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L. Bruce Railsback

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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

ABSTRACT

A new *Earth Scientist's Periodic Table of the Elements and Their Ions* presents the naturally occurring charged species commonly encountered by geoscientists, as well as elemental forms, and it is organized by charge. The new table therefore shows many elements multiple times, unlike the conventional table. As a result, trends, patterns, and interrelationships in mineralogy, soil and sediment geochemistry, igneous petrology, aqueous geochemistry, isotope geochemistry, and nutrient chemistry become apparent in this new table. The new table thus provides a more effective framework for understanding geochemistry than the conventional, and purely elemental, periodic table.

Keywords: geochemistry, mantle, minerals, nutrients, seawater, weathering.

INTRODUCTION

The *Periodic Table of the Elements* formulated by de Chancourtois, Meyer, and Mendeleev (Farber, 1969; Courtney, 1999) has clearly been of great utility in explaining and predicting relationships in chemistry. It has been of less utility, however, in the earth sciences. For example, it does not arrange lithophile, siderophile, and chalcophile elements into distinct groups, and it does not group elements into naturally occurring sets (e.g., elements concentrated in the mantle, in seawater, or in soil). Elements critical for biological processes are likewise not grouped in useful ways by the conventional periodic table. In these respects, the conventional periodic table has not provided a good framework for understanding the chemistry of Earth and its life.

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.

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.

DESCRIPTION OF THE TABLE

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 natural occurrence of sulfides, but not oxides, of the platinum group ions provides a converse example (Fig. 1). The differences between hard and soft cations are further illustrated by insets 3 and 6, which show that melting temperatures of oxides of cations of intermediate ionic potential decrease from hard to intermediate to soft cations. Inset 8 likewise shows that the relative solubility of halide compounds can be predicted from the division of hard and soft cations, in that solubility of halides of hard cations increases from F^{-} to I^{-}, whereas solubility of halides of soft cations increases from I^{-} to F^{-}. In igneous geochemistry, the failure of Cu^{+} to bond with O^{2-} and substitute for Na^{+} in plagioclase (Ringwood, 1955) provides an example of the different behavior of soft and hard cations, respectively. The failure of Tl^{+} to substitute for K^{+}, despite the similar size and charge of those two cations, is another example.

Another difference between the new table and its conventional predecessors is that the new table includes the naturally occurring ac-

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*E-mail: rlsbk@gly.uga.edu.

[1] GSA Data Repository item 2003109, sources of information used in constructing table, and explanatory notes, is available online at www.geosociety.org/pubs/ft2003.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

[2] Loose insert: Figure 1. An Earth Scientist's Periodic Table of the Elements and Their Ions. Sources of information used in constructing table and related notes are available in Appendix DR1 in GSA Data Repository (see text footnote one).

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

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

Figure 1. An Earth Scientist's Periodic Table of the Elements and Their Ions. Sources of information used in constructing table and related notes are available in Appendix DR1 in GSA Data Repository (see text footnote one).

An earth scientist's periodic table of the elements and their ions
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Figure 1
Supplement to *Geology*, v. 31, no. 9 (September 2003)

tinides with the hard cations. Th^{4+} thus falls below Hf^{4+}, and U^{6+} falls below W^{6+}. Trends in the symbols described in the next section extend across this unconventional but geochemically useful arrangement (Fig. 1).

The table also shows the atomic numbers, atomic masses, naturally occurring isotopes, and naturally occurring decay paths of the different elements. Names of elements and ionic forms are shown—e.g., ‘‘Sulfur as sulfate (SO_4^{2-})’’ for S^{6+}. Sizes of chemical symbols are scaled to abundance of the elements in Earth's crust; seven of the nine most abundant elements conveniently fall together in one part of the left side of the new table. Contours of equal ionic potential (charge ÷ radius, i.e., z/r) highlighted in blue and brown extend across the table and parallel trends in natural occurrences, as discussed in the next section.

