

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

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## 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  $\text{Si}^{4+}$ , 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*<sup>1</sup>. 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  $\text{O}^{2-}$  and  $\text{S}^{2-}$ , 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  $\text{O}^{2-}$  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)<sup>2</sup>. 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  $\text{Li}^+$ ,  $\text{Be}^{2+}$ ,  $\text{B}^{3+}$ ,  $\text{C}^{4+}$ , and  $\text{N}^{5+}$ . Al, Si, P, and S similarly appear on the left and within the left-to-right horizontal sequence  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Si}^{4+}$ ,  $\text{P}^{5+}$ , and  $\text{S}^{6+}$ . 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  $\text{S}^{2-}$ ,  $\text{S}^0$ ,  $\text{S}^{4+}$ , and  $\text{S}^{6+}$ ).

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  $\text{F}^-$  and  $\text{O}^{2-}$  but not to  $\text{S}^{2-}$ , whereas the soft cations bond strongly to  $\text{S}^{2-}$  and the larger halides,  $\text{Br}^-$  and  $\text{I}^-$  (Stumm and Morgan, 1996) (Fig. 1, Inset 8). These patterns are exemplified in nature by the absence of sulfide minerals of  $\text{Ca}^{2+}$  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  $\text{F}^-$  to  $\text{I}^-$ , whereas solubility of halides of soft cations increases from  $\text{I}^-$  to  $\text{F}^-$ . In igneous geochemistry, the failure of  $\text{Cu}^+$  to bond with  $\text{O}^{2-}$  and substitute for  $\text{Na}^+$  in plagioclase (Ringwood, 1955) provides an example of the different behavior of soft and hard cations, respectively. The failure of  $\text{Tl}^+$  to substitute for  $\text{K}^+$ , 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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<sup>1</sup>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](http://www.geosociety.org/pubs/ft2003.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

<sup>2</sup>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).

tinides with the hard cations.  $\text{Th}^{4+}$  thus falls below  $\text{Hf}^{4+}$ , and  $\text{U}^{6+}$  falls below  $\text{W}^{6+}$ . 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 ( $\text{SO}_4^{2-}$ )” for  $\text{S}^{6+}$ . 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  $\div$  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.,  $\text{Mn}^{4+}$  and  $\text{Fe}^{3+}$ ) 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  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Al}^{3+}$ ) to those coordinating with soft cations

(resulting in sulfides, bromides, iodides, and tellurides of  $\text{Ag}^+$  and  $\text{Au}^+$ ). From right to left, or from  $\text{Cl}^-$  and  $\text{F}^-$  to  $\text{O}^{2-}$  to  $\text{C}^{4-}$ , is the transition from anions making minerals with hard cations of low ionic potential (e.g.,  $\text{K}^+$  and  $\text{Na}^+$ ) to those making minerals with hard cations of higher ionic potential (e.g.,  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$ ). Minerals exemplifying this transition are carobite (KF), sellaite ( $\text{MgF}_2$ ), gibbsite ( $\text{Al}_2\text{O}_3$ ), quartz ( $\text{SiO}_2$ ), 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.,  $\text{K}^+$ ) to hydroxo complexes [e.g.,  $\text{Al}(\text{OH})_n^{3-n}$  and  $\text{Si}(\text{OH})_4^0$ ] to oxo-hydroxo complexes (e.g.,  $\text{COOOH}^-$  and  $\text{POOOOH}^-$ , more familiar as  $\text{HCO}_3^-$  and  $\text{HPO}_4^{2-}$ ) to oxo complexes (e.g.,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ) (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.,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Sr}^{2+}$ ) bond only weakly to  $\text{O}^{2-}$ , 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  $\text{O}^{2-}$  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.,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ ) form relatively strong bonds with  $\text{O}^{2-}$ , 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.,  $\text{P}^{5+}$ ,  $\text{N}^{5+}$ ,  $\text{S}^{6+}$ ) form very strong bonds with  $\text{O}^{2-}$  in radicals like  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , 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  $\text{OH}^-$  and/or  $\text{H}_2\text{O}$ ) built around  $\text{Si}^{4+}$  can accommodate 1+ to 4+ cations. Simple borates and phosphates, built around cations of higher ionic potential ( $\text{B}^{3+}$  and  $\text{P}^{5+}$ ), 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  $\text{N}^{5+}$ , 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  $\text{OH}^-$  and/or  $\text{H}_2\text{O}$  (e.g., hydrous nitrates accommodate 1+ and 2+ but not more highly charged ones, and  $\text{OH}^-$ -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.