Spectroscopy from Space

Roger N. Clark, Gregg A Swayze
U. S. Geological Survey
MS964, Box 25046 Federal Center
Denver, Colorado 80225, U.S.A.
rclark@usgs.gov
gswayze@usgs.gov

Robert Carlson
Jet Propulsion Laboratory, 183-601
California Institute of Technology
Pasadena, California 91109, U.S.A.
Robert.W.Carlson@jpl.nasa.gov

Will Grundy
Lowell Observatory
1400 West Mars Hill Road
Flagstaff, Arizona 86001, U.S.A.
W.Grundy@lowell.edu

Keith Noll
NASA/GSFC
MS 693
Greenbelt, Maryland 20771, U.S.A.
keith.s.noll@nasa.gov

ABSTRACT

This chapter reviews detection of materials on solid and liquid (lakes and ocean) surfaces in the solar system using ultraviolet to infrared spectroscopy from space, or near space (high altitude aircraft on the Earth), or in the case of remote objects, earth-based and earth-orbiting telescopes. Point spectrometers and imaging spectrometers have been probing the surfaces of our solar system for decades. Spacecraft carrying imaging spectrometers are currently in orbit around Mercury, Venus, Earth, Mars, and Saturn, and systems have recently visited Jupiter, comets, asteroids, and one spectrometer-carrying spacecraft is on its way to Pluto. Together these systems are providing a wealth of data that will enable a better understanding of the composition of condensed matter bodies in the solar system.

Minerals, ices, liquids, and other materials have been detected and mapped on the Earth and all planets and/or their satellites where the surface can be observed from space, with the exception of Venus whose thick atmosphere limits surface observation. Basaltic minerals (e.g., pyroxene and olivine) have been detected with spectroscopy on the Earth, Moon, Mars and some asteroids. The greatest mineralogic diversity seen from space is observed on the Earth and Mars. The Earth, with oceans, active tectonic and hydrologic cycles, and biological processes, displays the greatest material diversity including the detection of amorphous and crystalline inorganic materials, organic compounds, water and water ice.
Water ice is a very common mineral throughout the Solar System and has been unambiguously detected or inferred in every planet and/or their moon(s) where good spectroscopic data has been obtained.

In addition to water ice, other molecular solids have been observed in the solar system using spectroscopic methods. Solid carbon dioxide is found on all systems beyond the Earth except Pluto, although CO$_2$ sometimes appears to be trapped in other solids rather than as an ice on some objects. The largest deposits of carbon dioxide ice are found on Mars. Sulfur dioxide ice is found in the Jupiter system. Nitrogen and methane ices are common beyond the Uranian system.

Saturn’s moon Titan probably has the most complex active extra-terrestrial surface chemistry involving organic compounds. Some of the observed or inferred compounds include ices of benzene (C$_6$H$_6$), cyanoacetylene (HC$_3$N), toluene (C$_7$H$_8$), cyanogen (C$_2$N$_2$), acetonitrile (CH$_3$CN), water (H$_2$O), carbon dioxide (CO$_2$), and ammonia (NH$_3$). Confirming compounds on Titan is hampered by its thick smoggy atmosphere, where in relative terms the atmospheric interferences that hamper surface characterization lie between that of Venus and Earth.

In this chapter we exclude discussion of the planets Jupiter, Saturn, Uranus, and Neptune because their thick atmospheres preclude observing the surface, even if surfaces exist. However, we do discuss spectroscopic observations on a number of the extra-terrestrial satellite bodies. Ammonia was predicted on many icy moons but is notably absent among the definitively detected ices with possible exceptions on Charon and possible trace amounts on some of the Saturnian satellites. Comets, storehouses of many compounds that could exist as ices in their nuclei, have only had small amounts of water ice definitively detected on their surfaces from spectroscopy. Only two asteroids have had a direct detection of surface water ice, although its presence can be inferred in others.

**INTRODUCTION**

The remote detection, identification, and mapping of materials using spectroscopy and imaging spectroscopy has been a rapidly advancing and maturing science over the last two decades, and promises significant advances into the future. Spectrometers and imaging spectrometers are now flying on many spacecraft throughout the Solar System, providing a wealth of new data that has led to many new discoveries. As of this writing, spectrometers and imaging spectrometers are in orbit or have recently flown past Mercury, Venus, Earth, Earth’s Moon, Mars, several asteroids, Jupiter, Saturn, and on the way to Pluto. Aircraft-based sensors also play a key role in terrestrial imaging spectroscopy. This chapter will give a few examples of this very large and diverse field. The information is so vast, that the analogy for this chapter will be like taking a drink from Niagara Falls, thus we can cover only a small portion of the field. In order to limit the scope of this chapter, we limit discussions to spectroscopy of reflected solar radiation and thermally emitted light, and mostly exclude gamma-ray or radio wavelength spectroscopy. We only discuss remote detections across space (fly-by or orbiting spacecraft or in the case of the Earth, high altitude aircraft, above about 15 km). We exclude surface landers on other moons and planets.

Spectroscopy is a tool that has been used for decades to identify, understand, and quantify solid, liquid and gaseous materials, especially in the laboratory. In disciplines ranging from astronomy to chemistry, spectroscopic measurements are used to detect absorption features due to specific chemical bonds or electronic transitions, with detailed analyses used to determine the abundance and physical state of the detected absorbing species. Spectroscopic measurements have a long history in the study of the Earth and planets (e.g., Hunt 1977; Goetz et al. 1985; Pieters and Englert 1993; Clark 1999, Clark et al. 2003, 2007).
Reflectance and emittance spectroscopy of natural surfaces are sensitive to specific chemical bonds and transitions in materials, whether solid, liquid or gas. Spectroscopy has the advantage of being sensitive to both crystalline and amorphous materials, unlike some diagnostic methods, like X-ray diffraction. Spectroscopy’s other main advantage is that it can be used up close (e.g., in the laboratory) to far away (e.g., to look down on the Earth, or up at other planets). Spectroscopy’s historical disadvantage for materials identification is that it is sometimes too sensitive to small changes in the chemistry and/or structure of a material. The variations in material composition often cause shifts in the position and shape of absorption bands in the spectrum. Thus, with the vast variety of chemistry typically encountered in the real world, spectral signatures can be quite complex and sometimes unintelligible. However, that is now changing with increased knowledge of the natural variation in spectral features and the causes of the shifts. As a result, the previous disadvantage is turning into a huge advantage, allowing us to probe ever more detail about the chemistry of our natural environment (Pieters and Englert 1993; Clark 1999, Clark et al. 2003, 2007, 2013 and references therein).

Spectroscopic remote sensing from space, or high altitude aircraft requires the detection of reflected solar radiation at shorter wavelengths or thermally emitted light at longer wavelengths. The transition of predominantly reflected solar to predominantly emitted thermal radiation varies as a function of distance from the sun, and the object’s albedo. The transition from reflected solar to emitted thermal emission occurs at approximately 1.5 \( \mu \text{m} \) at Mercury, 2.5 \( \mu \text{m} \) for our Moon, 3 \( \mu \text{m} \) for the Earth, 3.5 \( \mu \text{m} \) for Mars, ~6 \( \mu \text{m} \) for Jupiter’s satellites, ~7 \( \mu \text{m} \) for Saturn’s satellites, and beyond about 10 \( \mu \text{m} \) for the Neptune system (e.g., see Clark 1979).

Ice is probably the most abundant single mineral found in the Solar System. Ice technically refers to the mineral ice, solid H\(_2\)O, that is found naturally on the Earth. In the planetary sciences “ice” has become known as any volatile material that is frozen. Thus, in the planetary literature we discuss water ice, CO\(_2\) ice, SO\(_2\) ice, benzene ice, methane ice, etc. This chapter will also review such ices found on the surfaces of planets, their satellites, and small bodies in the Solar System.

The major elements that formed the solar system were hydrogen, carbon, nitrogen, and oxygen, often referred to as CHON material. When chemically combined, these elements produce molecules with low condensation temperatures—volatiles—with H\(_2\)O being the most refractory of these. Sulfur can also contribute to the volatile inventory, and the abundances of CHON + S material can be appreciable. The inferred molar elemental abundances present in the protoplanetary nebula, relative to hydrogen, of O, C, N, and S are 0.085, 0.036, 0.011, and 0.002, respectively (Anders and Grevesse 1989).

Under the reducing conditions produced by the presence of H\(_2\), the expected closed-shell molecules are H\(_2\)O, CH\(_4\), NH\(_3\), and H\(_2\)S and these are observed as volatile gases or condensates in the atmospheres of the giant planets. Depending on thermal and chemical conditions in protoplanetary and protosolar nebulae, some or all of the above molecules, as well as those formed in more oxidizing conditions, will be incorporated in the forming satellites, comet nuclei, and dwarf planets. Examples of some stable volatiles formed under oxidizing conditions are CO, CO\(_2\), N\(_2\), and SO\(_2\). Minor species may include CH\(_3\)OH, HCN, HCNO, etc. These volatiles condense in varying proportions at rates that are highly dependent on temperature and molecular interaction energies, ultimately forming the diverse ices that are found on outer solar system bodies.

In their pure states, molecules can condense in crystalline or amorphous forms, with crystalline compounds exhibiting a variety of polymorphs. The occurrence of a particular phase depends on the formation conditions, particularly the temperature and starting state (gaseous or liquid), and the subsequent thermal and irradiation history. For example, the freezing of liquid water produces hexagonal ice whereas amorphous, cubic, or hexagonal ice can be produced by condensation of the vapor at different temperatures.
Most minerals on and within solar system bodies are not pure, but contain other minerals or impurities. These mixed minerals can exist in many forms. The minor constituent can be randomly dispersed as isolated molecules within the crystalline or amorphous matrix (a solid solution). These molecules can be substitutional or interstitial, or trapped within defects or closed channels, sometimes existing as micro-atmospheres in voids (e.g., spectroscopically interacting O$_2$ molecules in H$_2$O ice, (Johnson and Jesser 1997; Loeffler et al. 2006) or CO$_2$ gaseous inclusions in minerals.

