Earth and Planetary Materials

Spring 2013

Lecture 2
2013.01.09

Mineral Name

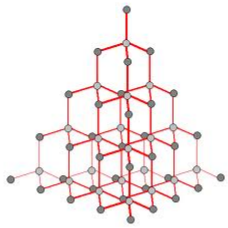
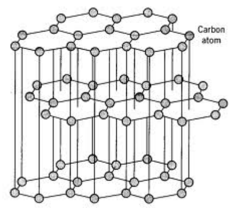
Implies two things

- Chemical composition
- A particular structure, or arrangement of atoms.

→ A distinct set of physical properties

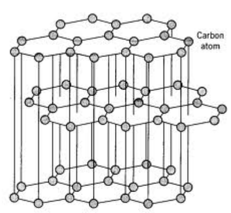
Polymorphs

- minerals that have the same chemical composition but different structure

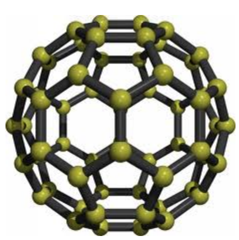
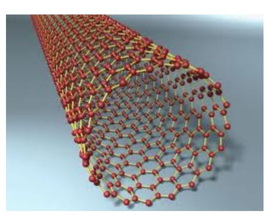
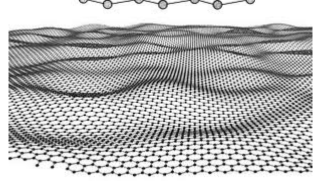




Examples

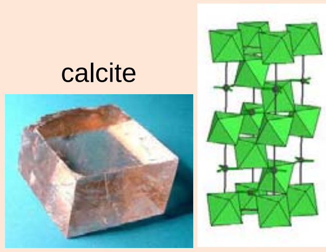
- C60 (fullerene, Nobel prize 1996)
- Carbon nanotubes (CNT)
- Graphite → graphene (2010, Nobel prize)
- Name a few different properties or applications for each?



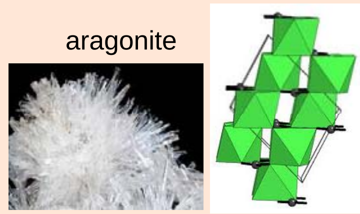
Will you consider them minerals?

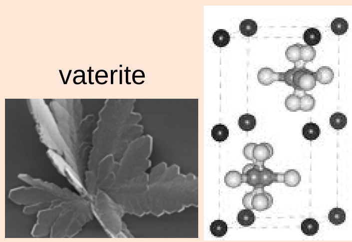
calcite



aragonite



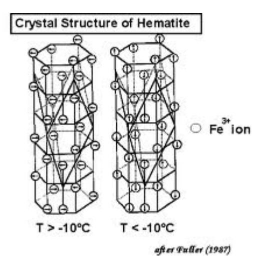
vaterite

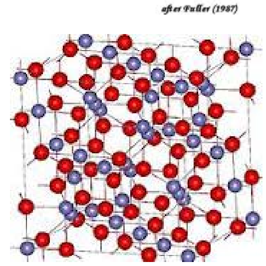


Examples?

Fe $_2O_3$

- α-Fe $_2O_3$: hematite
  - corundum structure, hexagonal close packing
  - antiferromagnetic below ~260 K
- γ-Fe $_2O_3$: maghemite
  - cubic structure, meta stable, converts to α- phase at high T
  - ferromagnetic





Minerals are chemical compounds

- **chemical compound**: stable combination of elements, electrically neutral

- **stoichiometry**: ratio of elements in a mineral

Example:

- The stoichiometry of quartz is Si and O in a 1:2 ratio (SiO_2)
- Sidorenkite $Na_3MnPO_4CO_3$

- Must be charged balanced!

