

Table 23.6. Sulfosalts		
	proustite	Ag_3AsS_3
	pyargyrite	Ag_3SbS_3
Tetrahedrite	tetrahedrite	$\text{Cu}_6\text{Cu}_4(\text{Fe},\text{Zn})_2(\text{Sb},\text{As})_4\text{S}_{13}$
	tennantite	$\text{Cu}_6\text{Cu}_4(\text{Fe},\text{Zn})_2(\text{As},\text{Sb})_4\text{S}_{13}$
	freibergite	$(\text{Ag},\text{Cu},\text{Fe})_{12}(\text{Sb},\text{As})_4\text{S}_{13}$
	hakite	$\text{Cu}_6\text{Cu}_4\text{Hg}_2\text{Sb}_4(\text{Se},\text{S})_{13}$
	giraudite	$\text{Cu}_6\text{Cu}_4\text{Zn}_2(\text{As},\text{Sb})_4(\text{Se},\text{S})_{13}$
	goldfieldite	$\text{Cu}_6\text{Cu}_4\text{Te}_2(\text{Sb},\text{As})_4\text{S}_{13}$
	argentotennantite	$\text{Ag}_6\text{Cu}_4(\text{Zn},\text{Fe})_2(\text{As},\text{Sb})_4\text{S}_{13}$
	cylindrite	$(\text{Pb},\text{Sn}^{2+})_8\text{Sb}_4\text{Fe}_2\text{Sn}^{4+}_5\text{S}_{27}$
	enargite	Cu_3AsS_4

Cu^{2+} being replaced by Sb^{3+} , As^{3+} , or Te^{4+} . Thus, the structure of **tetrahedrite**, $(\text{Cu},\text{Fe})_{12}\text{Sb}_4\text{S}_{13}$, is made from a cubic close-packed array of S^{2-} atoms with Cu^{2+} and Fe^{2+} in 6-coordination and Sb^{3+} in tetrahedral interstices. The trigonal pyramids formed by the tetrahedra are composed of a Sb^{3+} linked to three S^{2-} anions. Tetrahedrite is also an important Ag-containing mineral and the main mineral in the largest silver-mining district in the world—the so-called “Silver Valley” in northern Idaho.

Cylindrite ($\text{Pb}_3\text{Sn}_4\text{FeSb}_2\text{S}_{14}$) is an unusual sulfosalts worth mentioning because it is one of the few minerals to crystallize with circular habit. The structure is composed of two types of sheets: one with 4-coordinated sites and one with 6-coordinated sites. The misfit between the sites is believed to cause its curvature, much like the mis-

match between the tetrahedral and octahedral sheets in the fibrous form of serpentine—the most common of the asbestos minerals (i.e., chrysotile). This structure causes black crosses to be seen in reflected cross-polarized light.

The **enargite** (Cu_3AsS_4) structure is derived from that of wurtzite by replacing a quarter of the Zn^{2+} atoms with As^{3+} and three-quarters with Cu^{2+} . Thus, it has a ccp array of S^{2-} atoms with the Cu^{2+} and As^{3+} in tetrahedra interstices. It is sometimes mined as an ore of Cu^{2+} .

Oxides

Oxide minerals are grouped into classes on the basis of the number of different types of sites they possess. Thus simple oxides are generally those with only a single cation site; they tend to have formulas like XO_2 , XO , or X_2O_3 . Multiple oxides usually contain two or more different sites, usually one with 6-coordination and one with 4-coordination; their compositions are usually expressed as XY_2O_4 .

Simple oxides. You might think that simple oxides would have simple structures, but there is a wide variety among minerals in this class (Table 23.7). They all have O^{2-} as the main anion. They also have at least one predictable characteristic—these phases all have primarily ionic bonding, so coordination polyhedra obey radius ratio rules. The sizes and charges of the cations govern the size and complexity of the structures. For a more detailed overview of these minerals, we recommend volume 3 of *Reviews in Mineralogy* (Rumble,

