Part I

Theory of Remote Compositional Analysis Techniques
and Laboratory Measurements

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Electronic Spectra of Minerals in the Visible and Near-Infrared Regions

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1.1 Origin of Electronic Spectra of Minerals

Many of the spectral features of minerals in the visible to near-infrared region (VNIR; defined here as ~0.4–2.5 μm) arise from electronic transitions within and between transition elements and the anions chemically bound to them. Thousands of minerals have color or wavelength-variable properties in this portion of the spectrum. Metal ions including vanadium, chromium, manganese, iron, cobalt, nickel, and copper, usually in either the 2+ or 3+ oxidation state, are responsible for the color of many minerals. However, only a few of these elements, typically iron, titanium, and oxygen, are important in most remote sensing applications of rocky bodies. Many features arise from electronic transitions of electrons between the *d* orbitals of a metal ion, while some spectroscopic features arise from interactions between atoms.

1.2 Units

Wavelengths are commonly expressed in nanometers (nm) or micrometers (μm) and, in older literature, Ångstrom units. Literature on mineral spectroscopy and mineral chemistry often uses nm, while the remote sensing literature typically uses μm. The conversion among them is:

$$1000 \text{ nm} = 1 \text{ μm} = 10{,}000 \text{ Å}. \tag{1.1}$$

The spectrum can also be presented in energy units, usually wavenumbers, which are the reciprocal of the wavelength, and are usually expressed in reciprocal cm. The advantage of wavenumbers is that absorptions are symmetrical in energy coordinates but not in wavelength coordinates. Spectroscopic energies can also be expressed in electron volts, but this is more commonly encountered in the physics literature.

$$\text{Wavenumbers } \left(\text{cm}^{-1}\right) = 10{,}000{,}000/\text{nm} = 10{,}000/\text{μm})$$
$$1000 \text{ nm} = 1 \text{ μm} = 10{,}000 \text{ cm}^{-1}; \quad 400 \text{ nm} = 0.4 \text{ μm} = 25{,}000 \text{ cm}^{-1} \tag{1.2}$$
$$1 \text{ cm}^{-1} = 1.23984 \times 10^{-4} \text{ eV}; \quad 8065.54 \text{ cm}^{-1} = 1 \text{ eV} = 1239.8 \text{ nm}.$$

Spectra are usually displayed in either reflectance units or absorbance units. Reflectance spectra must be taken in comparison to a standard. In a laboratory setting, the standard can

be a colorless polytetrafluoroethylene-based plastic such as Spectralon®, aluminum, or, in the near-IR (NIR) region, gold. Spectra are presented as the percent (0–100%) or fraction (0–1) of sample reflectance relative to the standard versus wavelength. In spacecraft applications, the comparison standard is typically the solar flux. Reflected light data collected by spacecraft are typically expressed as I/F [radiance/(solar irradiance/π)]. For a given viewing geometry, these data can be further corrected for angular dependencies in scattering properties (see Hapke, 1981, for definitions of different types of reflectance).

Even though remotely obtained spectra are the composite response of many components in a field of view, many fundamental studies of mineral spectra are conducted with single crystals. In chemistry, such studies are usually presented in absorbance units, where

$$\text{Absorbance} = -\log_{10}(\text{Transmission}). \tag{1.3}$$

An absorbance of 1 means that 10% of the incident light is passing through the crystal; an absorbance of 2 means that 1% of the light passes through. Beer's law formulations ($I = I_0 e^{-\alpha d}$) are also sometimes used to derive an absorption coefficient (α) where the intensity of initial light (I_0) is compared to the intensity after transmission (I) through a given thickness of material (d).