PATTERNS AND TRENDS IN THE TABLE

Symbols in the *Earth Scientist's Periodic Table of the Elements and Their Ions* show natural occurrences or enrichments in minerals, natural waters, soils and sediments, igneous rocks, the mantle, and the atmosphere, and as critical nutrients (Fig. 1). These symbols fall in swaths that follow contours of equal ionic potential across the table, as one would expect from Cartledge (1928a, 1928b), Goldschmidt (1937), and Mason (1958). As a result, the new table makes apparent patterns of geochemistry that do not emerge from the conventional table. For example, many ions with ionic potential between 3 and 10 make oxide minerals, are concentrated in soil and ferromanganese nodules, enter early-forming igneous phases, and are least depleted the mantle. The result is a red-and-brown swath across the hard and intermediate cations in the new table (Fig. 1). The same swath of hard cations includes those that make oxides with the highest melting temperature, lowest solubility, greatest hardness, and greatest bulk modulus (insets 1–4 and 6).

On the other hand, hard cations with ionic potential <4 make fluoride minerals, include ions abundant in river water and seawater, and include ions important as nutrients. Cations with ionic potential >8 likewise include ions abundant in seawater, ions important as nutrients, and ions that form oxysalts, such as sulfates and arsenates. The results are blue-and-green swaths across the new table. Those swaths extend from the hard cations (which coincide with the lithophile elements) to the intermediate to soft cations (which coincide as a whole with the siderophile and chalcophile elements).

Contours of ionic potential continuing from the hard cations to the intermediate cations (e.g., Mn^{4+} and Fe^{3+}) continue the red-and-brown swath across the table, in that intermediate cations with ionic potential of 3–8 also make oxide minerals, are concentrated in soils, enter early-forming igneous phases, and so on. On the other hand, the contours for lowest ionic potential (1–2) set off the soft cations, which include the coinage metals (Cu, Ag, and Au) and form the center of a region characterized by yellow diamonds that mark ions forming sulfide, bromide, and iodide minerals.

The coinage metals and their neighbors are also shown in a section of the table highlighting elemental forms (the true ‘‘Table of the Elements’’ within the new table). Symbols and colored fields show that groups of these elements make alloys. For example, elements alloying with Os form a small distinct group, and elements alloying with Fe form a group overlapping little with elements alloying with Cu and Au.

On the right side of the table, patterns among the anions match those on the left side. Among the anions of low ionic potential, a blue-and-green swath of symbols pertaining to solutes mirrors that found in cations of low ionic potential. From top to bottom is the transition from anions coordinating with hard cations (resulting in fluorides and oxides of Na^+, K^+, and Al^{3+}) to those coordinating with soft cations (resulting in sulfides, bromides, iodides, and tellurides of Ag^+ and Au^+). From right to left, or from Cl^- and F^- to O^{2-} to C^{4-}, is the transition from anions making minerals with hard cations of low ionic potential (e.g., K^+ and Na^+) to those making minerals with hard cations of higher ionic potential (e.g., Al^{3+} and Si^{4+}). Minerals exemplifying this transition are carrobite (KF), sellaite (MgF_2), gibbsite (Al_2O_3), quartz (SiO_2), and moissanite (SiC).

Speciation of hard cations in aqueous solution also follows easily recognized trends in the new table (bold black lines in Fig. 1). From lower left to upper right across the hard cations, speciation progresses from hydration (e.g., K^+) to hydroxo complexes [e.g., $Al(OH)_n^{3-n}$ and $Si(OH)_4^0$] to oxo-hydroxo complexes (e.g., $COOOH^-$ and $POOOOH^-$, more familiar as HCO_3^- and HPO_4^{2-}) to oxo complexes (e.g., CO_3^{2-}, NO_3^-, and SO_4^{2-}) (Stumm and Morgan, 1996; Shock et al., 1997). A trend that is inscrutable in the conventional periodic table thus becomes readily apparent in the new table. This pattern of coordination, when extended from solution to solids, places in context the mineralogical existence of oxysalt minerals such as carbonates, nitrates, and sulfates, but no ‘‘calciates,’’ or ‘‘sodiates’’, and the existence of aluminate only as an aqueous species (Pokrovskii and Helgeson, 1997).

