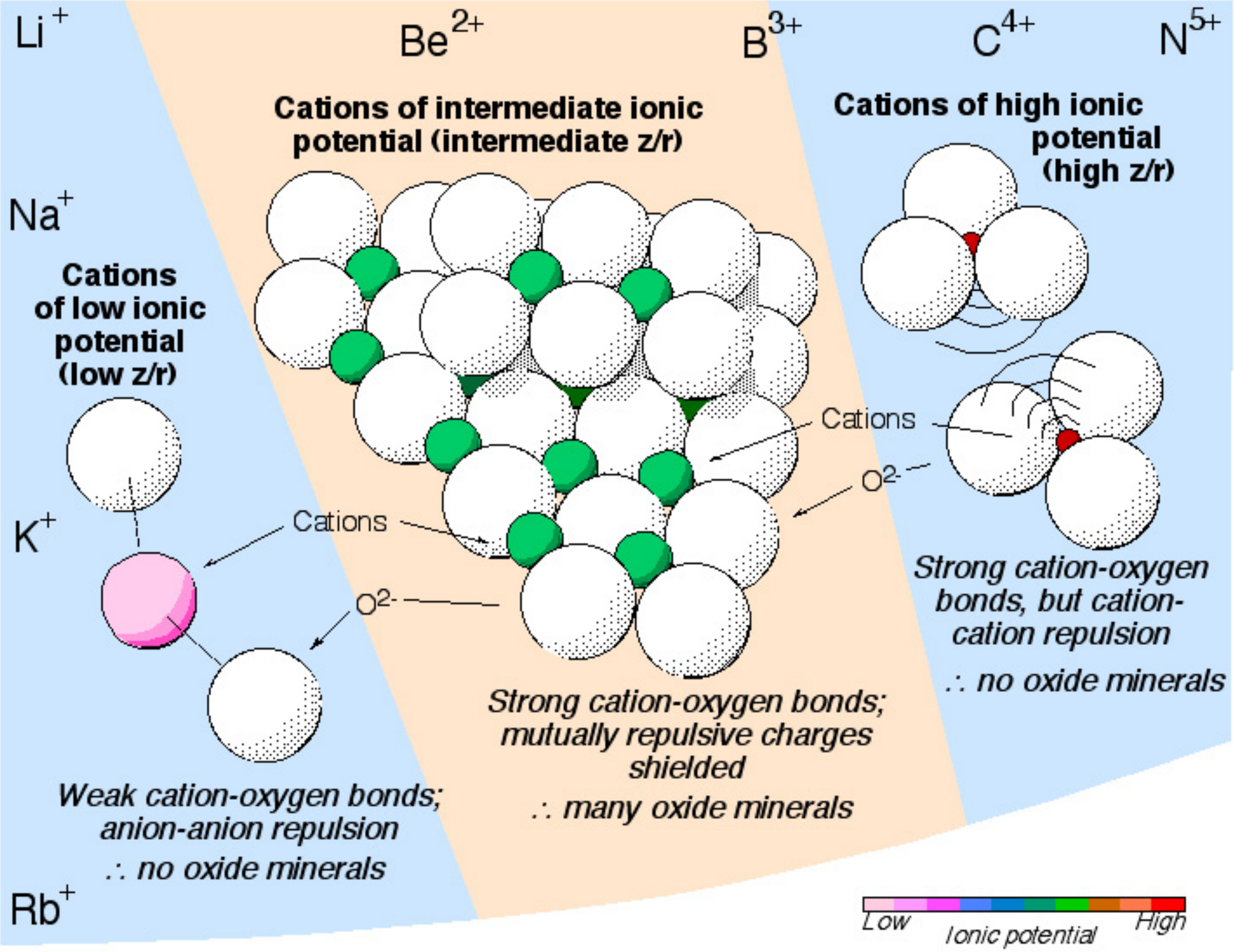
Consider the pattern on the left….

The **red** and **brown** symbols pertaining to ions residing well in solids fall in a swath down the middle of the hard cations.