Because most mineral crystals are anisotropic, fundamental studies of single crystals usually measure the spectrum with polarized light vibrating along the fundamental optical directions of the crystal. The refractive indices of a crystal for light traveling in different directions relative to the crystal axes form an optical indicatrix, mathematically, an ellipsoidal surface. Crystals that belong to the orthorhombic, monoclinic, and triclinic crystal systems will have three independent spectra that can display very different absorption properties (biaxial indicatrix). Crystals in the tetragonal and hexagonal systems will have two different spectra (uniaxial indicatrix), while isotropic, cubic crystals will have only one spectrum (spherical indicatrix). In general, spectra can be named either according to the crystal axes in which the vibration occurs (e.g., E\\$c$ or the c-spectrum) or by the symbol for the index of refraction that would be measured in the vibration direction. For biaxial crystals with three independent optical directions we have the α, β, and γ spectra (also called the X, Y, and Z spectra). For uniaxial crystals with two different spectra there are two independent optical orientations: the E$\perp c$ direction, also called the ω-spectrum, and the E\\$c$ direction, which is also called the ε-spectrum.

1.3 Crystal Field Transitions

The spectra of metal ions, particularly those of first-row transition elements, Ti through Cu, are often interpreted with the use of Crystal Field Theory. The d-orbital electrons are the valence (outermost) electrons in the case of these metals. For an isolated transition metal ion, electrons occupy any d orbital with equal probability. However, in a mineral, electrostatic fields produced by the anions (usually oxygen) surrounding the central metal ion separate the metal ion's d orbitals into different energy levels. This allows the d-orbital

electrons to undergo transitions between orbital energy states. Their transitions to different energy levels under the influence of VNIR light give rise to much of the color we see and the spectra we measure of minerals.

This can be understood for the case of a metal ion surrounded by six oxide ions (ligands) arranged in perfect octahedral symmetry. If the metal ion were floating in free space with no oxide or other anions near it, all five orbitals in the $3d$ level would have the same energy (Figure 1.1a). But when the metal ion is in an octahedral arrangement of oxide ions, the d orbitals split into groups of two different energies (Figure 1.1b) reflecting the different interactions the d-orbital electron clouds have with the surrounding ligands.

Iron in the 2+ oxidation state has six electrons, the valence electrons, in the $3d$ orbital. In an octahedral coordination environment, these go into the $3d$ orbitals as pictured in Figure 1.2a because the electrons are energetically more stable when pairing of electrons is minimized. An electronic transition will occur when light of an appropriate energy interacts with the Fe^{2+} ion and promotes an electron from a lower energy orbital to a higher energy
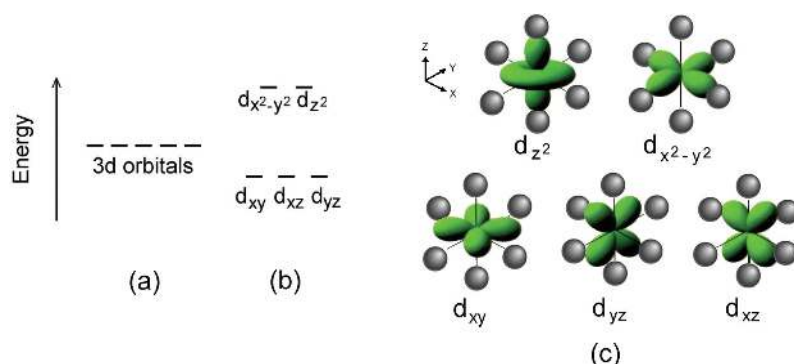

Figure 1.1 Energy diagram for $3d$ orbitals and their electron probability clouds. (a) Orbitals in free space. (b) Orbitals in an octahedron of oxide ions. (c) The electron clouds of the d orbitals in relationship to the oxide ions in an octahedral arrangement.
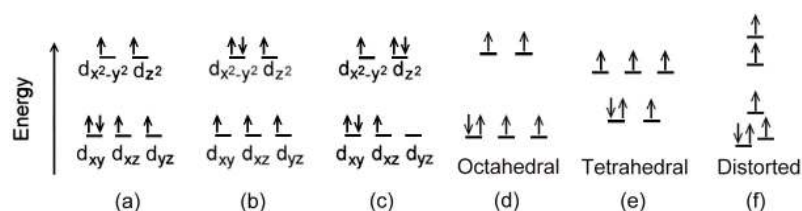