Closer to the sun, where temperatures in the solar nebula were hotter, rock forming minerals condensed in greater abundances. The solid surfaces of the terrestrial planets, Mercury, Venus, Earth and Mars are dominated by silicate and basaltic mineralogies and their weathering products.

DETECTION OF MINERALS AND THEIR SPECTRAL PROPERTIES

The main method for remotely detecting minerals and compounds is by studying sunlight reflected from the surface under study (reflectance spectroscopy), and/or the heat emitted in the thermal infrared (thermal emission spectroscopy). Materials absorb light at specific characteristic wavelengths, thus spectroscopy can be used to directly and unambiguously detect a compound (given sufficient spectral range, resolution and signal-to-noise ratio). Other methods of remote sensing, such as neutron absorption only sense the presence of atoms, so do not directly detect a specific chemical compound, and require instrumentation in close proximity to the surface (e.g., low orbit). Reflectance and emittance spectroscopy, however, can be used to probe surfaces both near and to the outer reaches of the Solar System from the Earth’s surface as well as from spacecraft. See Clark (1999) for a review of the different types of transitions and vibrations that lead to absorption features in spectra.

While absorption features are diagnostic of material identities, it is the scattering processes that control the light returned from a surface to a detector. Scattering occurs from mineral-vacuum (or gas) interfaces, grain boundaries or crystal imperfections, or from discrete impurities mixed in the surface of a material such as a particulate coating. In order to make an unambiguous detection of a particular material there must be a high enough intensity signal returned to the detector over a sufficient spectral range and with sufficient resolution to resolve diagnostic spectral features. Figure 1 illustrates the issue of sufficient spectral resolution for three operational terrestrial sensors compared to a laboratory spectrum.

A significant problem in detecting materials from space using reflected sunlight is correction of remotely sensed data for effects of the solar spectrum, and absorption and scattering from any atmosphere between the surface and spectrometer. Figure 2 gives an example. Remotely sensing surface composition through such an atmosphere poses challenges. The atmospheric transmission and scattering effects must be accurately corrected, however the atmospheric models are still evolving and correction methods are complex. Clark et al. (2002, 2003) discusses various methods for correcting terrestrial imaging spectroscopy data. Transmission and aerosol scattering is a significant problem on only 4 bodies in the Solar System where we can observe the surface: Venus, Earth, Mars, and Titan, Venus being the most difficult. Model transmissions for the Earth, Mars and Titan are shown in Figure 3. The mid-infrared transmittance of the Earth’s atmosphere is shown in Figure 4, which shows even less transmission, mostly due to absorption by water.

Another problem in remotely sensing compounds is that the apparent strength of spectral features changes with grain size of the material. Not only do the absorption features change shape, the overall shape of the spectrum can also change. This is illustrated in Figure 5 with Ice.
Figure 1. Comparison of sensors with different spectral resolutions. Landsat TM with 6 bands in the visible to near-infrared spectrum cannot resolve any absorptions typical in minerals. The MODerate resolution Imaging Spectrometer (MODIS) has enough spectral channels to barely resolve some spectral features in the visible portion of the spectrum, but not in the important near-infrared. The Airborne Visible and Infra-Red Imaging Spectrometer (AVIRIS), however, has sufficient spectral range and resolution to resolve many common absorption bands found in a wide variety of minerals and other compounds. The gray bands on the AVIRIS spectrum represent regions of the terrestrial atmosphere with strong absorptions. The spxnnnn entries are U.S. Geological Survey spectral IDs. Adapted from data in Clark (1999) and Clark et al. (2007).

Figure 2. Observed signal of sunlight reflected from the Earth’s surface measured at a height of 20 km by AVIRIS. The red line is the derived path radiance from the signal, light scattered by the atmosphere in the direction of the detector. To derive a surface reflectance spectrum, the solar spectrum, path radiance, and atmospheric absorption needs to be removed. DN stands for “Data Number” and is a relative scale. From Clark et al. (2002).
Figure 3. Model 1-way atmospheric transmission spectra for the Earth, Mars, and Titan. The dominant absorption in the Earth’s atmospheric transmission is water vapor, with ozone providing the UV drop. The dominant absorption in Mars’ atmospheric transmission is carbon dioxide and dust aerosol absorption plus scattering. The dominant absorption in Titan’s atmospheric transmission is methane and hydrocarbon aerosol absorption plus scattering. Earth spectrum from Clark (1999), Mars from P. Irwin (personal communication, 1997), and Titan from Clark et al. (2010a). The transmission of Venus’ atmosphere would be too low to register on this plot; transmission at 1 $\mu$m is $\ll 0.00002$ (Baines et al. 2000).

Figure 4. Atmospheric transmittance in the mid-infrared is compared to scaled grey-body spectra. Most of the absorption is due to water. Carbon dioxide has a strong 15-$\mu$m band, and the dotted red line shows the increased absorption due to doubling CO$_2$. Also shown is the black-body emission at 288 K and the grey-body emission from water and a sandstone scaled to fit on this transmittance scale. The water and sandstone curves were computed from reflectance data using: 1 - reflectance times a black-body at 288 Kelvin. Adapted from Clark (1999).
Spectroscopic characterization of minerals is well-covered in Pieters and Englert (1993), Clark (1999), and Clark et al. (2007), and references therein. Detection strategies are discussed in Clark et al. (2003) and references therein. Spectroscopy of ices are reviewed in Clark et al. (2013) and more briefly below.

Detection of a particular mineral on a planetary surface is only one aspect of understanding the geology and chemistry of the surface. Mapping the locations and geologic context greatly enhances our understanding of planetary surfaces, including their origin. Mapping solid and liquid compounds on a planetary surface is accomplished with imaging spectrometers. There are several types of imaging spectrometers. Two widely used diffraction grating types include whiskbroom scanners which collect spectra in a cross-track manner by using an oscillating mirror to sequentially reflect light from each spatial location in a scene to a spectrometer one pixel at a time, and pushbroom scanners which measure the spectra of all the pixels across an image simultaneously using an area array detector and the forward motion of the spacecraft. Whiskbroom scanner data are more easily calibrated because the same detector array measures the spectrum of every pixel in the scene, but dwell time on a given pixel is relatively short so images can be noisy. Pushbroom scanners have longer dwell times on each pixel so provide a less noisy image, but images are commonly plagued by along-track image artifacts caused by miscalibration of adjacent pixel array elements. See Goetz et al. (1985) and Clark et al. (2003) for more details. Whiskbroom systems include the NASA JPL classic Airborne Visible/Infrared Imaging Spectrometer (AVIRIS), flown on high altitude aircraft above the Earth (Green et al. 1990) and the NASA Visual and Infrared Mapping Spectrometer (VIMS) currently orbiting Saturn (Brown et al. 2005a). Pushbroom imaging spectrometers include the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) (Murchie et al. 2007) which is currently orbiting Mars on the Mars Reconnaissance Orbiter (MRO). Broadband imaging systems like the Mars Themis (Christensen et al. 2004) and HiRISE (McEwen et al. 2007) are not discussed because they are not spectrometers, nor imaging spectrometers.

**Figure 5.** Illustration of changing ice absorption band shapes and strengths with grain size. The near-infra-red spectral reflectance of A) a fine grained (~200 \( \mu \)m diameter) water frost, B) medium grained (~300 \( \mu \)m) frost, C) coarse grained (400-2000 \( \mu \)m) frost and D) an ice block containing bubbles and frost on the surface. The larger the effective grain size, the greater the mean photon path that photons travel in the ice, and the deeper the absorptions become. Curve D is very low in reflectance because of the large path length in ice but scattering from fine frost at the surface raises the reflectance. Adapted from data in Clark (1981), and Clark and Lucey (1984) with level corrections from the reflectance standard.
MINERAL AND FROZEN VOLATILES SPECTRAL SIGNATURES

H$_2$O (ice)

Water ice phases and spectral features as a function of temperature are discussed in detail by Mastrapa et al. (2013). Ice forms multiple crystal structures, including cubic (Ic), hexagonal (Ih), and amorphous solids (Hobbs 1975 and references therein) which might be encountered on planetary surfaces in the solar system. The spectra of crystalline water ice (Fig. 5, and see Grundy and Schmitt 1998) display particularly broad absorptions because the water molecules are orientationally disordered. In hexagonal or cubic ice, the oxygen atoms are in a well-defined crystal structure, but the hydrogen bonds point randomly toward neighboring oxygen atoms.

Mastrapa et al. (2008) measured the optical constants of crystalline and amorphous ice from 20 to 120 K and reviewed formation conditions for amorphous versus crystalline water ice. Below about 135 K, amorphous ice is expected to condense from the vapor phase if the rate of growth is slow. Thus, we might expect amorphous ice to be present in the Jupiter system and beyond. However, as we will see, with the probable exception of the Jupiter system, where surfaces are being irradiated by particles caught in Jupiter’s magnetic field, outer solar system surfaces are dominated by crystalline H$_2$O.

In amorphous ice, the absorptions shift to shorter wavelengths. The Fresnel peak near 3.1 $\mu$m also shifts to shorter wavelengths, and the temperature sensitive 1.65-$\mu$m absorption becomes very weak. See Clark et al. (2013).

SO$_2$ ice

SO$_2$, a colorless gas at room temperature, is a common terrestrial volcanic (and industrial) effluent and also present in Venus’s atmosphere, possibly from recent volcanic activity. It is the major component emitted from Jupiter’s volcanically active moon Io. SO$_2$ is a bent molecule of the form O-S-O and is a stable sulfoxide, with SO and S$_2$O being much less stable. Oxidation of SO$_2$ in the presence of H$_2$O produces sulfuric acid, evident in the Earth’s atmosphere as acid rain and in Venus’s atmosphere as the ubiquitous sulfuric acid clouds and haze.

