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## Geochemical Classification of Elements

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### Definition

Geochemists classify elements in various ways based on their abundance, behavior, and distribution in the Earth.

### Introduction

Elements can be qualitatively classified into **major** (>0.4 wt %), **minor** (0.1–0.4 wt%), and **trace** elements (<0.1 wt%). Major elements are those that define the primary structure of a given phase, which can be a mineral, liquid, or vapor. Major elements are abundant enough that they dictate a system's physical properties, including the assemblage of phases. Trace elements are not essential to the structure of a phase and do not directly influence the properties of a phase or system. Instead, trace elements occur passively as dissolved constituents or in the form of minor amounts of accessory phases. The distribution of elements on Earth is heterogeneous, ranging from the scale of hundreds to thousands of kilometers in the form of the Earth's layered structure (core, mantle, crust, ocean, and atmosphere) down to the scale of millimeters or less in the form of mineral grains or living organisms. Thus, although >99 % of the bulk Earth, which includes the crust, mantle, and metallic core, is composed of Fe, O, Mg, Si, S, Ni, Ca, and Al, in order of decreasing abundance by weight, much of the Fe and almost all the Ni are sequestered in the core, whereas most of the Earth's O is locked up in the mantle and crust in the form of oxides (O makes up nearly 50 % by weight of the mantle). The same element can be a major element in one geologic

environment and a trace element in another. For example, during certain petrogenetic processes, an element initially occurring at trace levels can become concentrated enough to be a major or minor element. Cu ore deposits or Li-rich pegmatites are examples where elements normally in trace abundances can locally become quite enriched. Other examples are H, N, and C, which are trace elements in the mantle but major constituents of the oceans, atmosphere, and life. Redistribution of elements throughout the Earth, a process called differentiation, is dominantly controlled by the formation and physical segregation of silicate liquids, aqueous fluids, and gases, which serve as potential carriers of all elements of the periodic table.

Exactly how elements are spatially redistributed in a planetary body depends on their chemical behaviors and how they partition into different phases during geologic and biochemical processes. Chemical behavior of elements is dictated by the "stability" of the outer electrons. Elements whose outermost electron shells are nearly filled tend to readily attract electrons (high electronegativity), forming anions in chemical bonds. Elements with only partially filled outer shells tend to donate electrons (low electronegativity) and become cations in chemical bonds. Elements with very different electronegativities (opposite ends of the periodic table) tend to transfer electrons between atoms, resulting in ionic bonds. In contrast, elements with similar electronegativities tend to share electron clouds in chemical bonds (covalent bonds), making such bonds very strong. Most of the rocks on Earth are silicates, which are composed of complexes of silica tetrahedra ( $\text{SiO}_4^{4-}$ ), where the similar electronegativities of Si and O result in significant degree of covalent character. Cations on the left side of the periodic table (alkali and alkali Earth metals), such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ , generate ionic bonds with the  $\text{O}^{2-}$  anions making up the apices of the silica tetrahedra to form, for example, the silicate minerals that make up most of the Earth's mantle (olivine,  $\text{Mg}_2\text{SiO}_4$ ) and crust (feldspar, e.g.,  $\text{CaAl}_2\text{Si}_2\text{O}_8$  and  $\text{NaAlSi}_3\text{O}_8$ ). Elements with filled energy shells, such as the noble gases, tend to be chemically inert.

## Partitioning Classifications

The efficiency to which an element partitions into a particular phase is controlled to first order by charge and ionic radius (cations are smaller and anions are larger than their respective atomic radii). During melting, elements can be classified into **compatible** or **incompatible** relative to the solid phase, that is, an incompatible element preferentially partitions into the melt phase, whereas a compatible element partitions into the solid phase. A cation becomes incompatible in a particular crystallographic site when excess electrostatic and strain energy is generated due to charge imbalance or when an ion is too big or too small for a particular crystallographic site (Wood and Blundy, 2003). These effects are manifested as general trends in partitioning behavior as a function of ionic radii for a given charge. For any given mineral/melt pair, there is an optimum ionic radii for maximum compatibility (Wood and Blundy, 2003). In the case of the rare earth elements in most mantle minerals, the heavy rare earths typically exhibit maximum compatibility because the lighter rare earths are too large. This variation in ionic radius, known as the “lanthanide contraction” of the f-orbital shell, thus manifests itself as a distinct decrease in compatibility toward the left-hand side of the periodic table for the rare earth elements.