Figure 1.2 Electron configurations for Fe^{2+}. (a) The ground state in an octahedral coordination environment. (b) The spin-allowed excited state that gives rise to the primary NIR absorption bands. Here, the total number of unpaired electrons has not changed in the excited state. (c) A spin-forbidden state in which the total number of unpaired electrons has changed in the electronic excitation. A comparison of the relative splitting of ground state d orbitals for Fe^{2+} ion in (d) regular octahedral, (e) regular tetrahedral, and (f) a representative distorted coordination.

orbital (Figure 1.2b). Each configuration of the electrons is an electronic state of the system. If the total number of unpaired electrons is not changed during the transition from the electronic ground state to a higher energy state, this is called a spin-allowed transition. If the total number of unpaired electrons changes, this transition is called a spin-forbidden transition because such a transition is about 100 times less likely to occur than a spin-allowed one.

The intensities of electronic bands relate to their spin-allowed or spin-forbidden properties. Spin-forbidden transitions produce absorption bands that are commonly much weaker than the spin-allowed bands. However, interactions between cations, as explained in a following section, can dramatically increase the intensity of formally spin-forbidden bands and produce other features of high intensity when cations in different oxidation states interact. In addition, electronic transitions that involve transfer of charge from anions to cations (Sections 1.4 and 1.5) can also be of much higher intensity, but are usually centered in the ultraviolet portion of the spectrum.

Qualitative predictions of the spectrum of metal ion complexes can be obtained from Tanabe–Sugano diagrams. These diagrams usually present energy states for complexes in ideal, octahedral coordination that can be used to interpret the number of spin-allowed and spin-forbidden absorption bands and their widths, and, with suitable experimental parameters, can provide predictions of where bands will occur. Most ions in minerals are not in ideal octahedral coordination, so these diagrams often do not accurately interpret mineral spectra, but they do indicate which absorption bands will split into multiple components for metal ions in crystal sites of low symmetry. These diagrams, along with other concepts previously discussed, are reviewed in more detail in several books and articles about mineral spectroscopy (Karr, 1975; Burns, 1993; Rossman, 2014).

Another important factor in determining the number and wavelengths of absorption bands from a metal ion is the symmetry and distances of the ions surrounding the central metal ion. The number and energies of absorption bands strongly depend on the symmetry (Figure 1.2d–f). In a perfectly regular octahedron, Fe^{2+} will have one possible transition from the lower to the higher set of orbitals (Figure 1.2b). In a perfectly regular tetrahedral coordination environment, the energy difference between the orbitals will be smaller; consequently, the absorption will occur at longer wavelengths, but still with only one absorption band. However, coordination environments of ideal symmetry are almost never encountered. In nearly all minerals, the metal ion is in a coordination environment distorted from ideal symmetry. In such cases, the energies of the orbitals will split and multiple absorption bands will be possible. This fact is crucial for understanding the relatively broad nature of absorption bands in spectra of common rock-forming minerals. For example, in olivine the broad Fe-related electronic absorption observed is, in reality, a set of overlapping absorptions, caused by the existence of numerous 6-coordinated sites of different dimensions and symmetries that occur as the atoms around the iron vibrate due to thermal energy. In pyroxene, the wavelength of the Fe-related electronic absorption in the distorted 6-coordinated M(2) site shifts systematically with Ca, Fe, and Mg substitution that changes the dimensions of the octahedral site.

Group theory provides symbolic names for each of the electronic states of the system. These names convey the spin state, degeneracy, and symmetry of the electron cloud (for further reading see Harris & Bertolucci, 1989; Cotton, 1990). For example, in a perfectly octahedral coordination environment, the Fe^{2+} ground state has a $^5T_{2g}$ symmetry designation, where the T indicates that the state is triply degenerate, the 5 is the number of unpaired electrons +1, and the $2g$ relates to the symmetry of the electron cloud. The excited state has a designation ^5E_g, where the E symbolizes a doubly degenerate state. A single absorption band occurs when the electron is promoted from the $^5T_{2g}$ state to the ^5E_g state. In coordination environments of lower symmetry, the T state can split into three different electronic states and the E state can split into two, each with a different energy. In orthopyroxene, the electronic ground state of Fe^{2+} in the low symmetry M(2) site splits into three different states labeled $^5A_1$, $^5A_2$, and $^5B_2$, and the excited state splits into a $^5B_1$ and a $^5A_1$ state, each of which is no longer degenerate (Goldman & Rossman, 1977).