Terms

- **Element**: simplest form of matter; can't be separated into different substances by ordinary chemical reactions

- **Atom**: smallest unit of matter that retains the properties of the element

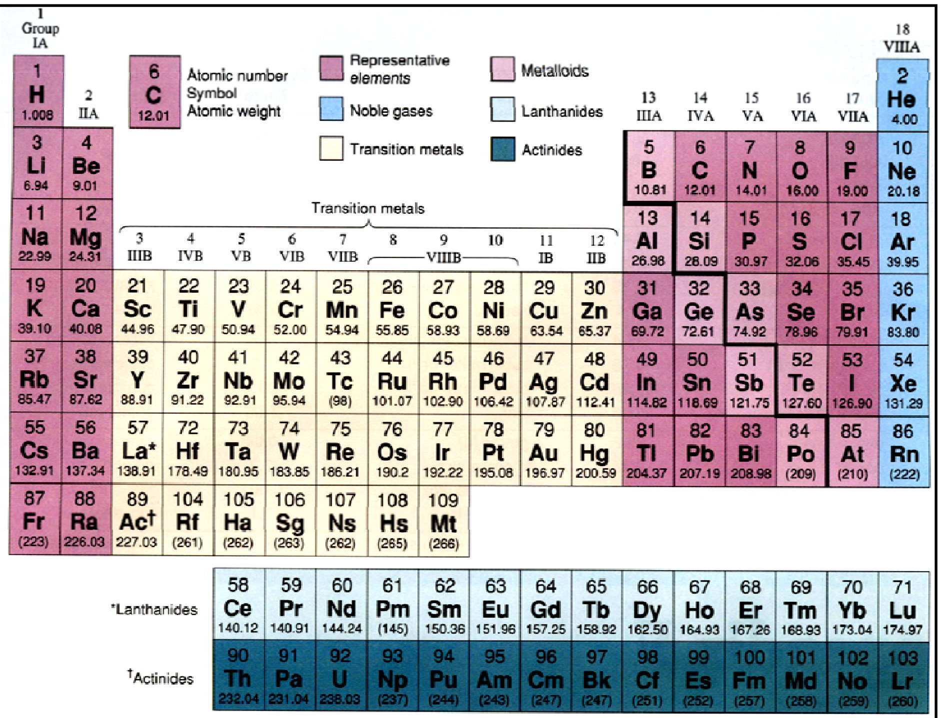
- **Atomic structure**:
  - nucleus
  - protons (charge=+1*e*; mass=1 amu)
  - neutrons (no charge, mass≈1 amu)
  - electrons (mass<<1 amu; charge = -1*e*)

Terms

- **Core electrons** (filled inner shells)
- **Valence electrons** (outer shell, available for chemical bonding interactions)
- **Atomic number:** number of protons in the nucleus; characteristic of the element

The Periodic Table of the Elements

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 Uun (271)	111 Uuu (272)	112 Uub (277)						
			58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	
			90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)	



Terms

- **Mass number**: # of protons + # of neutrons

- **Isotopes**: elements having same atomic number, but different number of neutrons.

  Examples:
  - ^{12}C, ^{13}C, ^{14}C are isotopes of carbon (mass number = 6)
  - ^{28}Si, ^{29}Si are isotopes of silicon (mass number = 14)

Terms

- **Atomic mass (weight)**: mass of 1 mole of that substance (6.02×10^{23} particles); averaged over the naturally occurring isotopes; given in periodic table

- **Neutral atom**: equal numbers of electrons and protons

- **Ion**: charged atom or tightly bound molecule

Bonding in Materials

(A) Electronic structure

- **Electronic structure**: provides an understanding of the ways and proportions that various elements occur in minerals.

- **Octet rule:** atoms tend to gain or lose electrons to gain a filled outer shell; which has eight electrons for elements below the second row. Stable configuration is for the outer shell to be either filled or empty - like that of a noble gas

Valence or formal charge on the ions

- Valence = oxidation state

- The charge of an atom after gaining or losing electrons to fill the outer shell

- The periodic table is arranged in such a way to make this easier

Basic orbital structure

- Example: Na; Z=11; neutral atom has 11 protons in the nucleus and 11 electrons:

_ _
↑↓ ↑↓ ↑↓↑↓↑↓ ↑ _ _ _ _ _ _ _ _ _ _

1s 2s 2p 3s 3p 4s 3d 4p

- Na can gain a filled outer shell by giving up one electron, acquiring the e^- structure of Ne
- Na ⇒ Na^+ + e^-
- Na is a cation with a +1 valence (or, formal charge; oxidation state)

Basic orbital structure

- Example: Cl; Z=17

_ _
↑↓ ↑↓ ↑↓↑↓↑↓ ↑↓ ↑↓↑↓↑ _ _ _ _ _ _ _

1s 2s 2p 3s 3p 4s 3d 4p

- Cl can gain a filled outer shell by gaining one electron, acquiring the e^- structure of Ar
- Cl + e^- ⇒ Cl^-
- Cl^- is an anion with a -1 valence (or, formal charge)

General Rules for assigning formal charge

- Alkali metals (first column): always +1 (Na, K, etc.)
- Alkaline earths (second column): always +2 (Mg, Ca, Sr, Ba)
- Halogens (column 7): always -1 (F, Cl, etc.)
- Column (III): Al, B, etc. are +3
- Si: +4
- C: can be anything from -4 to +4

Transition metals

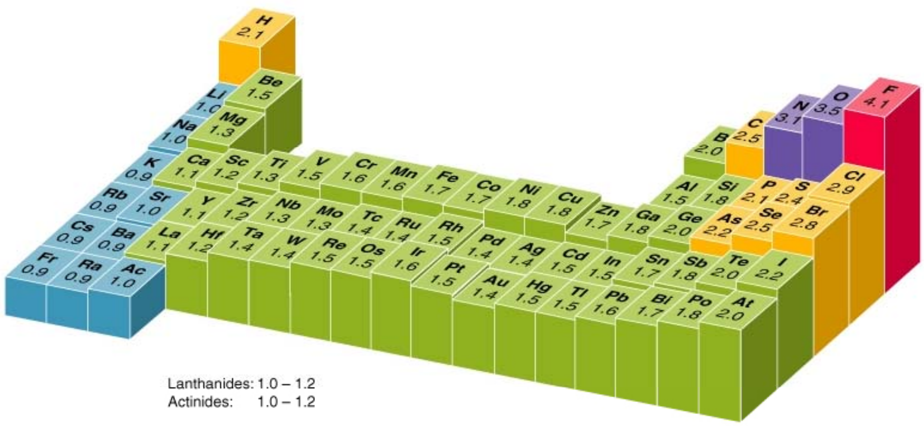
- correspond to filling of 3-d orbitals; more complicated
- can be tricky, some have several possible valence states
- most transition metals have a +2 charge from loss of 4s electrons (leaving the 3d electrons)

Some additional rules for Earth

1) O is always -2
2) H is always +1
3) valence for a native element is always 0
4) the charge of an ion is equal to the sum of the valence of the atoms:
5) the total charge of a mineral formula (or any chemical compound) is 0
6) rules 1-4 can be used to figure out the valence of something you don't know.

B) Electronegativity (EN)

- measure of an atom's ability to acquire an electron.
- useful concept for describing types of bonds.
- in periodic table: upper right are most electronegative (O and F)
- left and lower left have lowest EN (metals)
- difference in electronegativity can be used to deduce nature of bond: ionic (large difference) to covalent (little or no difference).