Most of the high mass trace metals, such as Sr, Rb, and Ba, and the rare earth elements tend to be incompatible during mantle melting because of their large cationic radii. First-row transition metals, with ionic radii more similar to the cation crystallographic sites in mantle minerals, tend to be compatible (Ni and Co) or moderately incompatible (Sc, V, Mn) during melting (Canil, 2004). Some highly charged transition metals, such as high field strength elements Ti, Zr, and Nb, are highly incompatible in common silicates due to charge imbalance. Some elements, however, can be highly compatible in a given phase, but exhibit overall incompatible behavior during melting if that phase represents a minor constituent in the rock. For example, Cu is highly compatible in sulfide, but because sulfides are low in abundance in typical mantle rocks, Cu behaves effectively as an incompatible element during mantle melting (Lee et al., 2012).

Partitioning behavior for a given element is rarely ever a constant due to many factors: (1) effective oxidation, which is controlled by the oxygen fugacity of the environment, (2) temperature, (3) pressure, (4) mineral composition, and (5) melt or fluid composition, which changes complexation behavior. An example of redox effects is seen in the difference in partitioning behaviors between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  and between  $\text{V}^{2+}$  and  $\text{V}^{3+}$  (Canil, 1997). An example of the influence of mineral composition is the effect of coupled substitutions. The presence of  $\text{Al}^{3+}$  as a major element in a pyroxene can enhance the compatibility of rare earth elements (+3) by providing a means of charge balance. Bridgmanite, a lower-mantle mineral with perovskite structure, can enhance the

compatibility of  $\text{Fe}^{3+}$  if  $\text{Al}^{3+}$  is contained in its structure (Frost et al., 2004). The subsolidus transformation of wadsleyite or ringwoodite, which contains minimal  $\text{Al}^{3+}$ , to bridgmanite has been suggested to lead to disproportionation of  $\text{Fe}^{2+}$  into  $\text{Fe}^0$  and  $\text{Fe}^{3+}$ , the latter dissolving into bridgmanite.

Another important quantity is the charge to ionic radius ratio, known as the **ionic potential**. Elements with high ionic potential are referred to as **high field strength elements** (HFSEs) and include  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ , and  $\text{Hf}^{4+}$ . Elements with low ionic potential are often referred to as **large ion lithophile elements** (LILEs) in the geochemical community. LILEs include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ . Low ionic potential elements readily form inner sphere aquo-complexes in aqueous solutions because they are large enough to be surrounded and coordinated to water molecules (Langmuir, 1997). This makes LILEs soluble in aqueous solutions. The high charge of HFSE and rare earth element cations reduces electron shielding within their outermost electron shell, resulting in significant reduction in ionic radii. Because of their small cationic radii and high charge, H is expelled from the solvation shell, preventing such elements from forming aquo-complexes and rendering them relatively insoluble in water (Langmuir, 1997). Only by complexing with other anions, such as halides and oxyanions, can such elements become more soluble in water. These are the reasons why geochemists generally consider LILEs **fluid mobile** and HFSEs **fluid immobile**, but even fluid immobile elements can become mobile under certain conditions.

## Geochemical Classifications

Elements are often categorized based on their general geochemical behaviors even though an element’s chemical behavior depends strongly on variables such as temperature, pressure, and chemical environment; the latter of which can dictate an element’s valence state and ability to form complexes. These classifications broadly follow Goldschmidt’s original classifications (Goldschmidt, 1937) with the addition of organophile and fluid-mobile elements.

**Lithophile** elements (“rock loving”) are preferentially partitioned into silicate minerals. These include cations that commonly form oxides, such as Ca, Mg, Mn, Ti, Na, K, the rare earth elements, U, Th, Si, and Fe in its oxidized states.