Many of these patterns can be explained by consideration of bond strength and shielding of charge in mineral structures, as is shown schematically in inset 7. Cations of low ionic potential (e.g., K^+, Na^+, Sr^{2+}) bond only weakly to O^{2-}, so they do not form oxide minerals and are not retained in oxide-forming and hydroxide-forming environments like soils. Instead, they are soluble in aqueous solution, entering natural waters and crossing cell membranes and root sheaths as nutrients. Their weak bonds to O^{2-} result in their incorporation into igneous minerals only at relatively low temperatures and thus relatively late in the crystallization sequence. Cations of intermediate ionic potential (e.g., Al^{3+}, Ti^{4+}) form relatively strong bonds with O^{2-}, and their tetrahedral to cubic coordination allows shielding of the cations' positive charges from each other. They thus form stable oxides and hydroxides in oxidizing environments, and many of them bond in igneous minerals at high temperatures and thus early in the crystallization sequence. Their stability as oxides and hydroxides results in low solubility and low concentration in natural waters and thus leads to their irrelevance as nutrients. Cations of high ionic potential (e.g., P^{5+}, N^{5+}, S^{6+}) form very strong bonds with O^{2-} in radicals like PO_4^{3-}, NO_3^-, and SO_4^{2-}, but their intense concentration of incompletely shielded positive charge and resultant repulsion preclude formation of oxides or hydroxide minerals. Thus, like cations of low ionic potential, they are soluble in aqueous solution, abundant in natural waters, and cross cell membranes and root sheaths as nutrients. Their concentration of positive charge causes them to enter igneous minerals so late that they are among the ‘‘incompatible’’ ions in crystallization of silicate magmas.

These considerations help explain the existence, and nonexistence, of oxysalt minerals (inset 6). Simple silicates (silicates without OH^- and/or H_2O) built around Si^{4+} can accommodate 1+ to 4+ cations. Simple borates and phosphates, built around cations of higher ionic potential (B^{3+} and P^{5+}), can only accommodate 1+ to 3+ cations, presumably because residual positive charge from borate and phosphate groups repels 4+ cations. Simple carbonates and sulfates, built around cations of even higher ionic potential, accommodate only 1+ and 2+ cations. Finally, simple nitrates, built around the tiny highly charged N^{5+}, only accommodate 1+ cations, presumably because the unshielded positive charge from nitrate groups repels any cations of 2+ or greater charge. The same trends, with shifted thresholds, exist in analogous minerals with OH^- and/or H_2O (e.g., hydrous nitrates accommodate 1+ and 2+ but not more highly charged ones, and OH-bearing sulfates and carbonates accommodate 1+ to 3+ but not 4+ cations). The result is a predictive model of the existence and nonexistence of oxysalt minerals of various cations.

GENERAL INSIGHTS

Perhaps the most general insight apparent in the new table is that chemical weathering at Earth's surface and the evolution of Earth to separate the mantle and continental crust are geochemically much the same process: the segregation of hard and intermediate cations of low and high ionic potential from those of intermediate ionic potential. The result is (1) concentration of many of the cations of intermediate ionic potential in the mantle and, at Earth's surface, in soil (the red-and-brown swaths in the table) and (2) the ultimate removal of ions of low and high ionic potential to the oceans (blue swaths in the table). The process continues in the oceans, in that cations of intermediate ionic potential are segregated to ferromanganese nodules and have a short residence time in seawater.

Another major Earth process—life—has followed rules similar to those dictating mantle evolution and weathering. Because life began and largely evolved in aqueous solution and because chemical entities must be dissolved to pass through cell membranes, life has utilized and depends on soluble chemical forms. The critical nutrients for life (green symbols in the table) are therefore coincident with the chemical species dissolved in natural waters (blue symbols in the table). The evolutionary transition of some life forms to land put them in an environment in which chemical weathering removes such ions from soils. The result is a conundrum for water-loving plant life: soils rich in nutrients are most common in arid regions where those nutrients have not been removed by weathering, and soils where wet conditions favor life are typically leached of nutrients. Utilization of ±1 ions by both plants and animals exemplifies this evolutionary challenge: modern farmers commonly must fertilize plant growth with K^+-bearing fertilizers, vertebrates frequent salt licks for Na^+, and premodern societies traded NaCl as a precious substance. Modern humans continue the trend, in that they consume I^--supplemented NaCl, drink F^--supplemented water, consume K^+-bearing sports drinks, and even take Li^+ pills.

