Geochemistry

Notes II: Characteristics of the elements, bonding, coordination number, ionic radius

I. Periodic Table and properties of the elements

II. Bonding

III. Coordination number, ionic radius

The chemical properties of an element depend on its electronic structure. Each electron is found in an orbital, which is, in essence, a volume in space in which there is a high probability of finding a particular electron (see figure 5.2). Orbitals are denoted by numbers and letters (e.g. 1s, 2s, 2p, 3d). A specific maximum number of electrons can fit in each orbital. There is a hierarchy in terms of energy among possible "sites" for electrons, so that under "normal circumstances" electrons occupy the lowest energy "sites" (see Table 5.2).

The most important point about this discussion is that atoms/ions are more stable when certain orbitals are full. In general neutral atoms do not have full orbitals (exception being rare gas elements). Therefore they react chemically to obtain full orbitals. This tendency is the basis for chemical bonds.

The Periodic Table (Fig. 6.1) organizes elements by atomic number and by chemical properties; mainly by how many electrons need to be lost or gained to attain a state where the orbitals are full. The rows are called periods and are characterized by the filling of a specific orbital or orbitals (Table 6.1). The columns are called groups and basically identify the number of electrons that must be lost to attain a stable electronic configuration. Elements in the same group have similar chemical properties. These chemical properties can be quantified in terms of parameters such as electronegativity and first ionization potential (Fig. 7.1).

One way in which atoms attain full orbitals is by losing or gaining electrons, thereby becoming electrically charged (an ion). A positively charged ion is a cation and a negatively charged ion is an anion. The charge an ion of a particular element attains after it has lost or gained enough electrons to have a stable electronic configuration is called the valence. It is important to know the valences of the most common elements in the earth (see Table 4.3, 7.3) as well as those of the elements that are important in isotope geochemistry.

Ionic bonds form when an electron or electrons from atoms of one or more element are lost to atoms of another element or elements. In this fashion the atoms attain stable electronic configurations and become ions. The attractive force between cations and anions is the basis for the ionic bond.

Covalent bonds form when atoms share electrons to attain stable electronic configurations. In reality most bonds are not strictly ionic or covalent and have some characteristics of each type of bond. Water is an important example of a molecule with both covalent and ionic characteristics.

Compounds are made up of either large numbers (10^{23}) of atoms bonded together in crystalline solids or finite numbers of atoms bonded together in discreet molecules. Chemical formulas stipulate either the actual number of atoms of each element in a molecule or the proportions of each element in a crystalline solid.

Solutions consist of one or more compounds dissolved in another compound. Solutions can be gaseous, liquid, or solid.

An important concept in understanding crystalline solids is a site, which is a type of location in a crystalline solid which has a particular geometry in terms of location within a crystal structure, shape, and size. Atoms or ions of one or more element may occupy a site.

In most rock-forming minerals, the main anion is O^{-2}. One can therefore consider sites occupied by cations in the spaces between the O^{-2} anions. Oftentimes these sites can be approximated by regular polyhedrons determined by connecting the centers of the anions with lines (Fig. 7.4). The site can then be described either by the number of anions surrounding the site (or number of vertices of the polyhedron), the coordination number, or by an adjective based on the name of the polyhedron (e.g. tetrahedral or octahedral). The size of a site increases with increasing coordination number.

The ionic radius of an ion of a particular element with a specified charge is a measure of the size of that particular ion. In crystals there is generally a good match between the ionic radius of an ion and the size of the site it occupies. One can calculate the size of a site from the coordination number and the ionic radius of the ion in the coordination complex (Fig. 7.4).

Ionic radius generally increases from (1) cation to anion, (2) low Z to high Z within a group, (3) high positive charge to low positive charge, (4) low negative charge to high negative charge, and (5) high Z to low Z over specific portions some periods (rare earths, actinides), (Fig. 7.5).

A solid solution is a crystal in which ions of two or more elements are mixed randomly in a particular site.