The **blue** and **green** symbols pertaining to ions that tend to go into solution, on the other hand, fall in swaths to the left and right of the central red-and-brown swath.

Here we have **generalizable patterns of geochemical behavior**, and a pattern that can never be shown coherently on a conventional periodic table.

Note also that the swaths of color that have emerged here follow the contours of equal ionic potential.

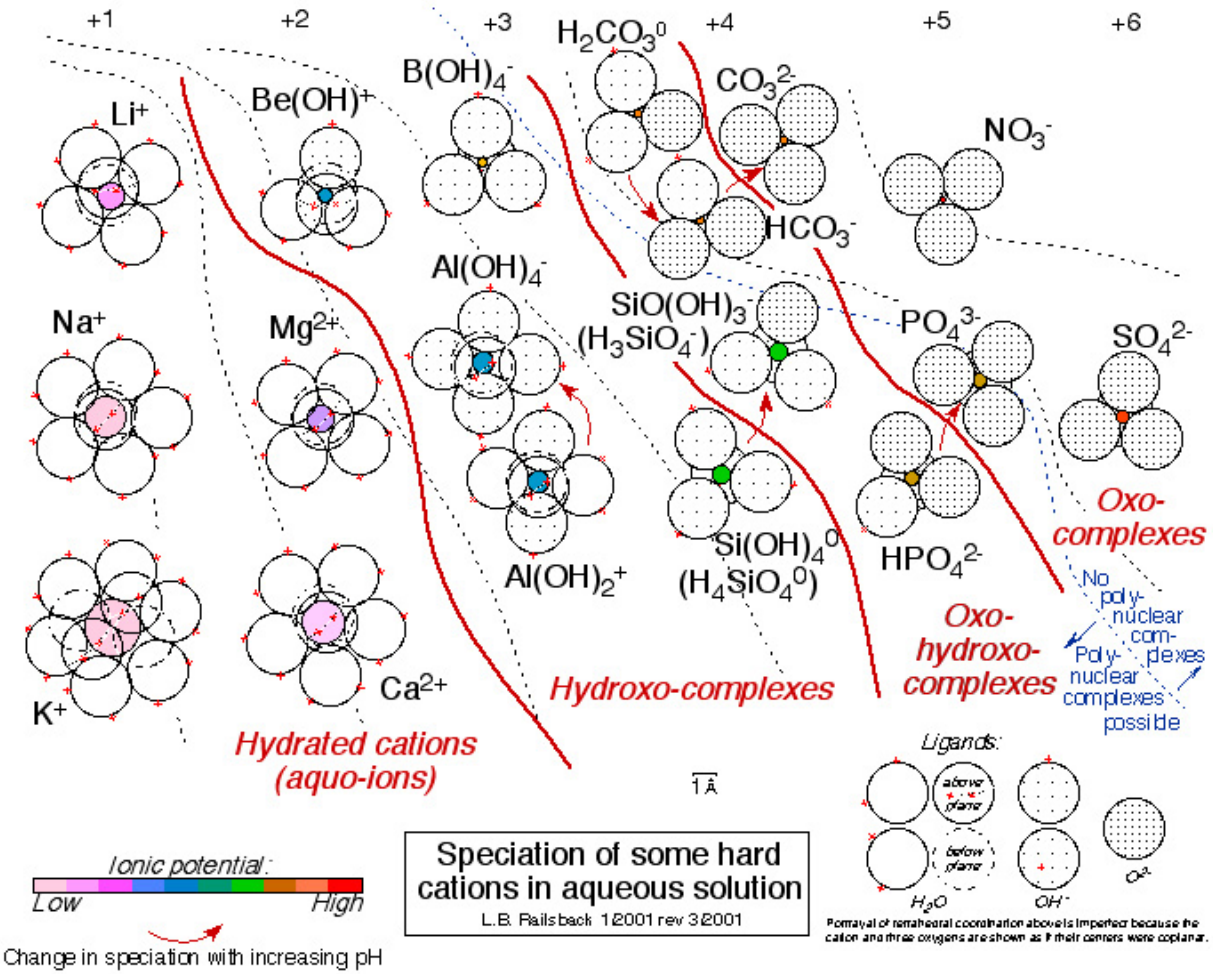


The pattern we've seen can be explained if we think about what **ionic potential** means in terms of interactions between ions.