SO$_2$ is more refractory than NH$_3$, it liquefies at ~263 K and freezes at ~200 K. Within the temperature range of 90 K to 120 K, appropriate for Jovian satellites, the SO$_2$ vapor pressure varies by five orders, from about 10$^{-4}$ nbar to 10 nbar. SO$_2$ is amorphous when condensed at temperatures < 70 K, but crystallizes at temperatures > 70 K (Schmitt et al. 1994). Condensed SO$_2$ forms many different textures (Nash and Betts 1998). The condensation, evaporation, and metamorphism of pure SO$_2$ and mixed ices have been discussed by Sanford and Allamandola (1993).

Useful reviews of SO$_2$ properties by Schmitt et al. (1998b) and Nash and Betts (1998) are found in the Solar System Ices book (Schmitt et al. 1998a). Infrared and ultraviolet spectroscopy of SO$_2$ is summarized in Carlson et al. (2007).

Nitrogen ice (N$_2$)

Although nitrogen is cosmochemically abundant, the high volatility of N$_2$ ice makes it unstable except at extremely low temperatures characteristic of the outer edge of the Solar System. There are two low-pressure phases of N$_2$ ice. Above 35.61 K, the stable form is beta N$_2$ ice, an orientationally-disordered hexagonal close packing solid (Scott 1976). It is difficult to detect spectroscopically, because N$_2$ is a non-polar molecule in which vibrational absorptions are not easily excited. Only when an N$_2$ molecule collides with another molecule is a dipole moment temporarily induced, enabling a photon around 4.25 $\mu$m to excite its 1-0 fundamental vibrational mode (e.g., Shapiro and Gush 1966; Sheng and Ewing 1971). This collision-induced absorption is relatively broad (~100 cm$^{-1}$ in wavenumber units), compared with gas-phase absorptions due to fixed dipole moments, owing to the modulation of the vibrational transition by the translational motion of the colliding pair. See Clark et al. (2013) for further review and references.
Hydrocarbons and other ices

Hydrocarbons are a diverse category of organic compounds, comprising numerous families without heteroatoms and with functional groups of solely hydrogen and carbon atoms. The simplest hydrocarbons are the alkanes – singly bonded molecules with no reactive functional groups. Hence, they tend to combust at relatively high temperatures, even though they are composed entirely of low atomic weight atoms, and have a generic chemical formula of $C_nH_{2n+2}$. If the carbon backbone contains a C-C double bond, the hydrocarbon is termed an alkene, and it has a formula of $C_nH_{2n}$ (e.g., propene, $C_3H_6$); with a C-C triple bond, it is called an alkyne whose formula is $C_nH_{2n−2}$ (e.g., propyne, $C_3H_4$). In the singly bonded alkanes, hydrogen atoms will bond to all the remaining positions on the carbon atom, and they are known as saturated hydrocarbons. Unsaturated hydrocarbons then, are those with doubly or triply bonded carbon atoms, and they will have less than their ‘full’ complement of hydrogen atoms. Together, these straight (or branched) chain hydrocarbons are known as ‘aliphatic’ compounds, and also include such derivatives as fatty acids (Wade 2005).

In general, spectra of different families share different spectral characteristics while spectral properties are similar within a family (also called group or series). For example, Figure 6 shows spectral differences among ices in the alkane, alkene, and alkyne groups from Clark et al. (2009). In alkanes, the C-H stretch fundamental occurs near 3.4 $\mu$m, whereas in the C-C double bonded alkenes, the C-H stretch shifts closer to 3.2 $\mu$m, and in the C-C triply bonded alkynes, the C-H stretch shifts to nearly 3.0 $\mu$m (Fig. 6).

The carbon skeleton can close in on itself in two ways: by creating a ring of singly-bonded carbon atoms of any length equal to or greater than three (cycloalkanes, known as alicyclic hydrocarbons), or by the overlapping of $p$ orbitals from adjacent carbon atoms into pi ($\pi$) bonds to create a benzene ring ($C_6H_6$). The benzene ring with overlapping $p$ orbitals is particularly stable, and forms the basis of the aromatic hydrocarbon family.

Most organic molecules are infrared active, displaying absorption features associated with stretching and bending vibrations. For example, the C-H stretch fundamental of aromatic

![Figure 6. Reflectance spectra of propane, propene, propyne and benzene ices. From Clark et al. (2009).](attachment:image.png)
hydrocarbons occurs near 3.3 \( \mu \text{m} \) (Fig. 6) and a bending mode absorption has been used to detect benzene ice on Saturn’s moon Titan. Because these transitions are specific to the atoms and their chemical bonds, and are similar regardless of the type of larger molecule within which they are contained, an examination of the IR spectrum will reveal an enormous amount of information about an unknown compound (e.g., as seen in Fig. 6). Clark et al. (2009) observed that the spectral complexity of organic ices first increases as molecular weight increases, then decreases at higher molecular weights. The loss of spectral structure at high molecular weights is probably due to many overlapping absorptions averaging out small details.

**Methane (CH\(_4\))**

Methane deserves special attention as the smallest and simplest alkane, as well as being the hydrocarbon most widely observed as an ice on solar system bodies. It is readily detected spectroscopically by means of numerous overtones and combinations of four fundamental vibrational transitions. These are a symmetric mode \( v_1(A_1) \) at 2914 cm\(^{-1}\) (3.43 \( \mu \text{m} \)), a doubly degenerate \( v_2(E) \) bending mode at 1526 cm\(^{-1}\) (6.55 \( \mu \text{m} \)), and triply degenerate stretching \( v_3(F_2) \) and bending \( v_4(F_2) \) modes at 3020 and 1306 cm\(^{-1}\) (3.31 and 7.66 \( \mu \text{m} \)), respectively (Grundy et al. 2002). Two different condensed phases occur at zero pressure. At temperatures below 20.4 K, CH\(_4\) exists as a cubic crystal, whereas above that temperature, it loses its orientational order and long-range coordination, resulting in broadened bands similar to (but not identical to) those of liquid methane (e.g., Ramaprasad et al. 1978; Martonchik and Orton 1994). Temperature-dependent spectra have been measured for methane ice between 0.7 and 5 \( \mu \text{m} \), revealing subtle changes with temperature that offer an as-yet unexploited potential for remote sensing of CH\(_4\) ice temperatures (Grundy et al. 2002). Methane molecules dispersed in nitrogen ice exhibit slightly different spectral behavior, characterized by subtle wavelength shifts toward blue wavelengths as well as the loss of a weak transition at 1.69 \( \mu \text{m} \) (Quirico et al. 1997b). This property provides a way to remotely distinguish diluted from pure CH\(_4\), as well as the potential to detect smaller quantities of nitrogen ice than can be readily detected through observation of the much weaker N\(_2\) ice absorptions, with specific applications discussed later in this chapter.

**MINERALS AND COMPOUNDS IN THE SOLAR SYSTEM DETECTED WITH SPECTROSCOPY**

We will now discuss the detections of minerals and other compounds on planets and their satellites in our Solar System.

**Terrestrial planets**

**Mercury.** Vilas et al. (2012), Izenberg et al. (2012), and Riner and Lucey (2012) have searched for spectral features in the MErcury Surface, Space Environment, GEochemistry, and Ranging (MESSENGER) spacecraft data of the planet Mercury. To date, no plausible spectral features for identifying mineralogy, for example, pyroxene absorptions like those seen on the Moon have been found. It appears that the surface of Mercury is intensely space-weathered, where the surface minerals are partially destroyed, leaving rinds enriched in nano-phase metallic iron. See Hapke (2001) and Chapman (2004) for more on terrestrial space weathering, and Clark et al. (2012) for space weathering effects in the outer solar system.

**Venus.** Venus has a thick highly scattering atmosphere, making it the most difficult surface to be detected from space (excluding Jupiter, Saturn, Uranus, and Neptune whose surfaces, if they exist are impossible to see with UV to far infrared light). Three spacecraft have detected thermal emission from the surface using near-infrared wavelengths: Galileo NIMS (Carlson et al. 1991), Cassini VIMS (Baines et al. 2000), and Venus Express VIRTIS (Müller et al. 2008, Titov et al. 2009 and references therein). Baines et al. (2000) showed that it could be possible to use a few windows in the Venetian spectrum to detect broad electronic absorptions due to iron.
in surface minerals and Hashimoto et al. (2008) have used these windows and suggested felsic materials in Venus’s highlands.

**Earth.** The Earth is the only planet whose temperature is near the melting point of water where both liquid and solid water exists on the surface. This condition enables a complex hydrologic cycle of both solid and liquid water eroding, reshaping and weathering the surface. Active plate tectonics recycles crustal minerals, and creates active volcanism which leads to a variety of important mineral-forming conditions. Over three thousand minerals have been found naturally occurring on the Earth (e.g., Fleischer and Mandarino 1995). Dozens of minerals have been detected at the Earth’s surface using spectroscopy from high-altitude aircraft (e.g., the NASA JPL Airborne Visible/Infrared Imaging Spectrometer, AVIRIS), commercial aircraft spectrometers, and spacecraft. The Earth’s high carbon and nitrogen environment, energy sources, and hydrologic cycle provide a unique surface composition with abundant water, organic compounds, and life. The Earth’s surface is dominated by liquid water, solid water, vegetation, and, in some locations, minerals in exposed rocks and soils.