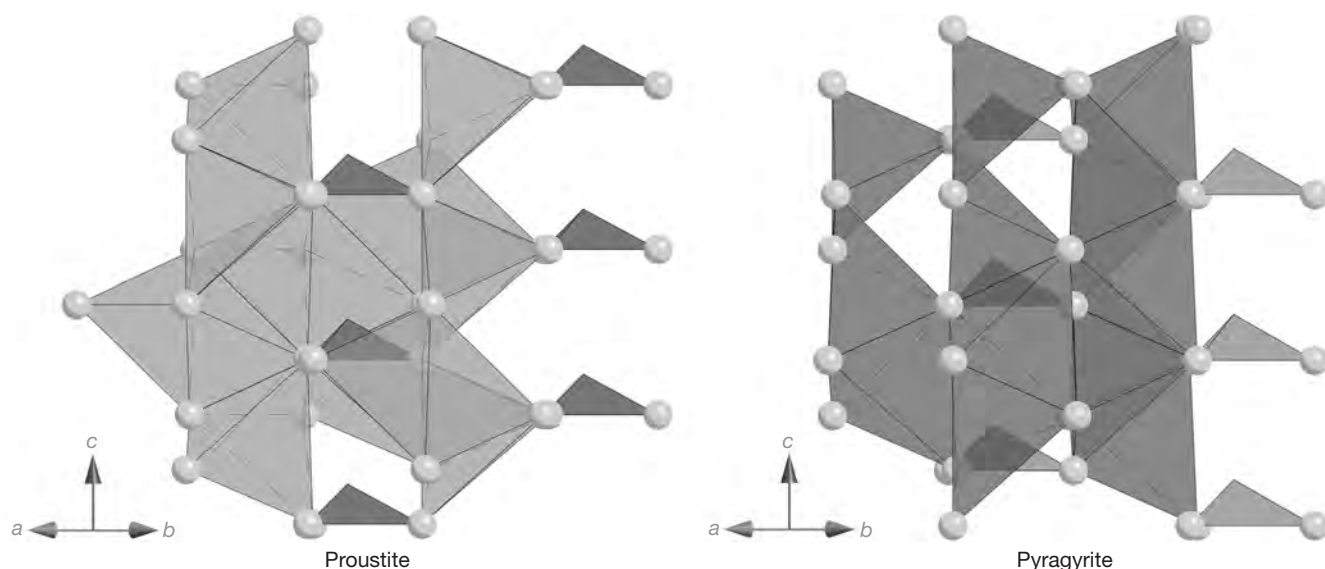


Figure 23.16. Proustite (left, Ag_3AsS_3) and pyargyrite (right, Ag_3SbS_3) are both composed of distorted Ag^{1+} polyhedra defined by S^{2-} ligands and flattened tetrahedra with three corners defined by S^{2-} and the fourth occupied by As^{3+} in proustite and Sb^{3+} in pyargyrite. The As^{3+} in proustite and the Sb^{3+} in pyargyrite are in tetrahedral coordination.

Table 23.7. Simple and Multiple Oxides

	cuprite	Cu^{1+}_2O	
	ice	H_2O	
Periclase	periclase	MgO	
	bunsenite	NiO	
	manganosite	Mn^{2+}O	
	monteponite	CdO	
	lime	CaO	
	wüstite	Fe^{2+}O	
	hongquite	TiO	
Corundum-hematite	corundum	Al_2O_3	
	hematite	$\alpha\text{-Fe}_2\text{O}_3$	
	eskolaite	Cr_2O_3	
	karelianite	V_2O_3	
Rutile	rutile	TiO_2	
	ilmenorutile	$(\text{Ti}, \text{Nb}, \text{Fe}^{3+})\text{O}_2$	
	struverite	$(\text{Ti}, \text{Ta}, \text{Fe}^{3+})\text{O}_2$	
	pyrolusite	Mn^{4+}O_2	
	cassiterite	SnO_2	
	plattnerite	PbO_2	
	argutite	GeO_2	
	stishovite	SiO_2	
	brookite	TiO_2	
	anatase	TiO_2	
Ilmenite	ilmenite	$\text{Fe}^{2+}\text{TiO}_3$	
	geikielite	MgTiO_3	
	pyrophanite	$\text{Mn}^{2+}\text{TiO}_3$	
	ecandrewsite	ZnTiO_3	
	melanostibite	$\text{Mn}(\text{Sb}^{5+}, \text{Fe}^{3+})\text{O}_3$	
	brizziite-III	$\text{NaSb}^{5+}\text{O}_3$	
	akimotoite	MgSiO_3	
Spinel	Al subgroup	spinel	$\text{Mg}[\text{Al}]_2\text{O}_4$
		galaxite	$(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})[\text{Al}, \text{Fe}^{3+}]_2\text{O}_4$
		hercynite	$\text{Fe}^{2+}[\text{Al}]_2\text{O}_4$
		gahnite	$\text{Zn}[\text{Al}]_2\text{O}_4$
	Fe subgroup	magnesioferrite	$\text{Fe}^{3+}[\text{MgFe}^{3+}]\text{O}_4$
		jacobsite	$\text{Fe}^{3+}[(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})\text{Fe}^{3+}]\text{O}_4$
		magnetite	$\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$
		franklinite	$(\text{Zn}, \text{Mn}^{2+}, \text{Fe}^{2+})[\text{Fe}^{3+}, \text{Mn}^{3+}]_2\text{O}_4$
		trevorite	$\text{Fe}^{3+}[\text{NiFe}^{3+}]\text{O}_4$
		cuprospinel	$\text{Fe}^{3+}[(\text{Cu}^{2+}, \text{Mg})\text{Fe}^{3+}]\text{O}_4$
		brunogeierite	$\text{Ge}^{2+}[\text{Fe}^{3+}]_2\text{O}_4$
	Cr subgroup	magnesiochromite	$\text{Mg}[\text{Cr}^{3+}_2]\text{O}_4$
		manganochromite	$(\text{Mn}^{2+}, \text{Fe}^{2+})[\text{Cr}^{3+}, \text{V}^{3+}]_2\text{O}_4$
		chromite	$\text{Fe}^{2+}[\text{Cr}^{3+}]_2\text{O}_4$
		nichromite	$(\text{Ni}, \text{Co}, \text{Fe}^{2+})[\text{Cr}^{3+}, \text{Fe}^{3+}, \text{Al}]_2\text{O}_4$
		cochromite	$(\text{Co}, \text{Ni}, \text{Fe}^{2+})[\text{Cr}^{3+}, \text{Al}]_2\text{O}_4$
		zincchromite	$\text{Zn}[\text{Cr}^{3+}]_2\text{O}_4$
	V sub-group	vuorelainenite	$(\text{Mn}, \text{Fe}^{2+})[\text{V}^{3+}, \text{Cr}^{3+}]_2\text{O}_4$
		coulsonite	$\text{Fe}^{2+}[\text{V}^{3+}]_2\text{O}_4$
		magnesiocoulsonite	$\text{Mg}[\text{V}^{3+}]_2\text{O}_4$
Ti sub-group	qandilite	$(\text{Mg}, \text{Fe}^{2+})_2(\text{Ti}, \text{Fe}^{3+}, \text{Al})\text{O}_4$	
	ulvöspinel	$\text{Fe}^{2+}_2\text{TiO}_4$	
	Chrysoberyl	BeAl_2O_4	
	Maghemite	$\gamma\text{-Fe}^{3+}_2\text{O}_3$	
	Arsenolite	As_2O_3	
Perovskite	Perovskite	CaTiO_3	
	Latrappite	$(\text{Ca}, \text{Na})(\text{Nb}, \text{Ti}, \text{Fe})\text{O}_3$	
	loparite-(Ce)	$(\text{Ce}, \text{Na}, \text{Ca})(\text{Ti}, \text{Nb})\text{O}_3$	
	lueshite	NaNbO_3	
	tausonite	SrTiO_3	
	isolueshite	$(\text{Na}, \text{La}, \text{Ca})(\text{Nb}, \text{Ti})\text{O}_3$	