SIX EXAMPLES ACROSS THE PERIODIC TABLE

Special Nature of Silicon

In addition to the trends already outlined, many important special cases in geochemistry become apparent with the new table. For example, Si^{4+} is unique in being very abundant (it is the second most abundant constituent in the crust) and in having an ionic potential at the boundary between the relatively insoluble cations of intermediate ionic potential (e.g., Al^{3+}, Ti^{4+}, and Sc^{3+} in the red-and-brown swath of the table) and cations of high ionic potential that form soluble radicals (e.g., C^{4+}, N^{5+}, P^{5+}, and S^{6+} in the blue-and-green swath). Si^{4+} is thus abundant both in residua from weathering (e.g., in sands and sandy or kaolinitic soils) and in natural waters, such as river water (where dissolved silica is the second most abundant dissolved species) and seawater (where it is the 11th most abundant dissolved species).

The abundance and borderline ionic potential of Si^{4+} also have important implications in igneous petrology. Most igneous minerals are silicates, but some of the first phases to form in igneous rocks (e.g., spinel and chromite) contain no Si at all, and the first Si-bearing minerals to form are forsterite (where Mg is more abundant than Si) and anorthite (where Ca and Al outnumber Si) (inset 3). Only in later-forming phases does Si^{4+} become the dominant cation, and only at the end of Bowen's reaction series (when incompatible elements enter solids) does SiO_2 form as quartz (inset 3). This paradox of Si^{4+} as a somewhat incompatible ion in the crystallization of silicate magmas arises because Si^{4+} is at the upper margin of ionic potentials that allow formation of stable oxides. In fact, Si^{4+} is just a step away from C^{4+}, N^{5+}, and P^{5+}, which do not make any such oxide at all because of their high ionic potential and are ''incompatible'' in igneous petrology.

The abundance and borderline ionic potential of Si^{4+} also lead to an interesting feature of plant physiology. Plants take in nutrients like NO_3^- as solutes, and the borderline ionic potential of Si^{4+} lets it be taken up as a solute [as $H_4SiO_4^0$, or more accurately as $Si(OH)_4^0$]. However, Si^{4+} is sufficiently insoluble that some plants build masses of opaline silica in their tissue (Meunier and Colin, 2001). These mineral accumulations within plants, called phytoliths, exist because Si^{4+} is sufficiently abundant and soluble to be taken up through roots in solution but sufficiently insoluble to be maintained as a solid mineral within wet plant tissue.

Extreme Nature of Gold

If Si has a special role in geochemistry because of its abundance and location at a threshold in ionic potential, Au is special for opposite reasons: it is extremely rare, it has an extremely low ionic potential as Au^+, and Au^+ is extremely ''soft'' in the spectrum from hard to soft cations. As a result, Au forms no oxide minerals and doesn't even form a sulfide of only Au; the only analogues of a hypothetical AuS_2 are two $AuTe_2$ minerals and an Au_2Bi mineral. Au's fondness for large anions is also seen in its extensive complexing with Cl^- in solution, to which is attributed much of the transport of gold to generate ore deposits (e.g., Murphy et al., 2000). On the other hand, the indifference of Au to oxygen is one of the reasons Au has been so valued by humans—it continues to shine as an unoxidized metal despite centuries of exposure to O_2. In the conventional periodic table, Au is simply one of many elements in the middle of that table, but isolation by contours of ionic potential illustrates its unique nature in the new periodic table.

Applications of Fe, Mn, and Ce as Paleoredox Indicators

The table's separation of cations and consideration of ionic potential shows why some cations have been used extensively in evaluation of paleoredox conditions. For example, Fe and Mn have been used in geochemical study of oxidation and reduction (e.g., Hem, 1972) because they are by far the most abundant elements that form nonhard cations. They are thus the most abundant elements that can undergo changes of one in oxidation state (e.g., between 2+ and 3+ for Fe). In oxidizing conditions, they are highly charged (= 3+) small ions that are insoluble because of their high ionic potential and resultant formation of hydroxides. In reducing conditions, they are lesser charged (2+) and larger ions that thus have lower ionic potential and are soluble. Fe therefore behaves like the soil-forming and oxide-forming Al^{3+} ion when oxidized to Fe^{3+}, but like the ''weatherable'' and soluble Mg^{2+} ion when reduced to Fe^{2+}.