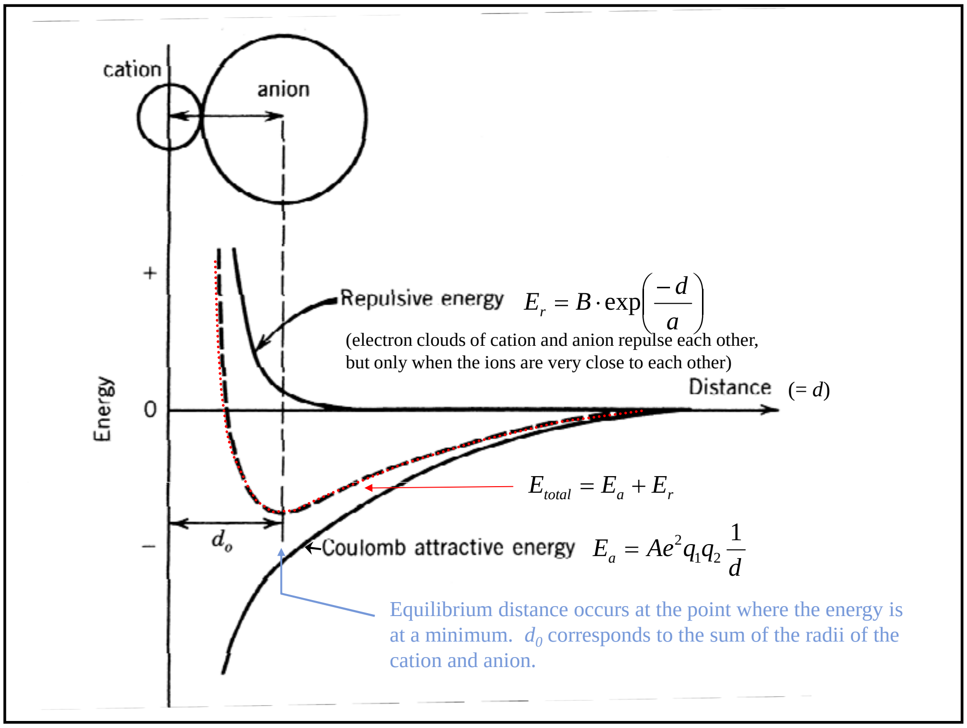
The noble gases are assigned electronegativities of zero and are omitted from this illustration.

FIG. 3.22 The electronegativities of the elements. (From J. E. Brady, J. W. Russell, and J. R. Holum, 2000, *Chemistry, matter and its changes*, 3rd ed., New York: Wiley.)

C) Types of bonding in minerals

Ionic bond

- Between elements with large EN difference (e.g., between Na and F)
- complete transfer of electrons from cation to anion
- moderately strong bond: brittle, moderately high melting point
- (Usually being) electrical insulators



C) Types of bonding in minerals

Covalent bond

- Between elements with similar, but high EN
- (example: C-C in diamond; C-O in carbonate ion)
- electrons shared between elements
- very strong bonds (= short bond distances)
- brittle; high melting point

C) Types of bonding in minerals

Metallic bond

- Between elements with similar, but low EN (e.g., Cu-Cu)
- All valence electrons given up to "conduction band"
- cationic metal cores with mobile electrons
- moderate melting point
- excellent electrical and thermal conductivity
- opaque; metallic luster (strong interaction with visible light)

C) Types of bonding in minerals

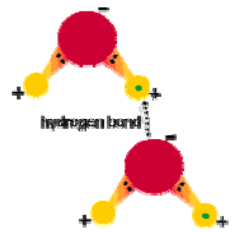
Van der Waal's bond

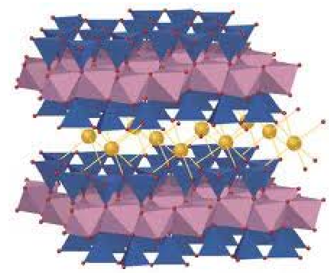
- Between neutrally charged particles
- polarization of electron distribution
- very weak bond
- often occurs between sheets in layered minerals (graphite, some clay minerals such as talc)