While there are many imaging spectrometers on the way to, or have recently flown by or orbited, or are currently orbiting planets and satellites throughout the Solar System, very oddly there is only one (non-military) true imaging spectrometer in orbit around the Earth, the aging EO-1 Hyperion system (e.g., Barry et al. 2001). Because the Hyperion instrument is relatively old and its near-infrared performance is significantly lower than that of aircraft systems, many studies rely on systems like the NASA JPL Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) system (Green et al. 1990) and other commercial systems which fly at lower altitudes.

The number of terrestrial applications of spectroscopy from space or aircraft is stunning, ranging from mineral mapping (e.g., Clark et al. 2003 and references therein) as shown in Figures 7a and 7b, acidic mine drainage and mineralization impact (e.g., Swayze et al. 2000), ecosystems mapping, vegetation species and chemistry (e.g., Kokaly et al. 2003; Clark et al. 2003; Ustin et al. 2009 and references therein), mapping chlorophyll in water (Clark et al. 2003; Clark and Wise 2011), assessments of environmental disasters (the World Trade Center Disaster: Clark et al. 2001, 2006; the 2010 Gulf of Mexico Deepwater Horizon oil spill: Clark et al. 2010b), and detection of fires/thermal hot spots through thick smoke, determining temperature and sub-pixel areal extent (Clark et al. 2003, 2006). Remote sensing had been tried for decades to derive a method to determine the amount of oil on the ocean’s surface without much success. But in the most recent disaster, the Gulf of Mexico 2010 oil spill, by using absorption features in oil and the spectral resolution of AVIRIS, Clark et al. (2010b) simultaneously solved for the oil:water ratio of intimate mixtures (e.g., water-in-oil emulsions), thickness of the mixture and their sub-pixel areal fraction to derive oil volume per pixel. Such unmixing is only possible using the many wavelengths provided by a visible to near-infrared imaging spectrometer.

**The Earth’s Moon.** Water ice is thought to exist in the permanently shadowed craters on the moon and neutron spectrometer data from Lunar Prospector (Feldman et al. 1998, 2000, 2001) showed that hydrogen is present in the lunar polar regions. More recently Clark (2009), Pieters et al. (2009), and Sunshine et al. (2009) reported that adsorbed water is extensive in the lunar surface raising the likelihood that some of it has migrated and is trapped in the polar regions. Coleprete et al. (2010) reported detection of water vapor and water ice in the ejecta from the NASA LCROSS impact into South Pole crater Cabeus A. They also claim detection of other volatile compounds. Paige et al. (2010) reported temperatures as low as 38 K in Cabeus A, where many volatile compounds might exist as ices.

The Chandrayaan-1 spacecraft with the Moon Mineralogy Mapper (M^3) is the only imaging spectrometer to orbit the Moon covering the reflected solar spectral range. The M^3 instrument
has been used to detect and map a variety of minerals on the Moon, including the pyroxene solid solution series, olivines, feldspars and spinels (e.g., Pieters et al. 2011 and references therein). Kramer et al. (2011) showed an interesting link between the enigmatic lunar swirls which seem to lack hydroxyl that occurs in the surrounding rocks and soils.

**Mars.** Orbital high spectral resolution mapping of Mars over the last two decades with the Thermal Emission Spectrometer (TES) on Mars Global Surveyor (Christiansen et al. 1992), Observatoire pour la Minéralogie, L’Eau, les Glaces et l’Activité (OMEGA) on Mars Express

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**Figure 7.** (a) Imaging spectroscopy mapping results from AVIRIS imaging spectrometer data over Cuprite, Nevada for absorptions in the 1-μm spectral region due to Fe$^{2+}$ or Fe$^{3+}$. All the Fe$^{2+}$ - Fe$^{3+}$ absorptions overlap making separation difficult. Yet through spectroscopic analysis, not only can the minerals be distinguished, but mixtures could be distinguished based on the shape of the overlapping absorption features. From Swayze et al. (2003) with modifications.
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(Bibring et al. 2004a), and the Compact Reconnaissance Imaging spectrometer for Mars (CRISM) on the Mars Reconnaissance Orbiter (Murchie et al. 2007) has led to numerous discoveries of mineral phases on the surface. One of the main goals that these imaging spectrometer share is the search for minerals formed during the early part of Martian history when water existed temporarily at the surface and for longer periods at depth. The spectral signatures of minerals frequently provide information about their environment of formation. Some minerals hint at metamorphic processes caused by elevated temperature and pressure caused by impacts. Clays and evaporites require water to form and are sensitive to formative pH conditions that can influence the preservation of fossils. Kaolin group minerals and the sulfate mineral alunite

Figure 7. (b) Imaging spectroscopy mapping results from AVIRIS imaging spectrometer data over Cuprite, Nevada. The results distinguish kaolinite, alunite, carbonate, mica and other minerals, separate kaolinite from alunite-dominated areas, and also indicate where both occur as mixtures. From Swayze et al. (2003) with modifications.
may indicate the past presence of hydrothermal activity around hot spring deposits or acidic paleolakes. In this way, spectroscopists can use orbitally detected minerals as proxies to focus rover missions on the most promising sites in the search for evidence of past life.

During its operation from 1996 to 2006 the TES interferometer, which measured mid-infrared wavelengths for 3 km pixels on the surface, was used to discover concentrations of hematite in Meridiani Planum (Christensen et al. 2000), leading to its selection as a landing site for the Mars Exploration Rover Opportunity. Other mineralogic discoveries include olivine in Nili Fossi (Hoefen et al. 2003), globally distributed pyroxene (Christensen et al. 2001), and possibly carbonate (Bandfield et al. 2003) and zeolite minerals (Ruff 2004) distributed globally in the Martian dust. Originally, Christensen et al. (2001) thought TES data indicated the presence of basalt in the southern highlands and more silica-rich andesite in the northern plains. Wyatt and McSween (2002) argued that these more silica-rich spectral detections are actually weathered basalts with thin coatings of silica glass. Nevertheless, TES may have revealed the presence of rare exposures of granitoid rocks in the central uplifts of two adjacent craters (Bandfield et al. 2004) suggesting the presence of mechanisms that can produce highly differentiated magmas.

OMEGA led the way in orbital visible–near infrared spectroscopic mineral discoveries on Mars with its typical 1-2 km pixel resolution. Detailed variations in Fe-pyroxene distribution were documented by Mustard et al. (2005). Gendrin et al. (2005) identified the monohydrated Mg-sulfate kieserite in layered deposits on the surface while gypsum-rich sand dunes were identified by Langevin et al. (2005) at circumpolar latitudes. Poulet et al. (2005) observed sparsely distributed phyllosilicates such as montmorillonite, Fe/Mg smectite, and nontronite consistent with an early stage of neutral to alkaline Martian hydrologic activity. Based on these and other mineral discoveries, Bibring et al. (2006) recognized several eras of mineralogic evolution on Mars: the “phyllocian” (~4.5 to 3.8 billion years ago) where aqueous alteration at more neutral pH formed phyllosilicates in the oldest terrain, the “theiikian” (~3.8 to 3.3 billion years ago) where sulfates were formed in a more acidic environment, and the “siderikian” (~3.3 billion years ago to the present) where anhydrous ferric oxides formed from slow weathering primarily in the absence of liquid water.

CRISM, the latest orbital visible-near infrared spectrometer to orbit Mars, is a pushbroom imaging spectrometer that has two data collection modes: a targeted hyperspectral mode that measures light from 0.36 to 3.92 μm over 544 spectral channels at a spatial resolution up to 18 m per pixel, and a multispectral imaging mode that collects subsets (e.g., 72, 94, or 262) of its 544 channels at a spatial resolution of 100 to 200 m per pixel (Murchie et al. 2007). The hyperspectral mode produces full spatial resolution 10 × 10 km hourglass-shaped images with 18 m pixels or half spatial resolution 10 × 20 km images with 36 m pixels. In targeted mode, CRISM spectral sampling is approximately 6.5 nm. CRISM is gimbaled so it can swivel to perform continuous spectral measurements on a target while the spacecraft flies over the location. This allows higher spatial and spectral resolution measurements to be obtained with better signal-to-noise ratios. Gimbaling also allows acquisition of up to 11 images of the same target at varying emission angles during an overpass to facilitate separating surface absorptions from atmospheric ones. Recently, CRISM began acquiring targeted hyperspectral images with along-track overlap to produce images with 3-12 m pixel resolution over the most interesting areas (e.g., rover sites).

CRISM data can be calibrated to apparent reflectance by first converting the data from instrument units to I/F (the ratio of the reflected intensity to the incident intensity of sunlight), next photometrically correcting it, then assuming Lambertian scattering applies, dividing it by the cosine of the incidence angle, and lastly correcting it for atmospheric gas absorptions by dividing by a scaled atmospheric transmission spectrum of Olympus Mons as explained in Mustard et al. (2008). Image noise can then be reduced using a filtering algorithm that
replaces outlier pixels in the spectral and spatial dimensions of the image cube (Parente 2008). Remaining noise is further reduced in each column by dividing individual pixel spectra by a spectral average calculated from pixels lacking narrow vibrational absorptions from that column. Alternatively, a DISORT-based radiative transfer model can be used to convert I/F data to surface Lambert albedo resulting in spectra nearly free of atmospheric gas artifacts (McGuire et al. 2008). This last method is compute intensive so has been applied to only a select group of CRISM scenes.