*Note that some of the formulas given here deviate in format from the "standard" formulations of Mandarino and Back (2004), in order to present the formulas in a comprehensible way that relates them to the crystal structure. See text for more details.

1976), as well as the chapter by Smyth et al. (2000) in vol. 40 of that same series.

In the **cuprite** (Cu_2O) structure (Figure 21.4), Cu^{1+} has an ionic radius of at least 0.77 \AA , and is found in linear 2-coordination with O. Each oxygen is bonded to a surrounding tetrahedron of Cu^{1+} atoms in a cubic unit cell. This structure can be envisioned as a body-centered lattice type with close packing of O^{2-} . If you divide that cubic structure into eighths, there will be a Cu^{1+} atom at the center of every other sub-cube.

The structure of **ice** (H_2O) is quite different from that of cuprite because the H "cation" (really just a proton) is so tiny relative to the O^{2-} anion (Figure 8.21 and 21.3). In ordinary ice, H_2O molecules with H-O-H angles of 104.5° form tetrahedra with four adjoining H_2O molecules (very much like Si in tridymite). Hydrogen bonding plays an important role in bonding the H_2O molecules to one other. Because of the large interstitial spaces that result, ice has a low density (which is why it floats). There are numerous ice polymorphs (at least nine), each designated with a roman numeral. Ordinary ice, the polymorph we find on Earth, is "ice I."

The **periclase group** includes minerals with divalent cations, the majority of which crystallize with a face-centered cubic lattice type like the halite structure. Both the cation and the anion are in 6-coordination (just as in halite). Of these mineral species, **periclase** (MgO) (Figure 8.13) is unusual because of its great stability when subjected to high temperatures and pressures. As a result, it is likely that periclase is an important phase in the Earth's interior, even under the high pressure conditions in the lower mantle.

Wüstite (FeO) is never completely stoichiometric (i.e., a 1:1 ratio of Fe:O), but is nearly so at pressures exceeding 10 GPa. Below that pressure, vacancies (usually indicated by the symbol " \square ") are needed to stabilize the structure, and a nominal composition of $\text{Fe}^{2+}_{1-3x}\text{Fe}^{3+}_{2x}\square_x\text{O}_2$, where x ranges from $0.04 < x < 0.12$, is found (Smyth et al., 2000). The amount of vacancy has a dramatic effect on its physical properties because it introduces defects into the structure, and Fe^{2+} may be oxidized to Fe^{3+} to maintain charge balance. The Fe^{3+} can occupy either the 6-coordinated site in the fcp array or the normally vacant 4-coordinated interstitial sites, resulting in a complex formula that can be expressed as ${}^{\text{VI}}[\text{Fe}^{2+}_{1-3x}\text{Fe}^{3+}_{2x-t}\square_{x+t}]^{\text{IV}}\text{Fe}^{3+}_t\text{O}_2$ (Smyth et al., 2000). Wüstite has been well-studied because of its potential significance at high pressures and temperatures in the Earth's mantle.

