Lecture 3: Transition Metal Chemistry; Crystal Field Theory
Transition Metal Chemistry
Transition Metals are Important

- Fe and Mn oxides are major soil and sedimentary minerals
- Fe and Mn involved in biogeochemical cycling, impact the cycles of C, N, S, and P
- V, Cr, Mn, Fe, Co, Ni, Cu, Zn have biologic functions
- Many of these element are used as proxies for reconstructing conditions in the geological past
- Many of these elements have technological or industrial applications
- Cr, Co, Ni, Cu, Zn are environmental contaminants
Mineral Color

Emerald: Cr$^{3+}$

Ruby: Cr$^{3+}$

Olivine: Fe$^{2+}$

Rhodacrosite: Mn$^{2+}$

Hematite: Fe$^{3+}$
Unique Properties of Transition Metals
 Ionic Radii Trends

### Lanthanide Contraction

- **(a)** cubic (8-fold) coordination
- **(b)** octahedral (6-fold) coordination

Figure 6.1 Ionic radii of the lanthanide cations in oxides. **(a)** Eight-fold coordination; **(b)** octahedral coordination (data from Shannon, 1976).

### Octahedral Ionic Radii of First-Series Transition Metal Cations

- **(a)** $M^{2+}$ ions
- **(b)** $M^{3+}$ ions

Figure 6.2 Octahedral ionic radii of first-series transition metal cations. **(a)** Divalent cations; **(b)** trivalent cations. Filled circles: high-spin cations; open squares: low-spin cations (data from Shannon, 1976).
Lattice Energy Trends

Figure 7.1 Lattice energies for transition metal compounds and minerals, (a) Metal(III) fluorides (TiF$_3$, V$_2$F$_3$, CrF$_3$ and FeF$_3$ are isostructural; ScF$_3$ and GaF$_3$ have the ReO$_3$ structure; MnF$_3$ has a distorted VF$_3$ structure); (b) Metal(II) oxides (ZnO has the wurtzite structure; the remainder have the NaCl structure); (c) Metal(II) sulphides (CaS has the NaCl structure; ZnS has either the sphalerite, wurtzite or NaCl structure; the remainder have the NiAs structure); (d) Metal(II) orthosilicates (Zn$_2$SiO$_4$ has the willemite structure; the remainder have the olivine structure). [Sources of data: George & McClure, 1959; Waddington, 1959; Ottonello, 1987.]
Hydration Enthalpy Trends

Figure 7.2 Heats of hydration of transition metal ions (a) $M^{2+}$ ions; (b) $M^{3+}$ ions. Filled circles: experimental; open circles: CFSE deducted. Note that experimental values lie on double-humped curves; when CFSE's (table 2.5) are deducted for each cation, the corrected values lie on smooth curves through the values for $3d^0$, $3d^5$ and $3d^{10}$ cations.

[Sources of data: George & McClure, 1959; table 2.5.]
Fig. 1.27: Water exchange rates of aqueous divalent transition metal cations.
Orthosilicate Dissolution Rate

**FIG. 2** Dissolution rates for endmember orthosilicate minerals at pH = 2 and 25 °C, plotted against the first-order rate coefficient, $k$ (s$^{-1}$), for water exchange from the solvent into the hydration sphere of the corresponding dissolved cation. The mineral and ions are identified by the divalent cation (for example, Mn refers to Mn$_2$SiO$_4$ and Mn(H$_2$O)$_6^{2+}$).

**FIG. 1** Dissolution rates of orthosilicate minerals (identified by the dominant divalent cation) at pH = 2 and a temperature of 25 °C. a. Rates for minerals containing alkaline-earth cations (filled symbols) vary with ionic radius of the divalent cation. Rates for minerals containing first-row transition metals (open symbols) vary considerably, although there is little variation in ionic radius. b. Dissolution rates of orthosilicate minerals containing transition metals (filled symbols, left-hand axis) compare well with the first-order rate coefficient$^{15}$, $k$ (s$^{-1}$), describing water exchange from the solvent into the hydration sphere of the corresponding metal ion (open symbols, right-hand axis). Measured uncertainties are commonly within the size of the plotted symbol.
### Partially Filled 3d Orbitals Unique to Transition Metals

Table 2.1. *Electronic configurations of the first-series transition elements occurring in minerals*