**Siderophile** elements (“iron loving”) are those that are preferentially partitioned into the metallic core, typically in the form of alloys with Fe. Elements exhibiting metallic behavior include the noble metals (Pt, Pd, Ir, Ru, Rh, and Os) as well as W, Ni, and Co. Some elements in their reduced states or at high enough pressures to impart

metallic behavior can alloy with Fe metal; these include Si, C, and some high field strength elements like Nb. Sulfur may dissolve in the core as a sulfide complex and, under these conditions, is also considered siderophile.

**Chalcophile** elements are those that commonly form sulfide-type minerals. These include Cu, Pb, Zn, Cd, Mo, Hg, Sb, Sn, Tl, Te, As, as well as noble metals.

**Atmophile** elements are those that readily form volatile compounds at relatively low temperatures (<300 K), many of which are preferentially concentrated in planetary atmospheres. Atmophile elements include C, O, H, N, S, and the noble gases.

**Organophile** elements are those that form or associate with organic compounds (hydrocarbon molecules) in biochemical and biogeochemical processes. These include C, H, N, S, and P, but also include various metal-organic complexes. Many metals, such as U, V, Ge, Pb, and Mo, can complex with organic molecules, generating organic-rich sediments with high metal contents.

**Fluid-mobile elements** are those that readily dissolve in fluids, typically water-rich fluids. Elements with high solubility in water tend to be low field strength elements, such as the alkali and alkali Earth group elements, which readily form inner sphere aquo-complexes or highly electronegative elements, such as the halogens. High field strength elements, in the absence of complexation, tend to be insoluble. Transition metals tend to have lower solubilities, but the presence of anions in the water can greatly enhance their solubilities through complexation. For example, noble metals and high field strength elements can become

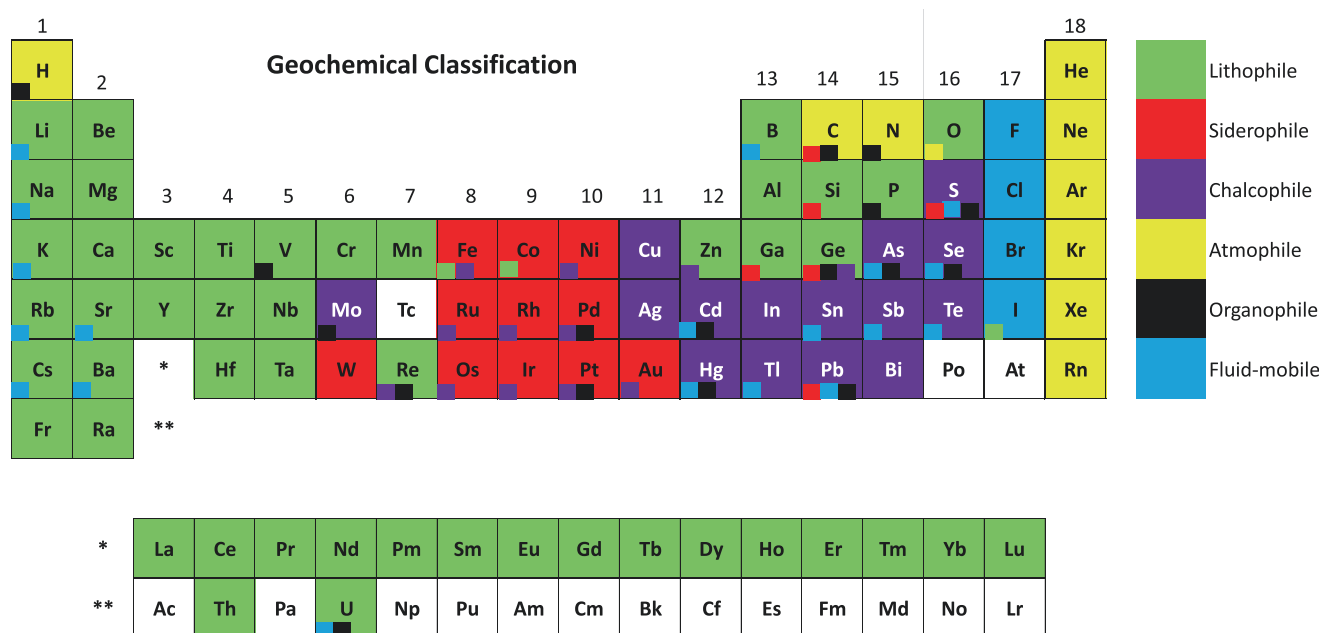
more soluble if complexed with certain halogens or oxyanions. Introduction of carbonate ions into fluids or silicate melts can also enhance solubilities of certain elements.