CRISM has allowed planetary scientists to leverage its fine pixel resolution to identify, in unprecedented detail, an even broader array of carbonates, phyllosilicates, opaline silica, sulfates, and zeolites on the Martian surface. Ehlmann et al. (2008) identified Mg-carbonate in the Nili Fossae region formed by alteration of olivine by hydrothermal fluids or near-surface water that were not destroyed by more acidic conditions later in Martian history. A number of researchers (Murchie et al. 2009; Mustard et al. 2008; Bishop et al. 2008; Noe Dobrea et al. 2010) have noted that extensive phyllosilicate-rich layers, in some cases hundreds of meters thick, blanket old eroded highland areas. At the highest spatial resolution, these layers resolve in places into a lowermost Fe/Mg-smectite unit, a middle montmorillonite unit, and an upper kaolinite-rich unit suggestive of a weathering profile as conditions became more acidic with time. Curiosity, the Science Laboratory rover, successfully landed in and has begun exploring Gale Crater where CRISM has identified diverse phyllosilicate and sulfate mineralogy in a 5 km high pile of layered rocks believed to have recorded climatic conditions during the first billion years of Martian history (Milliken et al. 2010). Gale crater is 152 km in diameter and is just 5º south of the equator. Stratigraphic exposure in the central mound is more than twice that of the Earth’s Grand Canyon (Thomson et al. 2011). The rover will traverse the central mound examining the lowermost section and then upper portion to determine if these sediments record the progressive “drying out” of Mars.

Ehlmann et al. (2009) summarizes spectral evidence for nontronite, Mg-rich smectite, chlorite, prehnite, serpentinite, kaolinite, K-mica, opaline silica, Mg-carbonate, and the Na-zeolite analcime in and around the Nili Fossae region. They suggest these minerals may indicate that low-grade metamorphism or hydrothermal aqueous alteration has occurred in this region in the past. Milliken et al. (2008) identified opaline silica on Mars based on CRISM spectra that were initially confused with the Al-rich smectite montmorillonite. Under terrestrial conditions opal has a broader 2.2-μm absorption compared to that of montmorillonite (Fig. 8). But under simulated Martian conditions weakly hydrogen bonded water normally present under relatively humid terrestrial conditions is lost causing the 2.2-μm absorption to narrow so it forms a better spectral match to CRISM spectra of widespread Martian surface rocks. Ehlmann et al. (2011) argue that spectroscopic evidence of minerals from assemblages formed under anoxic high temperature conditions, a high ratio of primary to secondary minerals, and observed stratigraphic relations indicate substantial amounts of clay formed by hydrothermal groundwater circulation and that cold, arid conditions with only transient surface water existed at the surface since the early Noachian period nearly 4 billion years ago. This explanation diminishes the need for an atmosphere thick enough to support persistent liquid water and clay formation by near-surface weathering (Bibring et al. 2006; Ehlmann et al. 2011).

Sulfate deposits on Mars are similarly detectable. Bishop et al. (2009) identified szomolnokite, a monohydrated Fe-sulfate in light-toned mounds within Valles Marineris and hydrated silica with hydroxylated ferric sulfate on the surround plateau. Lichtenberg et al. (2010) noted that a wide expanse of hydroxylated ferric sulfate underlies what is probably a layer of szomolnokite deposited as part of an evaporitic sequence in Arma Chaos. Several workers (Farrand et al. 2009, Milliken et al. 2008) have identified the yellow Fe-sulfate hydroxide jarosite in areas where water may have been present. Wray et al. (2011) used CRISM to map the distribution of a bathtub-ring of sulfates (i.e., gypsum, poly- and mono-hydrated
Mg/Fe sulfates, and jarosite) and phyllosilicates (i.e., kaolinite, montmorillonite, and Fe/Mg-smectites) deposited as an evaporative scum by the receding waters of 900-meter deep paleolake that once partially filled Columbus Crater. Swayze et al. (2008) identified K-alunite in light toned layers on the floor of Cross Crater in the southern highlands in association with kaolinite, montmorillonite, and opal (Fig. 9). These minerals form partially concentric zones with alunite at the core suggestive of terrestrial relict acid-sulfate hydrothermal deposits. The relatively low-temperature (<100 °C) spectral signature of the alunite and its presence at the foot of the crater wall suggest it may have formed by precipitation in hydrothermal springs where acidic-water discharged into a lake that filled the crater to several hundred meters depth. Deposits in this crater and those in Columbus Crater would be excellent sites for future rover missions looking for evidence of past life.

As a general rule, the relative timing of phyllosilicate and sulfate deposition on Mars appears to be controlled by a progressively drying climate. Thollot et al. (2012) have found an exception, where a closed depression in the Noctis Labyrinthus region of Mars holds several hundred meters of stratified material enriched in phyllosilicates and sulfates, and both formed in situ during the Late-Hesperian epoch (3.4 to 3.0 billion years ago) after the Noachian period.

**Figure 8.** Laboratory spectra of montmorillonite and an opaline coating on a 3,000-5,000 year old basalt from Mauna Loa, Hawaii, at terrestrial conditions and simulated Martian surface conditions compared with an average of 120 spectra from MRO CRISM scene HRL000044AC collected over the plains around Valles Marineris south of Melas Chasma. Artifacts due to CO$_2$ have been replaced by the dashed line to facilitate spectral comparison. Box encloses CRISM spectrum and lab mineral spectra measured at simulated Martian conditions. Figure modified from Swayze et al. (2007).
(4.1 to 3.8 billion years ago) when most phyllosilicates are thought to have formed. Their evidence suggests that the broadly diverse mineral assemblages formed from local volcanic activity and related hydrothermal alteration, and that geological setting may be just as important as geological timing when trying to understand orbitally detected mineral deposits.

Mars has seasonal and remnant polar caps of H\(_2\)O and CO\(_2\) ices, as well as permafrost and geologic features indicative of glacial flow and sublimation of water ice from below the surface. Mars’ seasonal polar caps extend down to about 50° latitude (e.g., James et al. 1993 and references therein). Due to present day obliquity, the southern hemisphere is drier than the northern hemisphere. The southern residual cap is dominated by CO\(_2\) ice while the northern residual cap is dominated by H\(_2\)O ice (Farmer et al. 1976; Kieffer et al. 1976). However, it has recently been confirmed that an H\(_2\)O cap underlies the southern CO\(_2\) remnant cap (Byrne and Ingersoll 2003; Bibring et al. 2004b).

More than 25% of the atmospheric CO\(_2\) condenses each year to form the seasonal caps (Forget et al. 1995; Kieffer and Titus 2001). The NASA Phoenix lander and Mars Reconnaissance Orbiter, Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), and the High-Resolution Imaging Science Experiment (HIRIS) instruments have quantified growth of the northern seasonal polar cap of H\(_2\)O and CO\(_2\) at 68° N latitude (e.g., Cull et al. 2010; Fig. 10). During winter, the CO\(_2\) ice grows to a depth of about 0.35 m with a thin layer of H\(_2\)O ice on the surface.

**Asteroids and comets**

Although asteroids generally show only silicate minerals on their surfaces, ice has been reported in two asteroids, 24 Themis (Rivkin and Emery 2008; Campins et al. 2009) and (65) Cybele (Licandro et al. 2011). Both objects have a weak absorption at 3-μm best described...
by water ice. However, strongly hydrogen bonded water can also display absorptions at the wavelengths where ice absorbs and higher signal-to-noise ratio spectra are needed to confirm this weak absorption. In addition, Themis has been reported to contain organic material (Campins et al. 2010; Rivkin and Emery 2010).

Comets are dark, with reflectances of only a few percent, and their surfaces are commonly thought of as carbonaceous lag deposits, the refractory remains left behind by the sublimation of dirty ice. While water is the major volatile species on comets, detection of water on the surface has been elusive. Davies et al. (1997) detected weak absorptions attributed to water ice in comet Hale-Bopp but the spectra included the coma. They also showed possible evidence for the ice being amorphous, but the low signal-to-noise ratio and weak absorption strength precludes a definitive detection when considering the far infrared spectrum of amorphous versus crystalline ice. Lellouch et al. (1998) also reported detection of ice in the coma of Comet Hale-Bopp. The temperatures they derived, 170 K, for their observations are too high for amorphous ice. A detection of ice on a comet nucleus without interference from the coma, comet Tempel 1, was reported by Sunshine et al. (2006) using the Deep Impact spacecraft where small exposures of ice were seen by the imaging spectrometer. The Deep Impact extended mission shows isolated patches of water ice on Comet Hartley 2 (Sunshine et al. 2012). While water ice has been detected on comets, to date, no other ices have been definitively detected via spectroscopy.

**Jupiter system**

Jupiter has four large moons, discovered 400 years ago by Galileo, and three of these (Europa, Ganymede, and Callisto) were found to have water ice surfaces (Kuiper 1957; Moroz 1965; Johnson and McCord 1971; Pilcher et al. 1972; Fink et al. 1973). Over the years these bodies have been studied using airborne (telescopes on terrestrial aircraft looking up) and ground-based spectroscopy using telescopes (Pollack et al. 1978; Clark 1980; Clark and McCord 1980), by infrared spectroscopy from the Galileo spacecraft in orbit around Jupiter (Fig. 11), and from the New Horizons flyby of the Jovian system (Grundy et al. 2007). While no water ice was found on the innermost of the Galilean satellites – Io – sulfur dioxide ice was identified by (Fanale et al. 1979; Hapke 1979; Smythe et al. 1979) on the surface of this moon, the most volcanically active object in the solar system. The vigorous heating that powers Io’s volcanoes is the periodic solid-body tidal flexing arising from this moon’s orbital eccentricity. An important aspect of Jupiter’s satellites is the energetic radiation environment they suffer, far

![Figure 10. CRISM spectrum of the Mars Phoenix landing site (solid line) from orbit and model results (dotted lines) obtained at Ls~19.3°. Water ice dominates the spectrum with smaller amounts of CO2 ice. The horizontal axis is the wavelength in microns. From Cull et al. (2010).](image-url)
Figure 11. Reflectance spectra of the Galilean Satellites. Geometric albedo spectra derived from ground-based and spaceborne instruments are shown top to bottom as a function of distance from Jupiter. Volcanic Io exhibits a rich infrared spectrum of SO$_2$ with possible but unidentified polysulfur oxide (PSO) absorption present. The blue edge of sulfur is evident along with a feature at 5 μm due to the S$_4$ molecule. SO$_2$ and possibly S$_4$ absorptions are found in the ultraviolet region. Europa has a leading (L)-trailing (T) side dichotomy so we distinguish these cases. SO$_2$, polymeric sulfur, and likely S$_4$ are present on the trailing hemisphere along with a hydrate shown at infrared wavelengths by distorted water bands. Nearly pure H$_2$O is present on Europa’s leading side and there is less blue and ultraviolet absorption on that face compared to the sulfurous trailing side. Hydrogen peroxide and carbon dioxide are also apparent in Europa’s infrared spectrum. Ganymede has less exposed ice and the geometric albedo is lower due to broad non-ice absorption. Callisto is almost completely covered with dark non-ice compounds and both Callisto and Ganymede show spectral features possibly due to a hydroxysulfide or carbonic acid, possibly SO$_2$, and potentially a CN compound. Trapped O$_2$ is present on all three of the icy satellites. The Galileo ultraviolet spectrometer data shown for Callisto and Ganymede were kindly provided by A. Hendrix and here normalized to the geometric albedos derived by Nelson and Hapke. Data from Clark and McCord (1980), Nelson et al. (1987), Noll et al. (1995), Spencer et al. (1995), Hendrix et al. (1999), Jessup et al. (2002), Geissler et al. (2004), and Hendrix and Johnson (2008).
more powerful than elsewhere in the solar system. Consequently, the surfaces of these bodies, and particularly that of Io and Europa, will experience modification by radiation chemistry (see review by Johnson et al. 2004).