Electronic absorption bands can be temperature sensitive. They typically broaden at higher temperatures and sharpen at lower temperatures. Fundamental studies of minerals and chemicals are often conducted at liquid nitrogen or even liquid helium temperatures to sharpen absorptions and allow determination of band centers at high spectroscopic resolution. Particularly for targets below ~150 K, consideration of shifts may be relevant in interpretation of remotely collected spectra.

Absorptions can also shift position or change intensity as mineral sites are distorted and metal–oxygen bond distances change at elevated temperatures (e.g., Aronson et al., 1970; Sung et al., 1977). High-temperature spectra are important in planetary science for interpreting the composition of bodies that are several hundreds of degrees warmer than Earth such as Mercury, Venus, and lavas on Jupiter's moon, Io.

1.4 Oxygen-to-Metal Charge Transfer

Another common feature in the spectra of many minerals is the oxygen-to-metal charge transfer transition. This feature arises from absorption of photons with enough energy to transfer charge density from an oxygen ligand to the central metal ion. Oxygen-to-iron charge transfer is most commonly encountered in common rock-forming minerals where the band is usually centered in the ultraviolet region. The higher the charge state of the central metal ion, the lower the energy of the absorption band will be. Oxygen-to-Fe^{3+} charge transfer bands sometimes tail into the visible portion of the spectrum, where they absorb in violet and blue and often produce a rusty orange-red color. Oxygen-to-metal charge transfer absorptions are normally much more intense than those arising from transitions within the *d* orbitals of metal ions.

1.5 Intervalence Charge Transfer

Intervalence Charge Transfer (IVCT) refers to a process in which two metal ions in close proximity to each other in a structure transfer an electron between them, thereby

temporarily changing the oxidation state of both cations. Absorption bands in the optical spectrum from IVCT can be comparatively intense, and only a little IVCT produces spectroscopic features and color in the visible spectral region. In the geological world, only two such interactions are commonly encountered: Fe^{2+}–Fe^{3+} and Fe^{2+}–Ti^{4+}. A third, Ti^{3+}–Ti^{4+}, is occasionally found in meteorites.

For these interactions to occur, cations need to be adjacent to each other in the mineral structure, often sharing a common edge or face of the coordination polyhedron. Both Fe^{2+}–Fe^{3+} and Fe^{2+}–Ti^{4+} IVCT are particularly common in terrestrial minerals such as micas, pyroxenes, amphiboles, and tourmalines and are the origin of the dark color of many minerals including magnetite and ilmenite. Fe^{2+}–Fe^{3+} IVCT in sites of near-octahedral coordination is found in the 630–820 nm region. Fe^{2+}–Ti^{4+} IVCT (Figure 1.3a) is typically found in the 425–460 nm region for 6-coordinated near-octahedral cations such as in pyroxenes (Mao et al., 1977; Mattson & Rossman, 1988). The Ti^{3+}–Ti^{4+} IVCT, observed in pyroxenes and hibonite from meteorites (Dowty & Clark, 1973; Burns & Vaughn, 1975), occurs near 690 nm in meteoritic hibonite from Murchison (Rossman, 2019).