On the left above, let's start with cations of low ionic potential - K^+ would be a good example. These ions are such weak fluffy concentrations of charge that they don't make strong bonds to O^{2-}, and so they don't go into high-temperature minerals of igneous rocks but instead stay in the melt, and in weathering they quickly break free from bonds to O^{2-} and go into solution.

In the middle of this sketch, we can consider cations of intermediate ionic potential - Al^{3+} and Ti^{4+} would be good examples. These ions are smaller and more highly charged and thus provide a more focused charge that allows stronger bonds to O^{2-} in solids. At the same time, the focus of positive charge is not so great that cations repel each other in those solids. As a result, these cations go into high-temperature minerals of igneous rocks, and in weathering they stay in solids and thus in soils.

At the right, we can consider cations of highest ionic potential - N^{5+} and S^{6+} would be good examples. These ions are still smaller and even more highly charged, and thus provide an extremely focused beacon of positive charge. That allows very strong bonds to O^{2-} to form radicals like nitrate and sulfate. However, the strength of positive charge is so great that O^{2-}s are hard-pressed to shield cations from each other, and so we end up with no CO_2 or SO_3 minerals, and these ions instead tend to break free in weathering and go into solution.



Speciation of some hard cations in aqueous solution

L.B. Railsback 1/2001 rev 3/2001

Portrayal of tetrahedral coordination above is imperfect because the cation and three oxygens are shown as if their centers were coplanar.

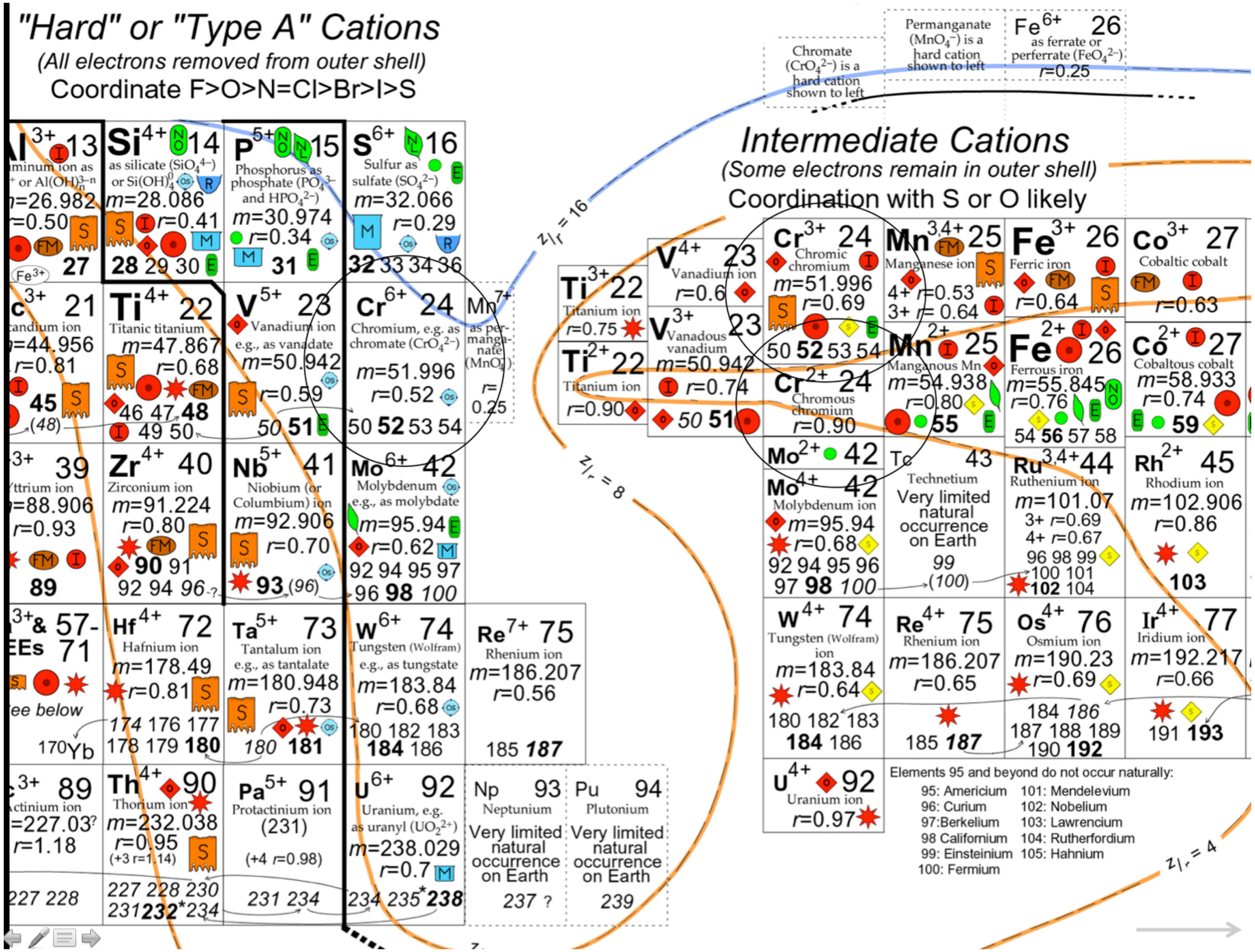
Cations of low ionic potential, at the left, attract the negative (O^{2-}) ends of water molecules, and are thus hydrated in solution.