Gravity data show that Io is a differentiated silicate body with an Fe or Fe + FeS core, whereas the outer three Galilean moons contain significant water ice, with increasing H$_2$O content as one moves outward from Jupiter. Europa is differentiated and may have an internal structure similar to Io’s but with an overlying 100-200 km H$_2$O mantle that comprises 10% of the satellite’s mass. This H$_2$O cover is thought to consist of a 2-20 km icy crust covering an ocean of up to 100 km thickness. As in the case of Io, tidal flexing provides the heat to sustain a liquid ocean which is likely in contact with the rocky mantle. Ganymede, the largest satellite in the solar system and larger than Mercury, has more water than Europa, contributing to approximately half of the satellite’s mass. An outer icy crust and mantle, about 200 km thick, is thought to cover an ocean that is sandwiched between layers of high-pressure ice in different phases. Beneath the H$_2$O mantle is a differentiated rocky body with a Fe-containing liquid core acting as a magnetic dynamo. Callisto is less differentiated than its sibling satellites, but has about the same relative water content and likely an ocean also, based on Galileo magnetic field data. However, due to their distance from Jupiter, tidal heating is much less efficient for these outer two satellites compared to Io and Europa.

In the following paragraphs we discuss the ice (SO$_2$ and H$_2$O) and non-ice surface compositions of Jupiter’s Galilean satellites. General reviews can be found in recent publications (Bagenal et al. 2004; Lopes and Spencer 2007; Pappalardo et al. 2009; Dalton et al. 2010; Clark et al. 2013). Io and Europa’s surface compositions are reviewed in Carlson et al. (2007) and Carlson et al. (2009), respectively.

**Io.** Io is the innermost of the four Galilean satellites and exhibits a young, volcanically active surface that is rapidly resurfaced at an average rate of about one cm per year. The surface is nearly completely covered by sulfur dioxide ice and elemental sulfur, the exceptions being in the hot volcanic areas and fresh lava flows where silicates may be exposed. Gaseous SO$_2$ is a volcanic effluent, derived from the degassing of hot magma, and is the dominant volcanic gas component, accompanied by minor amounts of SO and S$_2$ (Zolotov and Fegley 1998, 1999, 2000; Spencer et al. 2000) and other species such as NaCl (Lellouch et al. 2003), identified and mapped through ground-based microwave spectroscopy. SO$_2$ contributes nearly all of the absorption features in Io’s spectra (Fanale et al. 1979; Hapke 1979; Smythe et al. 1979; Schmitt et al. 1994; Nash and Betts 1995; Carlson et al. 1997). The global abundance and grain sizes of the SO$_2$ particles indicate that optically thick SO$_2$ deposits of mm-size grains are concentrated in Io’s equatorial regions (Carlson et al. 1997; Laver and de Pater 2008; 2009) and confirm earlier measurements of (McEwen 1988), who studied Io’s surface using ultraviolet and visible Voyager images. These equatorial deposits are strongly associated with active volcanoes and arise from volcanic venting of gaseous SO$_2$ into the plumes and atmosphere with subsequent deposition onto colder surfaces as frost. The relatively large grain sizes indicate sublimation and condensation metamorphism for these deposits.

In contrast, fine grained SO$_2$ frost was found at mid- and high-latitudes (Carlson et al. 1997; Doute et al. 2001; Laver and de Pater 2008, 2009). SO$_2$ frost sublimes during the day due to relatively high surface temperatures. Although most of it re-condenses locally during the nighttime, SO$_2$ molecules slowly migrate toward higher latitudes and colder regions (Matson and Nash 1983). The high-latitude SO$_2$ deposits appear transparent under normal-incidence illumination and therefore are thought to be optically thin (Geissler et al. 2001). They tend to remain as small grains as originally condensed because of the colder environment and rapid radiolytic destruction of the SO$_2$ grains at higher latitudes (Wong and Johnson 1996). The poles of Io appear red due to the radiolytic destruction of SO$_2$ and the production of elemental sulfur. The possible condensation of SO$_2$ during the ~2.5 hour eclipses of Io by Jupiter during each
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orbit has long been a subject of interest; see the recent review and time-resolved infrared spectra of Io at eclipse reappearance (Cruikshank et al. 2010a).

Sulfur dioxide is a thermochemical product of hot magmas and its presence is indicative of volcanic conditions. The ratios of SO and S\textsubscript{2} to SO\textsubscript{2} in the volcanic plumes are consistent with high-temperature volcanism in a silicate mantle that is deficient in Fe-metal (Zolotov and Fegley 2000). Being a high-temperature chemical product, SO\textsubscript{2} probably represents a very minor contribution to the satellites total mass. However, since it is a very volatile, it is likely that most of Io’s SO\textsubscript{2} is at or near the surface. The solid and gaseous forms of SO\textsubscript{2} are evident in the surficial ices and the overlying sublimational and plume-derived atmosphere, but there is evidence that liquid SO\textsubscript{2} forms a near-surface “aquifer.” Scarp and sapping channels provide one line of evidence (McCauley et al. 1979; McEwen et al. 2000; Moore et al. 2001) and uniform topographic infilling of a crater by SO\textsubscript{2} (Lopes et al. 2001) provides further evidence for SO\textsubscript{2} “ground water” (Fig. 12). It has been estimated that the upper 1 km of Io is rich in the volatiles SO\textsubscript{2} and sulfur (McEwen et al. 2000).

Io is intensely irradiated by Jupiter’s magnetosphere, forming sulfur trioxide. The signature of SO\textsubscript{3}, as well as S\textsubscript{8} and SO\textsubscript{2}, may be present in thermal emission spectra of Io (Khanna et al. 1995; Hanel et al. 2003). A related species, disulfur monoxide (S\textsubscript{2}O), was investigated by (Baklouti et al. 2008) but interference by strong SO\textsubscript{2} bands precluded its observation. Polysulfur oxides (PSO) may be present on Io and produce a broad absorption in the 4.5-\textmu m region (Baklouti et al. 2008). Ion irradiation can also sputter surface atoms and molecules into an atmosphere around Io and into escape orbits. Neutral and ionized toroidal clouds are formed around Jupiter and provide a source of sulfur, oxygen, sodium, potassium, chlorine, and other possible species to other satellites. This is particularly important for Europa, where the tori strike the trailing hemisphere and provide a source of sulfur and other elements.

Sulfur on Io is emplaced on the surface by volcanic plumes, primarily as S\textsubscript{2}, while sulfur volcanism may occur on Io and produce sulfur lava flows. Elemental sulfur can exist in a variety of forms (linear chains, cyclic) and with innumerable lengths. The most stable form is cyclo-octal and some of Io’s sulfur is likely in this form, the remaining being polymeric with some tetrasulfur S\textsubscript{4} (Fig. 11, top panel).

Figure 12. The interior of a volcanic caldera near Chaac (indicated by arrow) on the Galilean moon Io is filled with spectroscopically identified very pure SO\textsubscript{2} that appears white and to be topographically controlled inflows of liquid SO\textsubscript{2}.
The high temperatures of Io’s volcanoes, up to 1700 K, indicate silicate volcanism but the rapid resurfacing by plume and sublimated SO$_2$ has precluded definitive identifications of silicates on the surface. Geissler et al. (1999) found a region on Io with an absorption at 0.9 µm and suggested that it was caused by a ferrous iron feature present in Fe-containing magnesian orthopyroxenes. This is a plausible suggestion as such minerals are associated with the most primitive terrestrial rocks and possess a high melting temperature.

**Europa.** Europa orbits Jupiter at about 1.6 times the distance from Jupiter as Io and is the innermost of the water-ice-containing Galilean satellites. Although it contains less bulk H$_2$O than Ganymede or Callisto, the surface exhibits much more exposed water ice and hydrate than the other H$_2$O-icy Galileans due to its greater surface activity, a consequence of tidal heating (the crater age is a mere 50 My as reported by Zahnle et al. 2003). The leading hemisphere of Europa, in the sense of orbital motion, presents the purest ice as determined by infrared spectroscopy which probes the upper sub-millimeter depths of the surficial materials. Both amorphous and crystalline ice are present, with a greater proportion being the amorphous form (Hansen and McCord 2004). The presence of amorphous and crystalline phases are the result of two competing processes—the increase in disorder and amorphization of ice crystals by energetic particle bombardment, and thermally-induced phase transformation of amorphous ice to the lower energy cubic ice form or the even lower energy hexagonal ice phase.