Corundum group minerals are composed of a slightly-distorted, hexagonal close-packed array

of O^{2-} anions in which $\frac{2}{3}$ of the 6-coordinated sites are occupied by trivalent A cations, which can be Al^{3+} , Fe^{3+} , Cr^{3+} , or V^{3+} (Figure 21.9). The resultant structure is comprised of gibbsite-like sheets of rings of AO_6 octahedra in the (001) plane. The sheets link into a framework by sharing faces and corners of octahedra (Strunz and Nickel, 2001), giving the structure a hardness second only to diamond on the Mohs scale.

Corundum (Al_2O_3) has economic significance for many reasons. Because of its hardness, it is extensively used as an industrial abrasive. Historically, the brown form of corundum, which has the variety name emery, was mined for this purpose. Emery thus lends its name to the boards used as nail files, and is used in sandpaper. Corundum is fairly easy to create in the laboratory, so most modern commercial applications use synthetics. Purer varieties of corundum, usually in the form of sapphire rods and plates, are also used as gemstones and in the semiconductor industry as lasers (thanks to their fluorescence).

One interesting use of ruby lasers deserves mention here. The Apollo 11, 14, and 15 astronauts placed reflectors on the lunar surface; the Soviets also put reflectors on their Lunikhod roving vehicles. In several different experiments, a ruby laser pulse was sent by the MacDonal Observatory in Texas to the lunar surface, and the length of time it took for the reflection to be detected back on Earth was measured. From these experiments, we now know the distance from the Moon to Mount Livermore (near Ft. Davis, Texas) within about 15 cm! Interestingly, these experiments have also been used to demonstrate the "reality" of the Apollo landings to skeptics, because the return of the laser pulses cannot be explained by anything except human-made reflectors.

The gem varieties of corundum have been given a host of colloquial variety names. Strictly speaking, emery is brown corundum, ruby is red, padparadschah is orange, and sapphire is used for all the other colors, which include blue, green, purple, etc. The colors arise from very minor amounts of impurity (<1% of the Al^{3+} replaced by other cations) because the Al_2O_3 structure apparently does not tolerate substitutions. However, as noted in Chapter 7, these trace substitutions can cause intense colors. Ruby is red because of its Cr^{3+} content. Yellow sapphire owes its color to Fe^{3+} . Blue sapphire derives its color from $Fe^{2+} - Ti^{4+}$ and $Fe^{2+} - Fe^{3+}$ intervalence charge transfer. Green sapphires contain a mixture of the blue and green colors. Corundum varieties sold as gemstones are nearly always heated-treated to intensify (or in some cases, lighten) their colors; the heat treatment is done at the mines when they

remove the stones in a highly-accepted practice. Spectra of these minerals and more information on color can be found on the Mineral Spectroscopy server at Caltech.

The other common member of the corundum group is **hematite** ($Fe^{3+}_2O_3$), which is usually found in sedimentary or metamorphosed sedimentary rocks. It is a common mineral in soils all over the world, because it results from the breakdown of Fe-rich minerals in many different rock types. When present in equilibrium in metamorphic or igneous rocks, it is indicative of highly oxidizing conditions. Some hematite deposits reach tremendous thicknesses, such as those in Brazil, and thus they make convenient sources of iron ore for the iron and steel industries. The red color of hematite is very intense because the $Fe^{3+}O_6$ octahedra are somewhat asymmetric, intensifying the bands in the hematite spectrum. Magnetic coupling between Fe^{3+} cations further intensifies the red color. Thus hematite is used as a red pigment in many applications (including rouge).

Species in the **rutile group** have the general formula AO_2 , as discussed in Chapter 21, and the cation can be Ti^{4+} , Mn^{2+} , Sn^{4+} , Pb^{4+} , Ge^{4+} , Nb^{4+} , Fe^{2+} , Fe^{3+} , or even Sb^{5+} . Due to the different sizes and charges of these disparate cations, these structures generally do not tolerate cation substitutions, and thus are typically quite pure. The only exception to this rule is found in the species **rutile** (TiO_2), where Fe^{2+} , Fe^{3+} , Nb^{4+} , and Ta^{5+} commonly substitute (Figure 21.6). Although ionic bonding predominates in the other members of the rutile group, there is evidence to suggest that covalent bonding may be significant in rutile. The result is that the size of the unit cell does not appear to vary at high temperatures and pressures (Hazen and Finger, 1981).

Most of the AO_2 oxides can occur in many different structure types. Most preserve the octahedral coordination of the cation, but vary in the number of edges that are shared. For example, rutile, **brookite**, and **anatase** are all polymorphs of TiO_2 , but their octahedra share two, three, and four edges, respectively. As the number of shared edges goes up, so does the density. The denser structures are correlated with increased pressure of formation. The most common structure (as in rutile) is tetragonal, and composed of edge-sharing octahedra that link up to form chains in the c direction (Figure 21.6). The corners of the chains join to create a framework. In the resultant configuration, each oxygen atom is surrounded by three Ti^{4+} cations in a nearly planar arrangement.