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<tr>
<th>Atomic number</th>
<th>Element</th>
<th>Atom</th>
<th>Electronic configurations</th>
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<td>[Ar]3d&lt;sup&gt;10&lt;/sup&gt;</td>
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</table>

[Ar] = Argon core, 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>
Crystal Field Theory
d Orbital Shape

- 5 energetically identical orbitals
- \(d_{z^2}\) is a linear combination of two other orbital geometries
  - Looks different but actually is identical
- 3 point along diagonal directions, two along axes
When 3d Cations Surrounded by Anions (Ligands), All Orbitals are No Longer Equivalent.
Crystal Field Stabilization Energy (CFSE)

- \( t_{2g} \) and \( e_g \) orbitals differ in energy when a metal is coordinated to a ligand, e.g., \( O^{2-} \)
  - This difference in called the “crystal field splitting”, labeled as “\( \Delta_o \)” for an octahedral field
- There is a energetic benefit to filling \( t_{2g} \) before \( e_g \) (in an octahedral site)
  - Lower in energy then an idealized spherical field
  - This energy benefit is the CFSE:

\[
CFSE = 0.4 \Delta_o \times (\#e^- \text{ in } t_{2g}) - 0.6 \Delta_o \times (\#e^- \text{ in } e_g)
\]
Control on Spin State

• \(d^4\) through \(d^7\) ions can have two spin states
  – High-spin (hs): maximum number of unpaired e-
  – Low-spin (ls): maximum number of paired e-
• Adding a 2\(^{nd}\) e- to an orbital requires energy
  – Called the *spin-pairing energy (SPE)*
• Spin state is determined by relative size of \(\Delta_o\) and the spin-pairing energy
  – \(\Delta_o < \text{SPE}\): High-spin is lower energy state
  – \(\Delta_o > \text{SPE}\): Low-spin is lower energy state
Size of Crystal Field Splitting

• $\Delta_o$ is affected primarily by three parameters:
  – **Cation charge**: $\Delta_o$ increases with increasing charge
    • $\Delta_o$ for +3 cations nearly 2x that of 2+ cations
    • +3 cations more likely to be low-spin (but many are still hs)
      – e.g., Co$^{3+}$ is low-spin when substituting in Mn oxide minerals
  – **Nature of ligand**: $\Delta_o$ increases with strength of metal-ligand bonding interaction
    • Most ligands in natural systems produce weak $\Delta_o$
      – Favors high-spin states
      – Disulfide in pyrite is exception, as it produces low-spin Fe$^{2+}$, but substantial covalent bonding alter CF effects
  – **Atomic number**: $\Delta_o$ increases from 3d to 4d to 5d
    • Most 4d and 5d transition metals are low-spin ($\Delta_o > SPE$)
**CFSE For 3d Metals in Octahedral Coordination**

Table 2.2. *Electronic configurations and crystal field stabilization energies of transition metal ions in octahedral coordination*

<table>
<thead>
<tr>
<th>Number of 3d electrons</th>
<th>Cation</th>
<th>High-spin state</th>
<th>Low-spin state</th>
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<tr>
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<td>Electronic configuration</td>
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<td>4/5$\Delta$</td>
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</table>

Note: Table in reading has MAJOR typos in CFSE values
Figure 7.2 Heats of hydration of transition metal ions (a) $M^{2+}$ ions; (b) $M^{3+}$ ions. Filled circles: experimental; open circles: CFSE deducted. Note that experimental values lie on double-humped curves; when CFSE’s (table 2.5) are deducted for each cation, the corrected values lie on smooth curves through the values for $3d^0$, $3d^5$ and $3d^{10}$ cations. [Sources of data: George & McClure, 1959; table 2.5.]
Figure 6.2 Octahedral ionic radii of first-series transition metal cations. (a) Divalent cations; (b) trivalent cations. Filled circles: high-spin cations; open squares: low-spin cations (data from Shannon, 1976).
Figure 2.6 Arrangements of ligands about a transition metal ion in (a) tetrahedral and cubic coordinations, and (b) dodecahedral or cuboctahedral coordination. In tetrahedral coordination, the ligands may be regarded as lying at alternate vertices of a cube. In cubic coordination the ligands are situated on all eight vertices.
3d Orbitals in $T_d$ Coordination

- $t_2$
- $d_{zx}$
- $d_{yz}$
- $d_{xy}$
- $e$
- $d_{z^2}$
- $d_{x^2 - y^2}$

Figure 19-8
Shriver & Atkins Inorganic Chemistry, Fourth Edition
• $t_{2g}$ and $e_g$ reverse order for other coordination states