The second major constituent on Europa is a hydrated species, predominant on the trailing side and associated with the dark material that produces Europa’s hemispherical color dichotomy—the red, trailing hemisphere and the white, leading hemisphere. This icy hydrate is a complex of some molecule X (or groups of molecules) surrounded by hydration shells of water, often in stoichiometric proportions, as X$_n$·mH$_2$O. One suggested source of this hydrate is a salty subsurface ocean, the X being a salt such as MgSO$_4$, forming hydrates such as epsomite MgSO$_4$·7H$_2$O and others (McCord et al. 1998b, 1999). A second hypothesis is that radiolysis of exogenic (Iogenic) sulfur implanted on Europa’s trailing hemisphere produces hydrated sulfuric acid (Carlson et al. 1999b, 2002, 2005). The associated dark material is thought to be polymeric sulfur (Carlson et al. 1999b) since most salts and acids are colorless in the visible spectral region. The association of hydrate and dark material with geological features on the trailing side implies an endogenic process, either emplacement of material from the subsurface ocean or thermal modification of exogenically-derived material, forming lag deposits. Many hydrated salts exhibit spectral features in the infrared (Dalton et al. 2005; Clark et al. 2007). A linear (areal) mixing model has recently been applied and used to infer composition and variations across Europa’s surface (Shirley et al. 2010; Dalton et al. 2012, 2013; Cassidy et al. 2013). The model used many hydrated materials in the fitting, each with a constant grain size, and with areal rather than intimate mixing. Since spectral characteristics are strongly grain-size dependent, the uniqueness of the solutions and identifications must be viewed with caution. Suggestive evidence for the presence of epsomite (MgSO$_4$·7H$_2$O), based on a characteristic 2.07-µm feature, has been found recently by (Brown and Hand 2013). They suggest emplacement of Mg$^{2+}$ and other cations from Europa’s ocean as chlorides and subsequent radiolysis (see below) with H$_2$O ice and exogenic sulfur to produce sulfate salts. However, models with significant salt, like those proposed above, are incompatible with Europa’s 3-µm to 5-µm spectrum, which is very dark compared to salts (e.g., see salt spectra in Clark et al. 2007). Future models and interpretations need to include intimate mixtures and the full spectral range of data available for Europa.

The magnetospheric environment at the orbit of Europa is almost as damaging as at Io, and several radiolytic species are observed. As mentioned above, native sulfur exists on the surface and is radiolyzed to the polymeric form and as the red chromophore tetrasulfur (Carlson et al 2009; Hand and Brown 2013). Molecular oxygen is found on Europa (Spencer and Calvin 2002), and is radiolytically formed and trapped in H$_2$O ice, as is hydrogen peroxide H$_2$O$_2$. 
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Carlson et al. (1999a). SO$_2$ is observed and is a radiolytic product of sulfate decomposition (Johnson et al. 2004; Carlson et al. 2009; Hendrix et al. 2011). CO$_2$ is also found (Smythe et al. 1998; Hand et al. 2007; Hansen and McCord 2008) and this ubiquitous molecule could be from endogenic or exogenic sources (see discussions below). These minor species may exist in Europa’s near surface as mixed clathrate hydrates (Hand et al. 2006).

**Ganymede.** Ganymede is also a differentiated body, but is unique because it has an intrinsic magnetic field arising from dynamo motions within a molten iron core. Ganymede and Callisto contain more ice than Europa, but both exhibit darker, less icy surfaces than does Europa. The major source of this dark material is probably the direct infall of meteoritic material and from impact debris ejected from Jupiter’s more plentiful but smaller outer satellites. This process should also occur on Europa, but Europa’s vigorous current or recent surface activity has diluted and buried the meteoritic material within the ice shell.

Ganymede’s surface has roughly equal proportions of amorphous and crystalline ice (Hansen and McCord 2004); the small proportion of amorphous ice compared to Europa is presumably due to the lower incident flux of high-energy magnetospheric radiation and shielding by Ganymede’s magnetic field. Bright, icy polar caps are observed on this satellite and the boundary between the icy polar regions and the less icy lower latitudes closely coincides with the transition from open to closed magnetic field lines. This suggests surface brightening by energetic magnetospheric particles streaming in on open field lines and striking Ganymede’s polar surfaces. This brightening may be produced by ice grain disruption (Johnson 1997), creating smaller grains and more scattering sites, which decreases the absorption and increases the albedo, or by sputtering and thermal segregation (Khurana et al. 2007).

A hydrate, possibly similar to Europa’s, has been identified on Ganymede and suggested to have been formed from Mg$_2$SO$_4$-rich brine emplaced from the ocean below (McCord et al. 2001). Ganymede once had an active surface but any such emplacement must have occurred in the distant past since the surface age is ~ 2Gy (Zahnle et al. 2003). With subsequent meteoritic infall and gardening, it is unclear how these salt minerals could be present in the high concentrations that were observed. The geological process that erupts material from a 200-km deep ocean is also unclear. A second class of hydrate, associated with dark crater rays, has been identified by Hibbits and Hansen (2007) and found to be similar to C-type asteroid or Callisto non-ice materials. This hydrate may be material from, or modified by, the impactor.

Three water-related radiolytic species are found on Ganymede: molecular oxygen (Spencer et al. 1995; Calvin et al. 1996), ozone (Noll et al. 1996; Hendrix et al. 1999a), and possibly hydrogen peroxide (Hendrix et al. 1999b). Transient, localized SO$_2$ concentrations have been suggested (Domingue et al. 1998) and spectral information indicates the presence of other species. Since these features are similar to those found in spectra of Callisto, they are described in the following section.

**Callisto.** Callisto, the outermost icy Galilean satellite, has a bulk composition that is about half H$_2$O and half rocky silicates. In contrast to the inner three Galilean satellites, Callisto is only partly differentiated, with denser rocky components that slowly settled, or are currently settling, to the center (Schubert et al. 2004). The lack of tidal heating and the low rate of gravitational settling may not provide sufficient energy to cause geological activity on the surface. Callisto has a very old surface, mostly covered with a layer of dark material, presumably from meteoritic infall and outer satellite-derived ejecta material. Both impact cratering and mass wasting have exposed the icy “bedrock” over approximately 10% of this ancient surface, showing the presence of water ice that is predominantly crystalline with grain sizes (diameters) of ~ 200-400 µm (Hansen and McCord 2004). Water molecules tend to segregate by sublimation and condensation on cold, bright ice surfaces, but the dark material also has an H$_2$O component, probably including adsorbed H$_2$O. Because the temperatures attained by the dark material are
high (~ 150-160 K), some of these water molecules sublime during the day and re-condense at night, so thermal segregation is not complete. The radiolysis product $\text{O}_2$ has been observed on Callisto (Spencer and Calvin 2002) and $\text{H}_2\text{O}_2$ has been suggested (Hendrix et al. 1999b).

$\text{NH}_3$ has not been observed on the surface, but $\text{CO}_2$ is found on the surfaces of Callisto and Ganymede (Carlson et al. 1996; McCord et al. 1997; McCord et al. 1998a; Hibbitts et al. 2000, 2002, 2003) as well as on Europa as noted above. A tenuous $\text{CO}_2$ atmosphere has also been found on Callisto, indicating loss from the surface. The surficial $\text{CO}_2$ is not an ice, based on the spectral position of the absorption feature, and $\text{CO}_2$ ice is too volatile to be stable at Galilean satellite temperatures; instead the molecules appear to be trapped in the dark material. The source of $\text{CO}_2$ could be degassing from the interior (Moore et al. 1999) or an exogenic source or production mechanism. $\text{SO}_2$ has been suggested as a surface component based on ultraviolet (Lane and Domingue 1997; Noll et al. 1997) and infrared spectra (McCord et al. 1997, 1998a; Hibbitts et al. 2000). $\text{SO}_2$ is also quite volatile, and cannot exist as a direct condensate but could be trapped similar to $\text{CO}_2$. Hendrix and Johnson (2008) have questioned the ultraviolet $\text{SO}_2$ identification and interpreted Galileo ultraviolet spectra as absorption by carbonized organics. The radiolysis of organics in ice by energetic electrons as would occur in the Jovian magnetosphere does produce trapped $\text{CO}_2$ (Hand and Carlson 2012). Infrared evidence for the presence of aliphatic hydrocarbons has been suggested by (McCord et al. 1997, 1998a). Two other spectral features have been identified on both Callisto and Ganymede, one at 3.88 $\mu$m and thought to be due to a hydrosulfide compound (-SH) (McCord et al. 1997, 1998a) or the $\text{CO}_2$-related compound, carbonic acid ($\text{H}_2\text{CO}_3$) (Hage et al. 1998). Another common feature for these two satellites occurs at 4.57 $\mu$m and is possibly due to a –CN-containing tholin (McCord et al. 1997, 1998a).

**Saturn system**

It has long been known that the surfaces of Saturn’s rings and major satellites, Mimas, Enceladus, Tethys, Dione, Rhea, Hyperion, Iapetus, and Phoebe are predominantly icy objects (e.g., Fink et al. 1975; Clark et al. 1984, 1986, 2005, 2008a; Roush et al. 1995; Cruikshank et al. 1998a, 2005; Grundy et al. 1999; Owen et al. 2001; Filacchione et al. 2007, 2008; Cuzzi et al. 2009). Whereas the reflectance spectra of these objects (Figs. 13-16) in the visible range indicate that a coloring agent is present on all surfaces, only Phoebe and the dark hemisphere of Iapetus display spectra markedly different from very pure water ice (e.g., Cruikshank et al. 2005; Clark et al. 2005, 2012; Jaumann et al. 2009 and references therein). The relative purity of the ice in Saturn’s satellites and rings may be the result of a singular catastrophic event (e.g., Canup 2010; Asphaug and Reufer 2013).