Several species in the rutile group have special importance. Rutile is a major ore of titanium, and

is used as a white pigment in plastics, paper, and paint because its high refractive index causes it to reflect a greater portion of the incident light. **Pyrolusite** (MnO_2) is an important source of manganese, which is a key ingredient in the manufacture of steel. Manganese is also used in alloys with aluminum, and as an oxide in dry cell batteries. The ore is also used in livestock feed, fertilizers, and as a pigment for coloring bricks! Finally, **cassiterite** (SnO_2) is similarly important for tin production. Tin is mostly used in coatings or in alloys with other metals to make solders, glasses, and various chemicals.

Stishovite is a high pressure form of SiO_2 that forms when meteorites impact quartz-rich rocks. It is included here to compare its structure with that of the other minerals in this group, but it is really a silicate mineral because it forms from polymerization of the anionic complex $(\text{SiO}_6)^{12-}$.

The **ilmenite group** minerals (ATiO_3 , where A is Fe^{2+} , Mg^{2+} , Mn^{2+} , Zn^{2+} , and Sb^{5+}) are isostructural with corundum, though with the lower symmetry that arises from alternating the A cations with Ti^{4+} in the unit cell (Figure 21.9). This gives these minerals hexagonal unit cells. There are two different octahedral sites (the A location and the Ti^{4+} location) for the cations, and the structure is dense because the octahedra share faces. **Ilmenite** ($\text{Fe}^{2+}\text{Ti}^{4+}\text{O}_3$) is extremely common in both igneous and metamorphic rocks, where its presence often serves as a signature of high activity of TiO_2 saturation and/or relatively reducing conditions. Ilmenite typically contains some $\text{Fe}_2^{3+}\text{O}_3$ in solid solution and in favorable conditions can help indicate both the temperature and redox conditions under which it formed (see magnetite, below).

Multiple and related oxides. The large **spinel group** of multiple oxides comprises 22 minerals with the formula of $\text{X}^{2+}\text{Y}^{3+}_2\text{O}_4$, where X = Mg^{2+} , Mn^{2+} , Fe^{2+} , Zn^{2+} , Co^{2+} , Cu^{2+} , and/or Ge^{2+} , while Y = Al^{3+} , Fe^{3+} , Cr^{3+} and/or V^{3+} . The A cations have divalent charge and the B cations are trivalent. Each unit cell contains a (nearly perfect) close-packed array of 32 oxygen atoms with 64 tetrahedral and 32 octahedral sites between them. As we have discussed before, it is unlikely that all the tetrahedral and octahedral sites would be occupied. This would require face-sharing between adjacent tetrahedra and octahedra that would be unlikely in an ionically-bonded crystal.

The spinel formula suggests that there should be three cations for every four oxygens. Thus, the unit cell must contain $\frac{3}{4}$ of 32, or 24, cations. Many possible combinations of site occupancy present themselves for these 24 cations! An optimal configuration is for eight of the tetrahedral (A) sites to be filled, along with 16 of the octahe-

dral (B) sites. In the spinel group, there are thus two possibilities.

1. The mineral species **spinel**, which has a formula of MgAl_2O_4 , was the first spinel structure to be described (Barth and Posnjak, 1932), and thus was given the name “normal.” In **normal spinels**, the X (divalent) cations fill 8 A tetrahedral sites, and the Y (trivalent) cations occupy 16 B octahedral sites. Thus a “normal” distribution of cations in a spinel would be $\text{X}[\text{Y}^{3+}_2]\text{O}_4$. The tetrahedral site is listed first, and the octahedral site occupancy is given in brackets; this is reversed from the typical way formulas are written (i.e., going from the largest to smallest from left to right, respectively). Formulas in Table 23.7 are given using this nomenclature so you can figure out which ones are normal and which are inverse.
2. In **inverse spinels**, the Y (trivalent) cations occupy the tetrahedral site, and the octahedral sites contains a mixture of Y and X (divalent) cations, with a formula of $\text{Y}^{3+}[\text{XY}^{3+}]\text{O}_4$. Although these are more common in nature, they were described after the spinel species, and thus were given the name “inverse” to indicate that they were the opposite of what had already been described.

In other words, if the trivalent cations are all together on the 6-coordinated site, the occupancy is normal, and if they are split between the two types of sites, the spinel is said to be inverse. When the cations are disordered between the two sites, they are neither inverse nor spinel, but “random.” This nomenclature is important because mixing of cations with different charges on the 6-coordinated sites is very different (from a thermodynamic standpoint) than segregation of charges on distinct sites. Thus, cation distribution in spinels has profound consequences for their relative stabilities in different rock types. In practice, natural samples generally have a distribution of cations that lies between normal and inverse!