• Crystal field splitting is smaller than for octahedral fields:
  
  $\Delta_t = 4/9 \Delta_o$
  
  $\Delta_c = 8/9 \Delta_o$
  
  $\Delta_d = 1/2 \Delta_o$

Figure 2.7 Crystal field splittings of transition metal 3d orbitals in (a) cubic (8-fold); (b) dodecahedral (12-fold); (c) tetrahedral (4-fold); (d) spherical; and (e) octahedral (6-fold) coordinations (from Burns, 1985a).
CFSE For 3d Metals in Tetrahedral Coordination

Table 2.3. Electronic configurations and crystal field stabilization energies of transition metal ions in tetrahedral coordination

<table>
<thead>
<tr>
<th>Number of 3d electrons</th>
<th>Cation</th>
<th>High-spin state</th>
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<td>Electronic configuration</td>
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</table>

Note: Table in reading has MAJOR typos in CFSE values
Jahn-Teller Effect

- Distorted coordination environments alter energy levels
  - Ligands that move in raise energy
  - Ligands that move out lower energy

- Partially filling orbitals leads to a lower energy state
Jahn-Teller Distorted Mn(III) and Cu(II)
Water Exchange Rate Trends

Fig. 1.27: Water exchange rates of aqueous divalent transition metal cations.
Distortions Split Energy Levels

Figure 2.9 Relative energies of 3d orbital energy levels of a transition metal ion in low-symmetry distorted sites. (a) Regular octahedron (e.g., periclase); (b) trigonally distorted octahedron (e.g., corundum, spinel, approx. olivine M2 site); (c) tetragonally distorted octahedron (e.g., approx. olivine M1 site); (d) highly distorted six-coordinated sited (e.g., pyroxene M2 site); (e) regular cube; (f) distorted cube (e.g., triangular dodecahedral site of garnet).
Examples of the Impact of Crystal Field Effects in Geochemistry

• Relative weathering rates of orthosilicates
• Distribution of transition metals between different sites in silicate minerals
• Co(II) oxidation and incorporation as Co(III) in manganese oxides
• Stability and complexity of formation of pyrite
• Trace element substitution in calcite
Spinel \( (X^{2+}Y^{3+}_2O_4) \) Structures

- Many minerals have spinel structures
  - Some initial Fe and Al precipitates have spinel-like structures
- This structure is cubic, with both tetrahedral and octahedral sites
- “Normal” spinels have the 2+ cation in the tetrahedral site
- “Inverse” spinels have the 2+ cation in an octahedral site
- Distribution of cations between sites affected by Octahedral Site Preference Energy (OSPE)

\[
\text{OSPE} = \text{CFSE}_o - \text{CFSE}_t
\]
Molecular Orbital Theory

• Crystal field theory is a gross oversimplification that nevertheless explains many phenomena
• Molecular Orbital Theory is the modern method to describe the energetics of orbitals
  – Commonly applied in combination with Density Functional Theory calculations
• This is needed because minerals are not really ionic
  – Transition metal 3d orbital form bonds with ligand orbitals
  – This produces new hybrid orbitals that are mixtures of metal 3d and ligand orbitals
    • EX: In hematite, hybridization of Fe 3d and O 2p orbitals
Figure 11.2 Qualitative molecular orbital energy level diagram for the Fe$^{2+}$ ion in octahedral coordination. The diagram refers to σ-bond formation only.
Transition Metals Can Form Multiple Types of Bonds with Ligands

\(\sigma\) bonds

\(\pi\) bonds

Figure 11.3 Diagrammatic representation of metal–ligand bonds. (a) \(\sigma\)-bond formed by the overlap of a ligand \(s\) orbital and a hybrid metal orbital composed of the \(4s\), three \(4p\) and two \(e_g\) orbitals; (b) \(\sigma\)-bond formed by the overlap of a ligand \(p\) orbital and the hybrid metal orbital; (c) \(\pi\)-bond formed by the overlap of the ligand \(p_z\) orbital and a metal \(t_{2g}\) orbital; (d) \(\pi\)-bond formed by the overlap of a ligand \(3d\) orbital and a metal \(t_{2g}\) orbital. Signs of the wave functions are indicated; shaded regions represent areas of overlap.