Ce is less abundant than Fe and Mn, but otherwise analogous in that it precipitates in solids when oxidized to Ce^{4+} but is more soluble as Ce^{3+}. It thus provides an indicator of oxygenation in modern (de Baar et al., 1988) and ancient (Wright et al., 1987) oceans. Ce^{3+} and Ce^{4+} also exemplify patterns of coordination seen elsewhere in the table, in that the ion with lower ionic potential forms a fluoride mineral, fluocerite-(Ce), whereas the ion with higher ionic potential forms an oxide mineral, cerianite. The formation of those two minerals parallels the formation of fluorides by Na^+ and K^+ but formation of oxides by Al^{3+} and Sc^{3+} (Fig. 1).

Uranium, Thorium, and Dating Problems

Radiometric dating using the U-series method (Edwards et al., 1987) is a valuable means of determining the age of materials younger than ~500 k.y. old. One problem with this method, however, is that U at Earth's surface is in the U^{6+} state and thus in the soluble UO_2^{2+} oxo complex (Langmuir, 1978). Th, on the other hand, occurs as Th^{4+}, which is insoluble (e.g., Kaufman, 1969). As a result, parent U is commonly lost from materials but daughter Th remains, giving incorrectly old ages (e.g., Dabous and Osmond, 2000). This problem is not apparent from the conventional periodic table but is predictable in the new table, where U^{6+} falls in the blue-and-green swath of relatively soluble hard cations of high ionic potential and Th^{4+} falls in the red-and-brown swath of relatively insoluble ions of intermediate ionic potential.

From Silicates to Selenites

As already discussed, Si^{4+} is located at the boundary between cations of intermediate and high ionic potential in the new table. One result is that Si^{4+} is one of the few cations that make both an oxide mineral (quartz) and oxysalt minerals (the many silicates). V^{5+} and Mo^{6+} are hard cations with about the same ionic potential, and they also form oxides (shcherbinaite and molybdite) and oxysalt minerals (the vanadates and molybdates). If one follows the contour for $z/r = 8$ from those hard cations to the intermediate and soft cations (Fig. 1), one arrives at Se^{4+}, which likewise forms an oxide mineral (downeyite) and oxysalt minerals (the selenites). Like Si^{4+}, V^{5+}, and Mo^{6+}, Se^{4+} is also a cation essential to vertebrate nutrition (McDowell, 1992; Sunde, 1997). These similarities illustrate the continuity of trends along contours of equal ionic potential across the table. The principal difference in the behavior of Se is that it forms cations with multiple outer-shell electrons and thus exists as Se^{6+} as well as Se^{4+}. Se^{6+} also forms oxysalt minerals (the selenates) and is important in nutrition, but, just as one would expect after following the contour for $z/r = 16$ from P^{5+} and S^{6+} in the hard cations (Fig. 1), Se^{6+} does not form an oxide mineral.

Odd Role of Chloride—Jack of All Trades, Master of None

Cl^- is not as abundant as F^- in the crust, but Cl^- is more abundant than F^- in most natural waters. The reason for this paradox can be seen in the new table. Cl^- occupies an intermediate position among the anions at the right of the table, in that it coordinates with hard cations to make soluble minerals like sylvite and halite and coordinates with soft cations to make relatively rare minerals like chlorargyrite (AgCl) (Fig. 1). By comparison, F^- bonds with hard cations well enough to make insoluble minerals like fluorite and so is sequestered in them, leaving relatively low concentrations in natural waters. Cl^-, in contrast, bonds strongly with neither hard nor soft cations and so makes only relatively soluble minerals (inset 8). It therefore can reach high concentrations in natural waters and commonly only precipitates when it and a weakly bonding cation, Na^+, finally achieve saturation with respect to halite.

SUMMARY

Organizing the new *Earth Scientist's Periodic Table of the Elements and Their Ions* according to charge yields an arrangement more conducive to recognizing geochemical trends than that of the conventional periodic table. These trends in mineralogy, aqueous geochemistry, igneous petrology, mantle geochemistry, soil and sediment chemistry, and nutrient chemistry are largely controlled by coordination of cations with O^{2-}. This synthesis of geochemistry from mantle to soil to seawater provides a framework for understanding Earth systems and predicting geochemical relationships that is not recognizable with conventional, elementally constructed, periodic tables.

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