You cannot predict on the basis of a formula alone if a spinel will be normal or inverse. In fact, the patterns don't follow any obvious trends, and were considered to be anomalous until crystal field theory came along. As we discussed in Chapter 7, you can calculate a crystal field stabilization energy (CFSE) for any transition metal cation by weighting the contributions of electrons in various orbitals (see Table 7.9). Recall that CFSE can be calculated for a cation in various types of coordination polyhedra, and a high value of CFSE means that a cation will be energetically preferred in a coordination polyhedron with that coordination type. For example, in Table

7.10 we noted that Cr^{3+} has one of the highest values for CFSE of any transition metal in high-spin octahedral coordination, which means that Cr^{3+} really prefers to be in octahedral coordination. You can do the same set of CFSE calculations for tetrahedral coordination, and then compare the results, as shown in Table 23.8 for oxides.

The difference between the octahedral and tetrahedral crystal field splitting energies for various cations is termed the **octahedral site preference energy** (OSPE) and is a measure of a cation's preference for octahedral sites relative to tetrahedral ones. We see here again how Cr^{3+} much prefers octahedral over tetrahedral coordination. Thus, in a spinel containing Cr^{3+} we would expect to find the Cr^{3+} in the octahedral site, forming a normal spinel. Similarly, both Ni^{2+} and Cu^{2+} have relatively large values of OSPE; spinels with divalent cations in octahedral coordination are inverse. Cations like Fe^{3+} and Ti^{4+} , which have zero OSPE, will have no preference for either tetrahedral or octahedral coordination, and thus will form both normal and inverse spinels depending on the site preferences of the other coexisting cations. The spinel structures predicted by crystal field theory match the experimentally-measured ones extremely well (see Table 6.2 in Burns, 1993). In Table 23.7 of this text, we have written the formulas to show the typical distribution of cations in each mineral species. For more information on this topic, consult the book by Burns (1993).

The subgroups in the spinel classification (Table 23.7) are defined on the basis of the atom in the B (octahedral) position. Their cation site occupancies are easily understood in terms of the preceding discussion. For example, all the minerals in the

Cr^{3+} subgroup are normal spinels because Cr^{3+} has such a high preference for octahedral coordination. On the other hand, those in the Fe^{3+} subgroup are a mixture of inverse and normal spinels depending on the OSPE of the other cation in each one.

The spinel structure itself has great significance for studies of the Earth's interior. As you will recall from Chapter 20, the upper mantle's mineralogy is dominated by olivine, orthopyroxene, clinopyroxene, and spinel or garnet, with small amounts of amphibole (usually kaersutite) and mica (usually phlogopite). Deeper in the mantle, the pressure increases, and the minerals eventually become unstable. At about 400 km, the olivine structure is no longer stable. It changes spontaneously from the olivine structure to a spinel-type structure, which takes up 8% less space; the composition remains the same (though we now call it $\beta\text{-Mg}_2\text{SiO}_4$). This causes a seismic discontinuity at about 300–400 km depth that is the boundary to the transition zone.

Magnetite has particular importance because of its magnetic properties (see Text Box). You can probably guess how this mineral earned its name. Because of its ubiquitous presence in the geologic record, magnetite and other oxides have been useful in preserving a geological record of the changes in the direction of Earth's magnetic field. This is the field of paleomagnetism, which measures magnetic behavior in oxide minerals belonging to two solid solutions: ulvöspinel-magnetite and ilmenite-hematite, as shown in Figure 23.17. The bottom of the ternary represents the solid solution between the Fe^{2+} oxide, wüstite (FeO), and its more oxidized equivalent, hematite ($\text{Fe}_2^{3+}\text{O}_3$). As you go to the top of the diagram, Ti^{4+} substitutes for Fe^{3+} , creating titanomagnetite and hemoilmenite. Magnetite is magnetic because it is a ferrimagnet (see Text Box). Thus, as a magnetite crystal grows, it will record the direction of the magnetic field at that time. If the magma happens to be Ti-rich, the effect of the unpaired Ti^{4+} electrons is to reduce the strength of the magnetic field to zero; the pure ulvöspinel endmember is antiferromagnetic (again, see text box). A related phenomenon occurs between hematite, which is antiferromagnetic, and ilmenite. It has only recently been recognized that fine-scale intergrowths of hematite and ilmenite can produce ferromagnetic interactions at the atom scale due to coupling in the layers between them (Robinson et al., 2002). Thus magnetite and hemoilmenite/ilmeno-hematites contribute to retaining the magnetic signatures of planets.