In a number of terrestrial minerals adjacent sites may have different coordination polyhedra including edge-shared octahedra and tetrahedra in cordierite or edge-shared octahedra and distorted cubes in garnets. In these cases, the wavelengths of the IVCT bands will differ from those of the edge-shared octahedra. A number of different mineral examples are reviewed in Burns (1981).
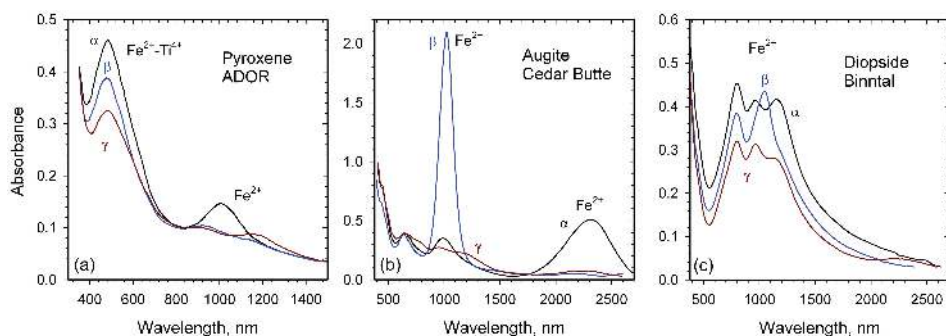

Figure 1.3 Transmission spectra. (a) Clinopyroxene from the Angra dos Reis meteorite showing Fe^{2+}–Ti^{4+} IVCT near 480 nm and the Fe^{2+} features near 1000 and 1200 nm discussed in Section 1.6. (Modified from Mao et al., 1977.) (b) A 200 μm thick augite crystal showing the absorption bands from Fe^{2+} in the geometrically distorted M(2) site near 1000 and 2400 nm, and the weaker bands from Fe^{2+} in the nearly octahedral M(1) site near 970 and 1200 nm. Weak absorption from Cr^{3+} appears near 450 and 650 nm. (c) A 200 μm thick diopside crystal showing comparatively weak absorption bands from Fe^{2+} in the geometrically distorted M(2) site near 1000 and 2400 nm, and the stronger bands from Fe^{2+} in the nearly octahedral M(1) site near 1000 and 1200 nm. Absorption near 800 nm arises from Fe^{2+}–Fe^{3+} IVCT.

1.6 Spectra of Key Minerals

There are currently more than 5400 known mineral phases, but only a small number of them contribute electronic absorptions routinely associated with remotely sensed spectra in the VNIR region. These phases include pyroxenes, olivines, feldspars, iron-bearing layered silicate minerals, and iron oxides. A number of other phases such as iron carbonates, iron sulfates, and other sulfur species are occasionally encountered. While they are only components contributing to the whole spectroscopic signature of an object, these minerals and their electronic absorptions carry important information for revealing the geological history of an object. In this section, we review the spectra of select, important phases. Many examples of the spectra of mineral single crystals with other cations are presented in Rossman (2014).

Iron is the element most commonly causing absorptions in the VNIR spectral region and is responsible for the color of common rock-forming minerals. In the primary igneous minerals, iron is usually found in the 2+ oxidation state, often either in sites that are somewhat distorted from ideal octahedral 6-coordination or in irregular sites of higher coordination number. Frequently, iron occurs in more than one distinct site in the crystal structure of the host mineral. Sulfur species of mixed oxidation state are important on some outer Solar System bodies (e.g., Io: Nash et al., 1980; Carlson et al., 1997). Other metal cations such as V, Cr, Mn, Ni, and Cu are important contributors to the spectra of terrestrial minerals and are responsible for the spectacular colors of many museum-quality minerals. To date, they have not played a significant role in remotely sensed spectra of other planetary bodies.

1.6.1 Pyroxenes

Pyroxenes, $(Ca, Mg, Fe)_2(Si, Al)_2O_6$, are important minerals in many planetary bodies and are an excellent example of how structural distortion affects spectral properties. The two components of the pyroxene absorption bands of Fe^{2+} become increasingly separated as the sites become more distorted from octahedral geometry due to cation substitutions. In the case of the pyroxene M(2) site, the two components can be separated by about 1000 nm (Figure 1.3b).