It is important to recognize that elements can behave in different ways. Obviously, oxygen in its molecular form can be atmophile, but it also forms oxides and dominantly behaves as a lithophile element in the presence of metals. Elements like Ge can be lithophile, organophile, chalcophile, and siderophile, depending on oxidation state and chemical environment (Figure 1).

**Cosmochemical Classifications**

There is a cosmochemical classification of elements that is primarily used to describe the temperature interval over which elements condense from a gaseous state to a solid or liquid state during nebular condensation and planetary accretion. These classifications are based on theoretical condensation temperatures calculated from a nebula with a solar composition and a pressure of 10<sup>-4</sup> bar (at the 50 % condensation level) and are most applicable in the study of meteorites, impact processes, and planetary accretion (Lodders and Fegley, 1998):

- Highly refractory (>1700 K)** – Re, Os, W, Zr, and Hf
- Refractory (1500–1700 K)** – Al, Sc, Ca, Ti, most rare earth elements, Th, and U



**Geochemical Classification of Elements, Figure 1** Cosmochemical classification of elements: Cosmochemical classification of elements based on 50 % condensation temperatures at 10<sup>-4</sup> bar using data from Lodders and Fegley (1998)

**Moderately refractory** (1300–1500 K) – Be, Mg, Si, Cr, Fe, Co, Ni, Nb, Ce, Yb, Pt, and Pd

**Moderately volatile** (1100–1500 K) – Cu, Ba, Mn, Sr, P, and Au

**Volatile** (700–1100 K) – Na, K, B, S, Rb, Cs, Ga, Sn, and Se

**Highly volatile** (<700 K) – Pb, Zn, Tl, In, Bi, O, C, N, H, and noble gases

The use of these classifications should generally be restricted to cosmochemical processes or during the high temperatures of planetary accretion instead of for differentiation within an already condensed planetary body. For example, refractory elements, in a cosmochemical sense, can be siderophile, lithophile, or even chalcophile during planetary differentiation. Care must also be taken when using the terms atmophile and volatile. For example, Pb and Zn are considered highly volatile from a cosmochemical perspective, but would not be considered atmophile. Nevertheless, under unusual situations, such as during a meteorite impact or volcanic processes, Pb and Zn can be volatilized briefly into the atmosphere before recondensing out of the atmosphere upon cooling. Ge can be volatile in a cosmochemical sense, but can be lithophile or siderophile in a geochemical sense (Figure 2).