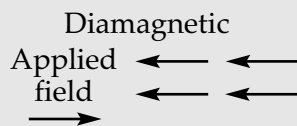
Many organisms (including humans) are known or suspected to have magnetite crystals in their brains that apparently trigger impulses in

Table 23.8. Octahedral Site Preference Energies (OSPE) for Transition Metals in Oxide Structures (after Burns, 1993, Table 6.3)

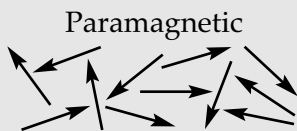
Number of 3d electrons	Cations	Octahedral CFSE (kJ/mole)	Tetrahedral CFSE (kJ/mole)	OSPE (kJ/mole)
0	Ca^{2+} , Sc^{3+} , Ti^{4+}	0.0	0.0	0.0
1	Ti^{3+}	-87.4	-58.6	-28.8
2	V^{3+}	-160.2	-106.7	-53.5
3	Cr^{3+}	-224.7	-66.9	-157.8
4	Cr^{2+}	-100.4	-29.3	-71.1
4	Mn^{3+}	-135.6	-40.2	-95.4
5	Mn^{2+} , Fe^{3+}	0.0	0.0	0.0
6	Fe^{2+}	-49.8	-33.1	-16.7
6	Co^{3+}	-188.3	-108.8	-79.5
7	Co^{2+}	-92.9	-61.9	-31.0
8	Ni^{2+}	-122.2	-36.0	-89.2
9	Cu^{2+}	-90.4	-26.8	-63.7
10	Zn^{2+} , Ga^{3+} , Ge^{4+}	0.0	0.0	0.0

Why are some minerals magnetic, and how are some minerals able to record the direction of the Earth's magnetic field? Really, all minerals are magnetic, but we routinely think of magnetism as the property of being attracted to a magnet. Magnetism arises fundamentally from the spin and orbital motions of electrons, though spin is most important in common Fe and Ti-rich materials. There are five types of magnetism and all materials will exhibit one of these.

1. **Diamagnetism** is found in all matter, such as helium, water, and copper. It occurs in materials in which all outer orbital shells are filled and there are no unpaired electrons. In this situation, electrons with opposite spins and equal energy pair up to cancel each other out. Although these materials generally have no magnetic moments, they can acquire weak magnetization in the opposite direction to an applied magnetic field because of weak currents created by changes in the orbital motions.

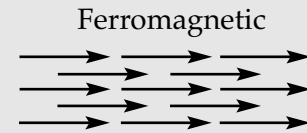


2. **Paramagnetism** results when some of the atoms in a material have unpaired electrons in partially-filled orbitals. If the electrons do not interact, there is no magnetization. But when a magnetic field is applied, the atomic motions may align with it. If you place an ion with unpaired outer electrons in a crystal structure, it will normally be paramagnetic. Thus, most minerals are paramagnetic at room temperature, including such examples as pyrite, siderite, and phlogopite.

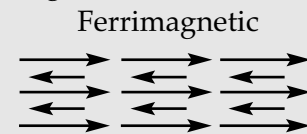


3. If the atoms containing unpaired outer electrons are close together within a crystal structure, their spins can interact, and electrons in adjacent sites will acquire parallel alignments. These materials will take on their own, strong magnetization, and are considered to be **ferro-**

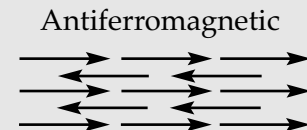
magnetic. Examples of this include Fe, Ni, Co, and many of the related alloys. Note that when ferromagnetic materials are cooled, they eventually reach a point at which the electronic forces between adjacent electrons can no longer interact, and effectively "quenched." This occurs at a (somewhat) diagnostic temperature for each material, and is called the **Curie temperature.**



4. **Ferrimagnetism** is a more complex form of ferromagnetism in which two sets of magnetic fields are created within the same crystal structure, usually separated by oxygen anions. One set of atoms spontaneously aligns in one direction, and a second set, equally spontaneously, pairs off in the opposite direction. However, the magnetic moments of the two opposing fields are not equal, and thus these materials have a strong net magnetic field above the Curie temperature. Magnetite, pyrrhotite, and feroxyhyte are all ferrimagnets.



5. **Antiferromagnetic** materials also contain two set of atoms with exactly equal and opposite magnetic moments. In this case, the moments cancel out perfectly, and the material will have no magnetic moment. Many minerals such as ilmenite, goethite, and troilite are all antiferromagnets at room temperature. When they are cooled to low temperatures, however, thermal vibrations cause them to lose their antiferromagnetic structure, and they become paramagnetic; the temperature at which this occurs is called the **Néel point.**



surrounding nerves in response to changes in magnetic field. This capability is probably what allows many migratory animals to navigate.

Magnetite crystals have been found in the brains of homing pigeons, for example, as well as many fish species.

Finally, the spinel species **magnetite** has petrologic importance because it is found in a huge range of different rock types. The equilibrium between quartz, olivine, and magnetite is used as a reference to specify a commonly-occurring oxygen pressure typical of rocks formed at or near the Earth's surface. In addition, magnetites in many igneous and metamorphic rocks are titaniferous (containing ulvöspinel, Fe_2TiO_4 in solid solution). Titaniferous magnetites coexisting with ilmenite solid solution are sensitive to both temperature and redox conditions (oxygen fugacity), and in favorable conditions the compositions of both phases can indicate the temperature and oxygen fugacity at which they formed.