Cations of a little higher ionic potential have enough positive charge to repel some of the H^+ ions of potential hydrating water molecules.

They thus instead have OH^-s around them and they form hydroxocomplexes.

Moving farther to the right, you encounter cations of still higher ionic potential, so that their positive charge repels still more H^+ ions, stripping some oxygens of both H^+ ions. They thus form oxohydroxo complexes.

Farthest to the right, cations of highest ionic potential repel all H^+ ions and thus have nothing but O^{2-}s around them, and so they form oxocomplexes like the familiar nitrate of N^{5+} and sulfate of S^{6+}. On the other hand, we don't talk about "calciates" and the like because of the much lower ionic potential of Ca^{2+}.



Chromium is one elements that exist both as hard cations and as intermediate cations.

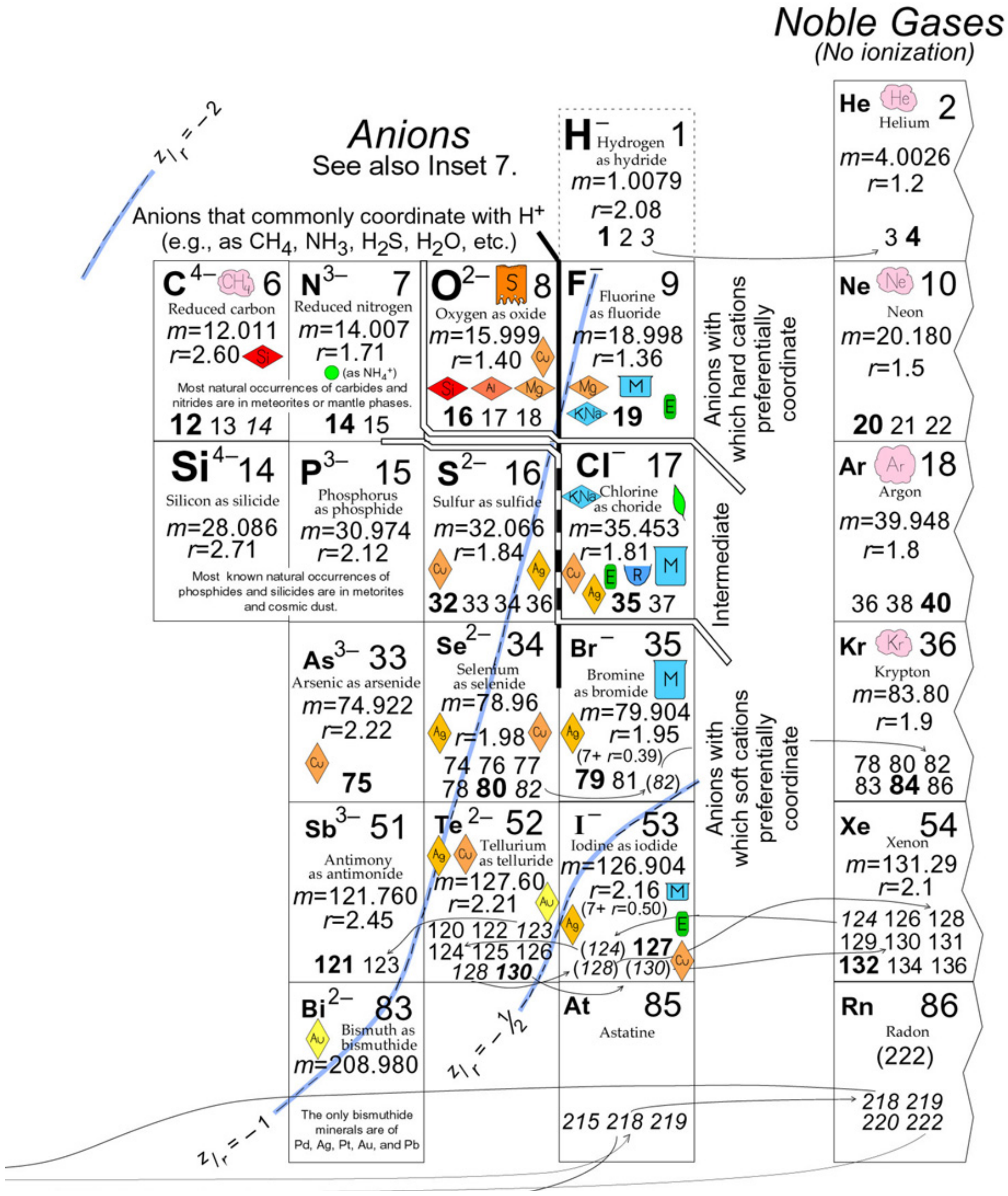
Cr^{3+} an **intermediate cation**, isn't very soluble, enters early-forming igneous minerals, and stays in soil in weathering - Cr^{3+} it has a great affinity for solids. Thinking along those lines, Cr^{3+} predictably makes both an oxide mineral and a sulfide mineral.

On the other hand, Cr^{6+}, the **hard cation**, has a high ionic potential and so falls in the blue swath of cations that make oxysalts, in this case chromates. It's relatively soluble.

All this has **environmental implications**, in that reducing groundwater will leave behind Cr as Cr^{3+} on aquifer solids, but more oxidizing groundwater pumped as drinking water may bring with it chromium as soluble Cr^{6+}, which is poisonous and a major problem in some groundwater (as in Bangladesh).

Cr^{6+}, the hard cation, has a high ionic potential and so falls in the blue swath of cations that make oxysalts, in this case chromates, and it's relatively soluble. Cr^{3+}, on the other hand, is less soluble, enters early-forming igneous minerals, and stays in soil in weathering - Cr^{3+} has a greater affinity for solids. Thinking along those lines, Cr^{3+} predictably makes both an oxide mineral and a sulfide mineral. All this has environmental implications, in that reducing groundwater will leave behind Cr as Cr^{3+} on aquifer solids, but more oxidizing groundwater pumped as drinking water may bring with it chromium as Cr^{6+}, leading to a toxicity problem.