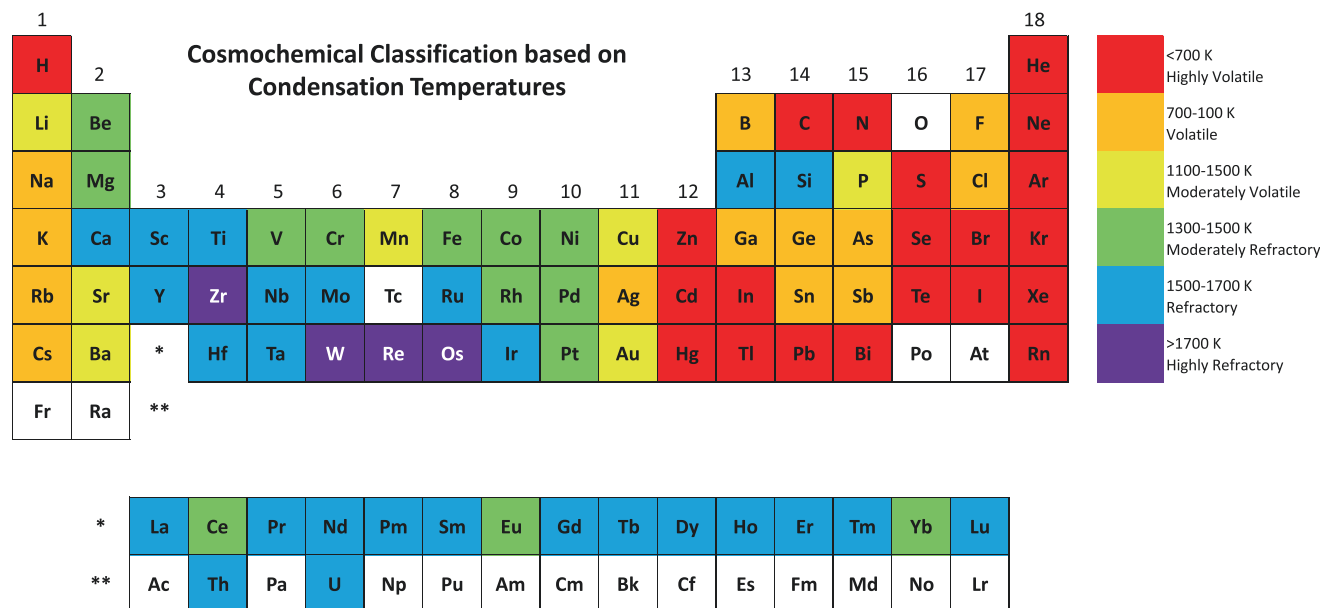
### Using Elements in Geochemistry and Cosmochemistry

Major elements are best used for determining how phase assemblages evolve during petrogenesis of rocks. Compatible

and moderately compatible trace elements can also be used to evaluate phase assemblages. Together, major elements and moderately incompatible to compatible trace elements can be powerful tools for unraveling the mineralogy of the source regions of magmas. Incompatible trace elements are less diagnostic of mineralogy because effects of fractionation strongly accentuate changes in incompatible trace element abundances. For example, continental crust is highly enriched in incompatible elements owing to extreme magmatic differentiation. Contamination of mantle-derived magmas with small amounts of continental crust or fluids can lead to significant changes in trace element signatures with only minor change in major element systematics. Because some trace element systems are associated with radioactive isotopic systems, a full understanding of the geochemical behavior of parent and daughter elements is critical for interpreting isotopic evolution of the Earth.

Because many factors influence element partitioning, some elements can be used to track various intensive variables, such as temperature, pressure, and oxygen fugacity, when used judiciously. For example, rare earth element partitioning between solid and melt and at subsolidus conditions can be used indirectly as a qualitative barometer by signaling the presence of high-pressure minerals (garnet) or as a quantitative thermobarometer with proper calibration (Liang et al., 2013). Variations in the oxidation state of Fe, Eu, and Ce influence their geochemical behaviors, allowing them to be used for tracking oxygen fugacity in the mantle, crust, oceans, and atmosphere through time.

Finally, elemental abundances provide first-order constraints on how different reservoirs interact and how elements



**Geochemical Classification of Elements, Figure 2** Geochemical classification of elements

are cycled through these reservoirs. For example, the abundance of an element in the ocean may shed light on the element's residence time, that is, elements in high abundance tend to be soluble and have long residence times (Na and Cl), whereas elements in low abundance tend to be insoluble and have short residence times (e.g., rare earth elements). Temporal variations in seawater composition have been used to reconstruct past variations in climate, ocean circulation, and weathering (Holland, 1984). Similar approaches can be applied to better understand magma chamber dynamics.

## Summary

The elements of the periodic table provide many different ways of investigating how the Earth system operates. In many cases, however, the study of major and trace elements is often treated separately. Many of the most interesting advances in geochemistry have come from a holistic understanding of the periodic table.

## Cross-References

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- ▶ [Nobel Gas Elements](#)
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- ▶ [Partitioning and partition coefficients](#)
- ▶ [Periodic Table](#)
- ▶ [Siderophile Elements](#)
- ▶ [Solubility](#)
- ▶ [Trace Elements](#)

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