There are several minerals closely related to those in the spinel group. **Chrysoberyl** (BeAl_2O_4) has the same structure as olivine, with Al^{3+} in the octahedral (Fe,Mg) sites and Be^{2+} in the Si^{4+} tetrahedral sites. It is similar to the spinel structure as well, though the smaller Be^{2+} in the tetrahedral site makes the structure orthorhombic rather than isometric. Other simple oxides like **maghemite** ($(\text{Fe}^{3+}, \square)_3\text{O}_4$) have a spinel structure with both Fe^{3+} and vacancies in both the 4- and 6-coordinated sites. **Arsenolite**, As_2O_3 (Figure 21.8), is made from four pyramids with O^{2-} at the base and As^{3+} at the tip; these form As_4O_6 molecules linked by weak van der Waals bonds.

The **perovskite** group minerals (Table 23.7; note that these are, strictly speaking, "simple" oxides) have a nearly-cubic structure in which Ca atoms replace O's in a cubic close-packed

arrangement; thus, the Ca^{2+} atoms are in 12-coordination with O^{2-} . Ti^{4+} and other small cations occupy some of the octahedral interstices in coordination with oxygen atoms; these octahedra share corners to create a framework (Figure 21.12). The resulting minerals have a general formula of ABO_3 , where $\text{A} = \text{Ca}^{2+}$, Na^{1+} , Ce^{3+} , and/or Sr^{2+} , and B is either Ni^{2+} or Nb^{3+} . The perovskite structure is important within the transition zone in the Earth's mantle, where Ca garnet transforms to a perovskite structure, resulting in a density increase.

One last oxide that has great political and economic importance is the oxide **uraninite** (UO_2), which is the major ore of uranium. Uraninite crystallizes with a body-centered cubic lattice type; O^{2-} anions lie at the corners of the cube and U^{4+} is in the center in 8-coordination. Uraninite was first mined in the early 20th century for its minor radium contents (radium was used in making luminescent dials for watches, and other unhealthy applications). Of course, uranium itself became important during the Manhattan Project in World War II for the development of the atomic bomb and after for both weapons and generation of electricity. Extensive mining operations were then undertaken in the U.S., Canada, and the Belgian Congo. We now know that Australia has the world's largest reserve of uranium, though strict laws regulate its export only to uses involving the production of electricity (e.g., in nuclear power plants). Uranium is also exploited by geologists because the long half-life of the ^{238}U isotope (4.51×10^9 years) makes it well-suited for radiometric dating of rocks.

Hydroxides and oxides containing hydroxyl.

The addition of H^{1+} to oxide structures, usually incorporated in the form of hydroxyl $(\text{OH})^{1-}$, changes the possible structures only slightly because the H^{1+} is so small. These minerals contain structural $(\text{OH})^{1-}$ and not structural H_2O . There is often confusion over these two terms because the $(\text{OH})^{1-}$ content of a mineral may be expressed as the weight percent H_2O . However, OH-bearing minerals *do not contain molecular water* so they are not considered hydrated minerals.

Perhaps the most important of these phases are the three mineral species that make up the valuable aluminum ore, bauxite: **diaspore**, **gibbsite**, and **boehmite**. The rock type "bauxite" occurs in nature as a heterogeneous mixture of these three phases, and forms in area of very high weathering rates—like the tropics. It is primarily mined to make the aluminum metal used in many materials in our everyday lives: kitchen appliances, cars, ships, airplanes, glass, aluminum foil, and even electrical transmission lines. Aluminum is pre-

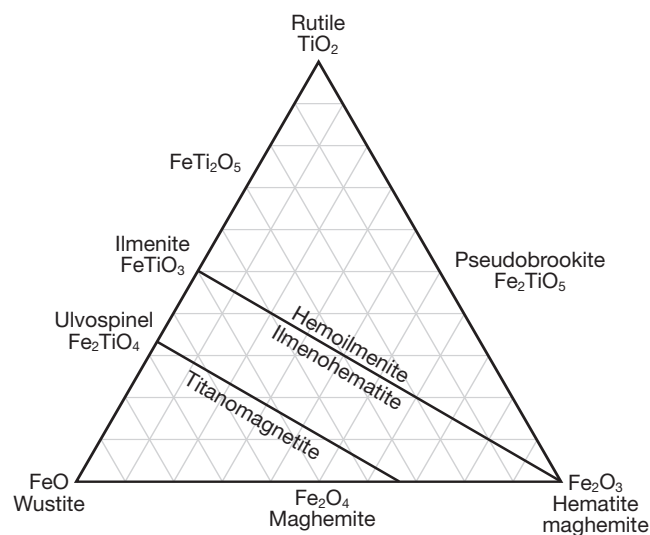


Figure 23.17. Ternary diagram for the iron oxides showing the interrelationships among Fe^{2+} , Fe^{3+} , and Ti^{4+} . Substitution along the hemoilmenite and titanomagnetite lines toward Ti causes a decrease in the magnetic remanence of the phases.