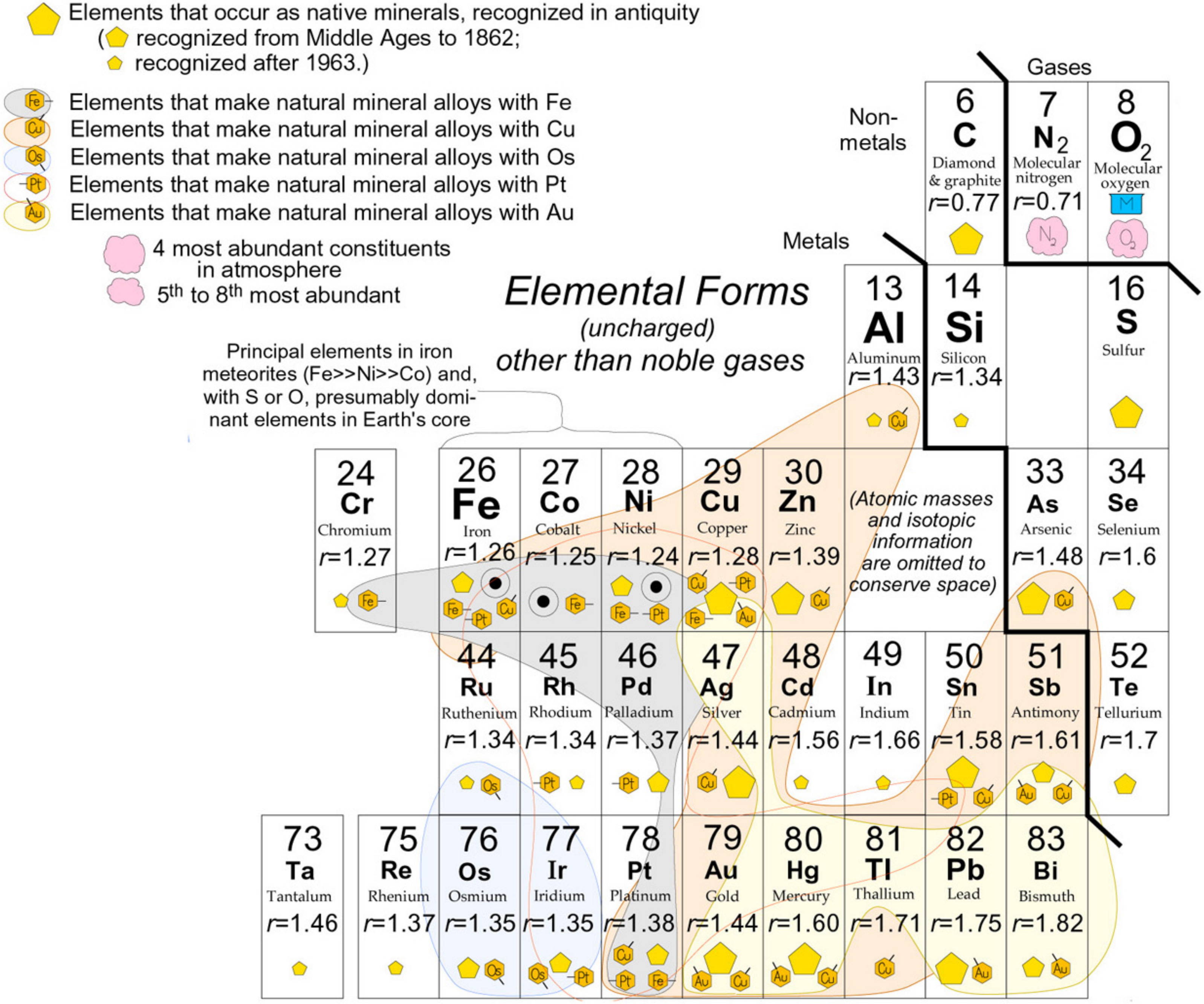
There is little to say here on the **anion side**, in part because ionic potential does not change as much as on the left (cation) side (-0.5 to -2.0 here; 0.5 to 50 among cations)