The spectrum of augite in Figure 1.3b, a terrestrial clinopyroxene, shows prominent absorptions at about 1000 nm in the beta polarization and near 2300 nm in the alpha direction. These two bands arise from Fe^{2+} in the M(2) site of pyroxene, which is highly distorted from an octahedral geometry. Two weaker bands near 970 and 1200 nm are due to Fe^{2+} in the less distorted M(1) site. Small, sharp spin-forbidden transitions are observed at wavelengths less than 1.0 μm. In contrast, the spectrum of diopside in Figure 1.3c has comparatively little contribution from the M(2) site and is primarily dominated by Fe^{2+} absorption from the M(1) site.

Pyroxenes are among the most widespread rock-forming minerals in the Solar System. The absorptions caused by Fe^{2+} in distorted M(1) and M(2) sites can be detected in remote sensing reflectance spectra and related to pyroxene crystal chemistry (Figure 1.4a–c),
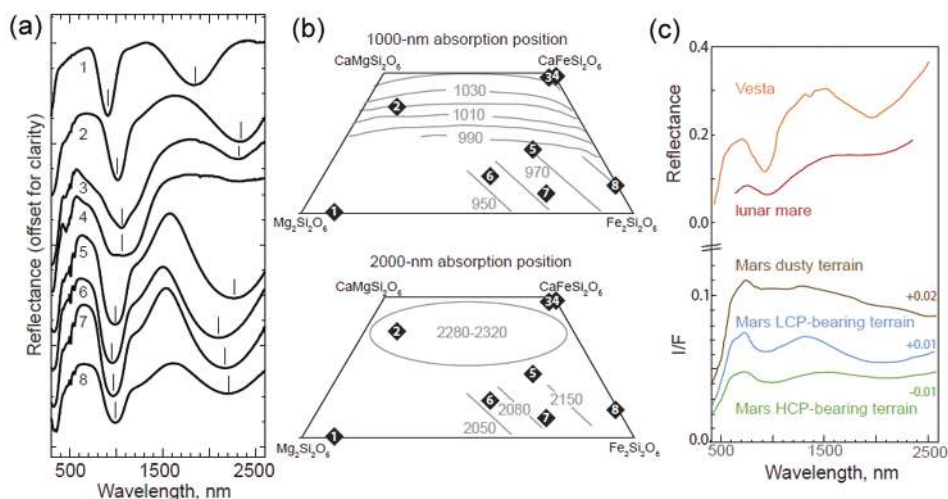
Figure 1.4 Reflectance spectra of pyroxenes. (a) Spectra of a variety of pyroxenes from Klima et al. (2011). (b) Pyroxene absorption band positions systematically shift with the crystal chemistry, here represented on a pyroxene quadrilateral. Apices are diopside ($CaMgSi_2O_6$), hedenbergite ($CaFeSi_2O_6$), enstatite ($Mg_2Si_2O_6$), and ferrosilite ($Fe_2Si_2O_6$). (c) These changes have been essential for identifying distinct geologic units with low-Ca and high-Ca pyroxene (LCP and HCP) on Mars (spectra from Mustard et al., 2005), pyroxenes on Vesta (spectra from DeSanctis et al., 2012), and high-Ca pyroxenes in lunar lavas (spectra from Pieters, 1986).

which in turn can be related to magmatic processes occurring on Solar System bodies. For example, 1 µm and 2 µm absorptions in dark lunar mare terrains were used to establish their volcanic origin and map distinct lava flows (e.g., Pieters, 1978; Staid et al., 2011; Whitten & Head, 2015). Strong pyroxene absorption bands observed for the asteroid Vesta and its family were used to identify it as the parent body for the HED meteorite suite and later mapped with spacecraft data (e.g., McCord et al., 1970; DeSanctis et al., 2012). On Mars, an observed transition from older lavas with low-Ca to younger lavas with high-Ca pyroxenes is inferred to result from thermal evolution of the martian mantle (Mustard et al., 2005; Baratoux et al., 2013). For more reading on pyroxene spectroscopy, see Klima et al. (2011).