C) Types of bonding in minerals

Hydrogen bond

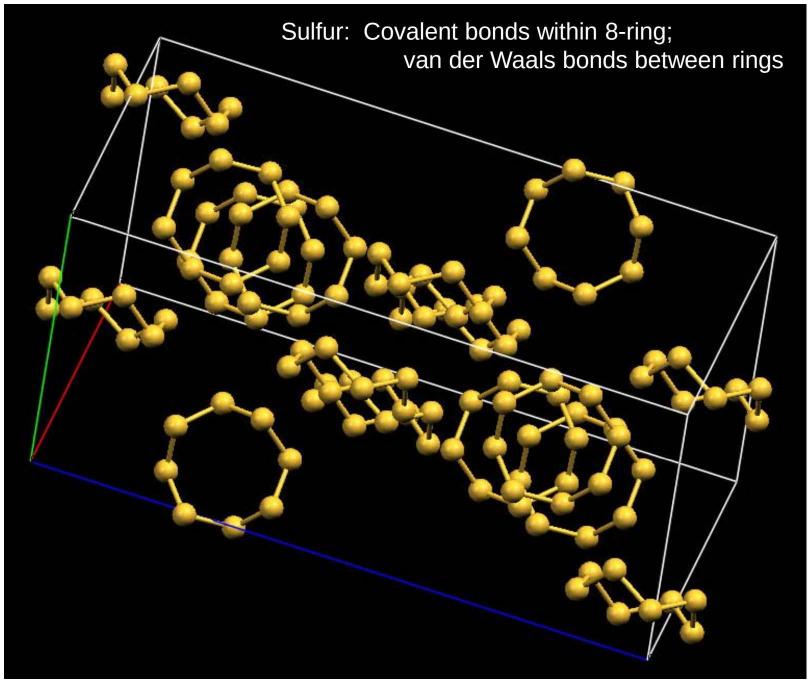
- Between OH group (hydroxyl, or water), and lone e^- pair on adjacent oxygen
- weak bond, but important in some minerals (ice, clay minerals, gypsum)
- Extremely important in biological systems (stabilizes and determines the structure of large macromolecules, e.g. proteins and nucleic acids)