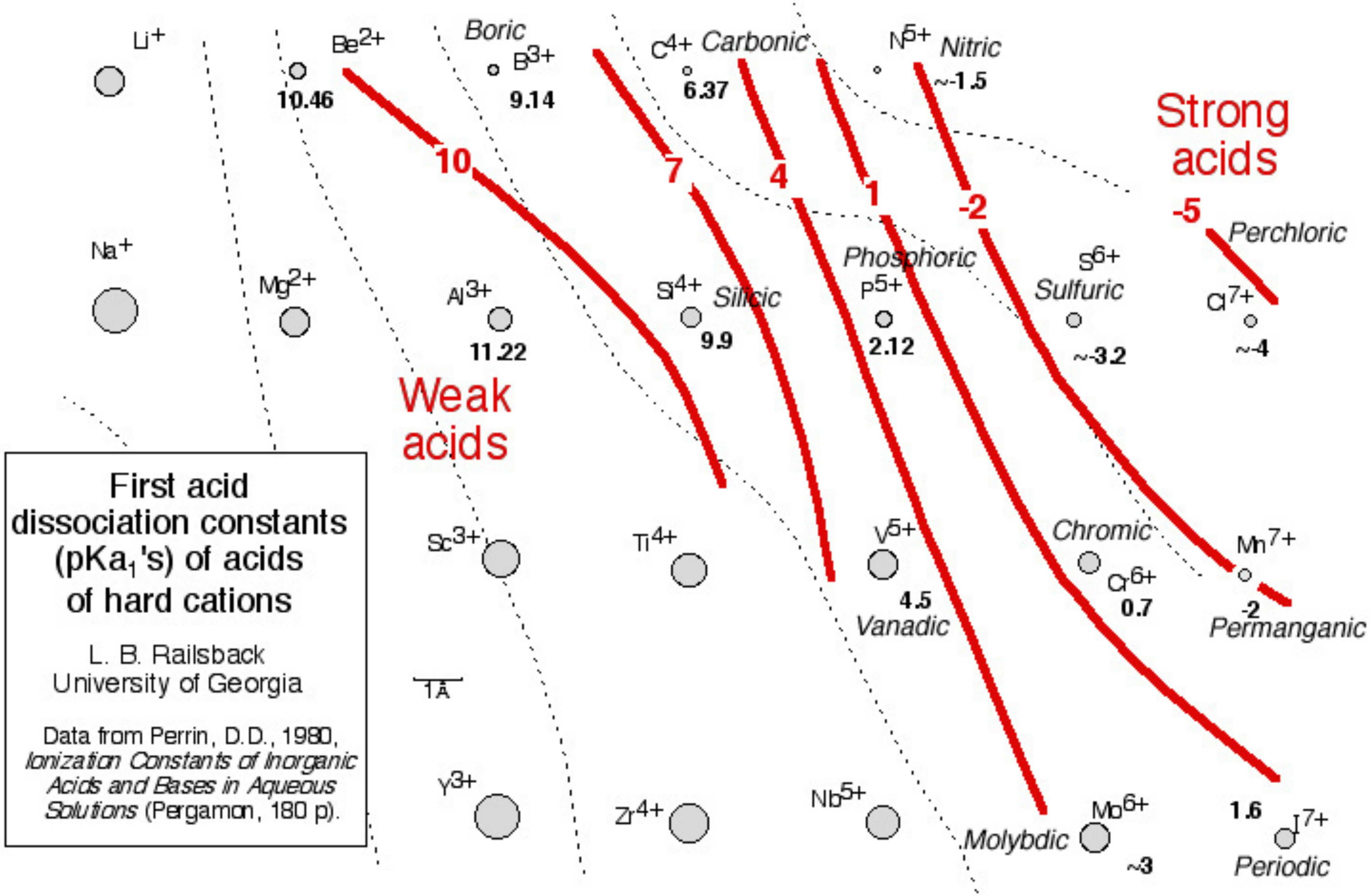


Elemental Forms

(uncharged)

other than noble gases





First acid dissociation constants (pKa_1's) of acids of hard cations

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Data from Perrin, D.D., 1980, *Ionization Constants of Inorganic Acids and Bases in Aqueous Solutions* (Pergamon, 180 p).