1.6.2 The Olivine Series

The spectrum of forsterite provides another example of the role of Fe^{2+} in two distinct sites in the crystal of $(Mg, Fe)_2SiO_4$. Each of the 6-coordinated sites for the metal cations, known as the M(1) and M(2) sites, is significantly distorted from purely octahedral symmetry. Consequently, each site produces a pair of Fe^{2+} NIR absorption bands, which correspond to the crystal field splitting between the lower energy orbitals and the excited states (Figure 1.5). Because olivine is orthorhombic, the 3 spectra in Figure 1.5a represent polarizations along the *a*-, *b*-, and *c*-axes of the crystal which correspond to the γ, α, and
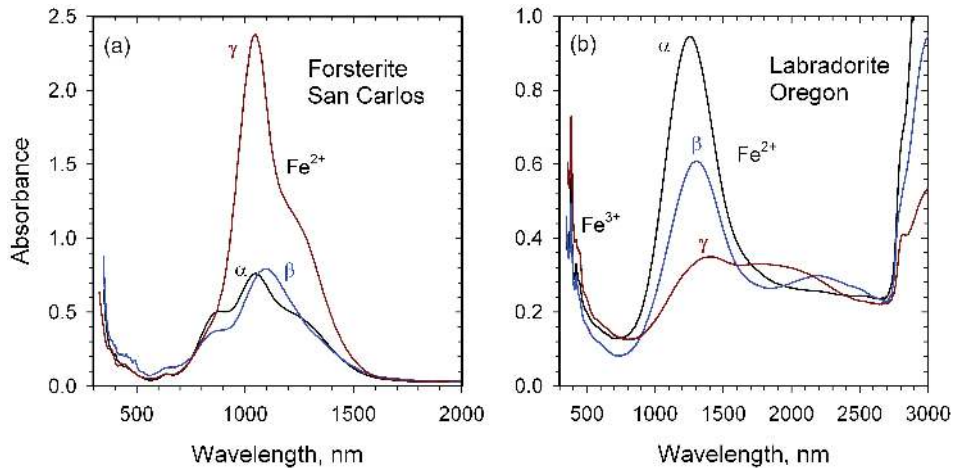
Figure 1.5 Absorption spectra. (a) Olivine (forsterite) from San Carlos, Arizona. (b) Fe-bearing plagioclase feldspar from Lake County, Oregon.

β spectra, respectively. The absorption in the 700–1600-nm region of the forsterite spectrum represents spin-allowed bands of Fe^{2+}. There are absorption bands centered near 830 nm, 1060 nm, 1100 nm, and 1310 nm. The two most intense bands displayed in the γ-spectrum are from iron in the M(2) site. Weak features at less than 800 nm are either spin-forbidden bands of Fe^{2+} or features from other minor components. The diffuse reflectance spectrum convolves the three spectra, as shown in Figure 1.6. The band positions shift with increasing Fe/(Mg + Fe) ratios. Figure 1.6a compares the spectra of an Mg-poor and an Mg-rich olivine. Olivine spectroscopy is further discussed in Sunshine et al. (1998), Isaacson et al. (2014), and Chapters 4 and 18.

1.6.3 Feldspars

Plagioclase feldspars (e.g., $CaAl_2Si_2O_8$) can have iron substitution and thus an Fe^{2+} absorption in the NIR region (Figure 1.5b). The dominant absorption centered near 1300 nm arises from Fe^{2+} in the Ca site, which is significantly distorted from any standard coordination geometry. Features in the 300–500 nm region are from Fe^{3+} in the Al sites, and features near 3000 nm are from the OH content of the feldspar. The Fe^{3+} bands are absent in the spectrum of lunar plagioclase returned by the Luna 20 mission (Bell & Mao, 1973; Chapter 18). Plagioclase spectroscopy is further discussed in Cheek (2014).

1.6.4 Spinels

The spinel group minerals of the general formula (XY_2O_4) are phases that commonly contain Fe^{2+} in a tetrahedral environment, substituting for Mg. Because there is less