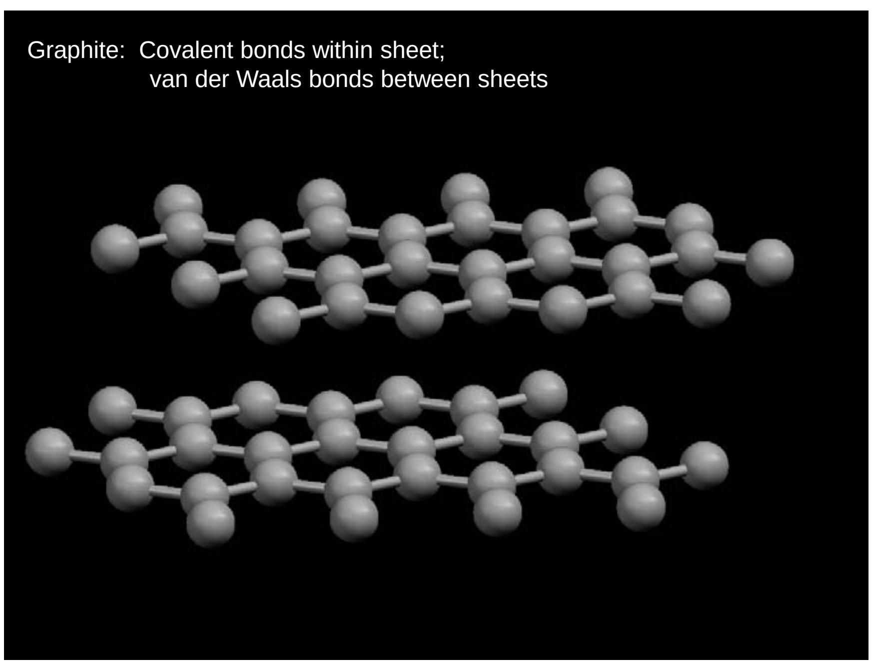




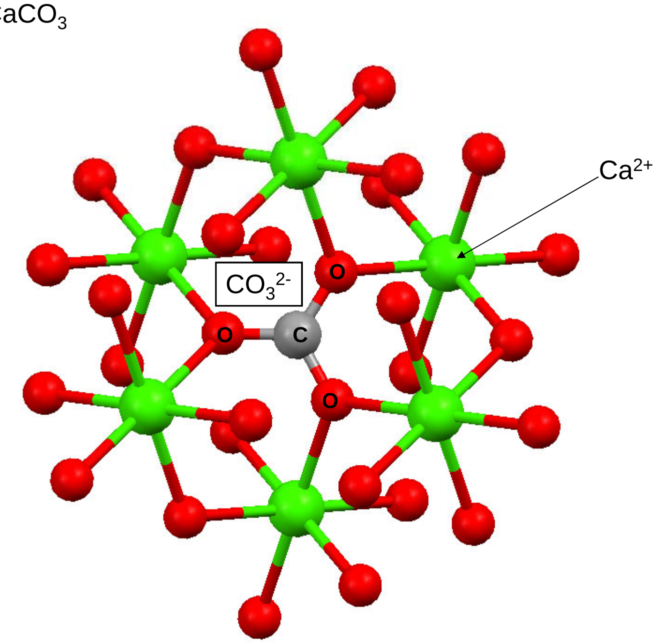
C) Types of bonding in minerals

- It is very common for minerals to exhibit more than one type of bonding


Sulfur: Covalent bonds within 8-ring;
van der Waals bonds between rings

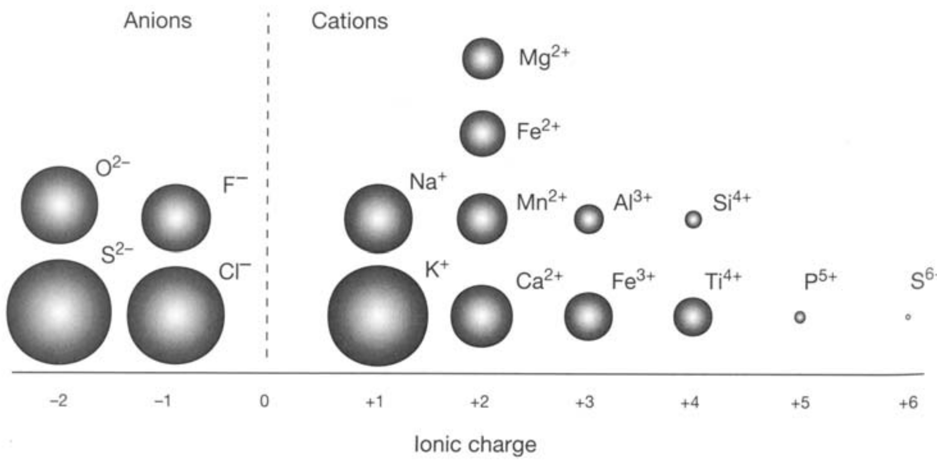

Graphite: Covalent bonds within sheet;
van der Waals bonds between sheets

calcite $CaCO_3$



Bond energy, bond length

- Bond energy (*E*): the measure of bond strength in a chemical bond
- Relates to bond length (distance): we can use atomic radius (metallic, ionic, or covalent) of each atom in the molecule to determine the bond strength
- Only general trend



Perkins (2002) *Mineralogy*, 2nd Ed; p. 274

Example

Bond type	Bond length (pm)	Bond energy (kJ/mol)
C–C	154	348
C=C	134	614
C≡C	120	839

TABLE 3.12 Some Common Ions (Exclusive of Hydrogen) that Occur in Rock-Forming Minerals, Arranged in Decreasing Ionic Size

Ion	Coordination Number with Oxygen		Ionic Radius Å
O^{2-}			1.36 [3]
K^{+}	8–12		1.51 [8]–1.64 [12]
Na^{+}	8–6	cubic to octahedral	1.18 [8]–1.02 [6]
Ca^{2+}	8–6	cubic to octahedral	1.12 [8]–1.00 [6]
Mn^{2+}	6	octahedral	0.83 [6]
Fe^{2+}	6	octahedral	0.78 [6]
Mg^{2+}	6	octahedral	0.72 [6]
Fe^{3+}	6	octahedral	0.65 [6]
Ti^{4+}	6	octahedral	0.61 [6]
Al^{3+}	6	octahedral	0.54 [6]
Al^{3+}	4	tetrahedral	0.39 [4]
Si^{4+}	4	tetrahedral	0.26 [4]
P^{5+}	4	tetrahedral	0.17 [4]
S^{6+}	4	tetrahedral	0.12 [4]
C^{4+}	3	triangular	−0.08 [3]