Dark material was first inferred in the Saturn system by J. D. Cassini (1672), and verified by Murphy et al. (1972) and Zellner (1972). The nature of the dark material has been studied by numerous authors, sometimes with conflicting conclusions, including Cruikshank et al. (1983), Vilas et al. (1996), Jarvis et al. (2000), Owen et al. (2001), Buratti et al. (2002), and Villas et al. (2004). The new Cassini VIMS data provide a greater spectral range (0.35 to 5.1 $\mu$m in 352 wavelength channels) in reflected solar radiation, with higher precision, and show new absorption features not previously seen in these bodies (e.g., Buratti et al. 2005; Clark et al. 2005, 2008a, 2012; Cruikshank et al. 2007, 2008). These new VIMS observations also spatially resolve the satellite surfaces enabling maps of compounds to be made, leading to additional insights into the nature of the icy satellite surfaces. The spatial resolution of derived maps of materials from VIMS data is variable depending on fly-by distances, and ranges from tens of kilometers per pixel to sub kilometers per pixel.

The Cassini spacecraft entered the Saturn system in 2004, and the Visual and Infrared Mapping Spectrometer (VIMS) began obtaining spatially resolved spectra of Saturn’s satellites and rings (Brown et al. 2005a; Figs. 13-16). The VIMS has provided a wealth of spatially
resolved compositional data on the satellites (e.g., Phoebe: Clark et al. 2005; Iapetus: Buratti et al. 2005, Cruikshank et al. 2007, 2008; Enceladus: Brown et al. 2006; Jaumann et al. 2006; Dione: Clark et al. 2008a; Jaumann et al. 2009; Clark et al. 2012) and rings (e.g., Nicholson et al. 2008; Cuzzi et al. 2009). The satellites and rings are dominated by crystalline H$_2$O ice with trace amounts of CO$_2$ (Fig. 15) and dark material (e.g., Fig. 14 and Fig. 16 spectra B and C) although it is not clear if the CO$_2$ is an ice, trapped, or both (Cruikshank et al. 2010b). Trace

Figure 13. Cassini VIMS reflectance spectra of Saturn’s rings corrected for fill factor. The spectra are dominated by absorptions from water ice and an UV absorber. Adapted from data in Cuzzi et al. (2009).

Figure 14. Spectra of bright and dark regions on Saturn’s satellite Dione. Inset shows weak CO$_2$ observed in areas with dark material. From Clark et al. (2008a).
organics and ammonia absorptions are seen in some satellites but again, it is not clear if the absorptions are due to ices or trapped molecules. Unusual colors and spectral shapes of the satellites and rings in the UV to visible are currently explained by a combination of Rayleigh scattering by small particles (ice grains as well as contaminants) and an UV absorber by one of

Figure 15. CO$_2$ on icy objects in the Saturn system detected by the absorption near 4.25 $\mu$m. No CO$_2$ has been detected in spectra of the rings. CO$_2$ absorption appears strongest on satellites with dark material. From Clark et al. (2008a).

Figure 16. Spectra of Iapetus, showing a sequence from regions of dark material (black spectrum) to higher concentrations of water ice (blue). From Clark et al. (2012).
the contaminants (Clark et al. 2008a,b, 2012; see reviews by Jaumann et al. 2009; Cuzzi et al. 2009; Hendrix et al. 2012).

The surface composition of Titan is still enshrouded in a cloud of mystery despite the initial flood of data from the Cassini spacecraft and the Huygens probe. Although the composition of Titan’s atmosphere is known (Coustenis et al. 1999, 2003, 2005, 2006a,b, 2007; Flasar et al. 2005; Teanby et al. 2009 and references therein), with most of the observed gases having been predicted using models of UV photolysis and reactions of atmospheric methane and nitrogen (Yung and DeMore 1999; Vuitton et al. 2008 and references therein), the many less volatile molecules that coat and/or make up the solid surface have yet to be identified. Tholins are the solid end products of photolysis and electron discharge experiments done in terrestrial laboratories with gases common in Titan’s atmosphere and are one type of mixture of compounds theorized to exist on Titan (e.g., Sagan et al. 1992; Imanaka et al. 2004; Quirico et al. 2008). Table 1b in Clark et al. (2010a) lists known solid compounds on Titan through 2009, and include benzene (firm), with many tentative or inferred compounds including ices of cyanoacetylene (HC$_3$N), toluene (C$_7$H$_8$), cyanogen (C$_2$N$_2$), acetonitrile (CH$_3$CN), H$_2$O, CO$_2$, and NH$_3$.

The Cassini RADAR has provided the highest spatial resolution images of Titan’s surface from Saturn orbit but is a mono-frequency system that provides compositional information only through the dielectric constant of the surface at its operating wavelength of 2.16 cm (Elachi et al. 2005). Only the Descent Imager-Spectral Radiometer, DISR, on the Huygens probe and VIMS from the Cassini Saturn orbiter have the capability to provide combined spectral plus spatial information about the surface (Tomasko et al. 2005; Schroeder and Keller 2008; Sotin et al. 2005; Barnes et al. 2005, 2007, 2008; McCord et al. 2006, 2008; Rodriguez et al. 2006; Brown et al. 2008; Nelson et al. 2009; Soderblom et al. 2009; Clark et al. 2010a). The DISR was limited in wavelength range out to 1.7 $\mu$m but obtained very high spatial resolution over a limited area during the descent of the Huygens probe; VIMS measures wavelengths out to 5.1 $\mu$m (Fig. 17) and can cover large parts of the surface of Titan, but at much more limited spatial resolution (a few km /pixel are common and a few small areas have been spectrally imaged.

![Figure 17. Reflectance spectra of Titan’s bright (red line) and dark (blue line) regions. The gray areas in the plot are regions of strong absorption from atmospheric methane through which the surface is not detected. From Clark et al. (2010a).](image)
at sub 300 meters). Terrestrially synthesized tholins do not match the spectral slope in data from the Huygens DISR (Tomasko et al. 2005; Schroeder and Keller 2008) or Cassini VIMS (McCord et al. 2006). The DISR spectra of Titan’s surface show a blue spectral slope from 1 to 1.6 μm that is distinctly “un-tholin” like and show what qualitatively appears to be a water-ice absorption, but the complete H₂O feature was not covered by the spectrometer (Tomasko et al. 2005; Schroeder and Keller 2008). Schroeder and Keller concluded the absorption did not match water ice. Also, the 1.25-μm H₂O absorption was not observed even though expected in the models presented by Tomasko et al. (2005) and Schroeder and Keller (2008). In situ analyses have detected methane, ethane, and tentatively identified cyanogen, benzene, and carbon dioxide on the surface from the Huygens GCMS (Niemann et al. 2005). Ammonia and hydrogen cyanide were the main pyrolysis products of the aerosols measured by the Huygens in situ pyrolysis experiment during its descent (Israel et al. 2005) and those aerosols could rain down to the surface, but pyrolysis products are not necessarily compounds in the aerosols. Higher in Titan’s thermosphere, benzene was first detected in the stratosphere by ISO and CIRS (Coustenis et al. 2003, 2007), and the Cassini Ion and Neutral Mass Spectrometer (INMS) instrument has detected high abundances of benzene along with toluene above 900 km (Waite et al. 2007). Toluene is an interesting molecule after benzene because toluene consists of a benzene ring with a methyl functional group, -CH₃, replacing one of the hydrogen atoms attached to the benzene ring. Toluene is a possible larger organic molecule that may be compatible with VIMS surface spectra of Titan.

Clark et al. (2010a) presented evidence for surface deposits of solid benzene, (C₆H₆) (Fig. 18), solid and/or liquid ethane, (C₂H₆), or methane (CH₄), and clouds of hydrogen cyanide (HCN) aerosols using diagnostic spectral features in data from the Cassini VIMS. Cyanoacetylene (2-propynenitrile, HC₃N) is indicated in spectra of some bright regions, but the spectral resolution of VIMS is insufficient to make a unique identification although it is a closer match to the feature previously attributed to CO₂. Acetylene (C₂H₂), expected to be more abundant than benzene on Titan according to some models, was not detected. Water ice, if present, must be covered with organic compounds to the depth probed by 1-μm to 5-μm wavelength photons: a few millimeters to centimeters. While many organic compounds have now been detected in the atmosphere and on Titan’s surface, we still have only a small spectral database of solid organic compounds measured at Titan temperatures (about 92 K) to compare with spectra of Titan. Spectra of additional compounds are needed, along with higher spatial and

![Figure 18](image_url). Spectra of Titan showing an absorption attributed to benzene ice. From Clark et al. (2010a).
Spectroscopy from Space

Saturn’s moon Titan has a close analogy to Earth’s hydrologic cycle where instead of liquid water, methane and ethane exist as liquids at the surface. Similar to liquid water lakes and rivers on the Earth, Titan has liquid methane and ethane lakes and rivers in a currently active methanologic cycle. These two bodies are unique in the Solar System in that regard.

Uranus system

The Uranus system was investigated by the Voyager II spacecraft in 1986, but that probe had no near-infrared spectral-imaging capability. Accordingly, compositional studies of the Uranian satellites and rings have relied on ground-based telescopic observations, progressing in parallel with advances in infrared instrumentation technology. Prior to the Voyager encounter, low spectral resolution (bandwidths ~2% of the wavelength) circular-variable filter (CVF) spectrophotometry led to detection of broad water ice absorptions at 1.5 and 2 μm on the five major satellites of Uranus: Miranda, Ariel, Umbriel, Titania, and Oberon (Cruikshank 1980; Cruikshank and Brown 1981; Soifer et al. 1981; Brown 1983; Brown and Clark 1984; Brown et al. 1991). Spectrometers based on infrared detector arrays enabled higher quality near-infrared spectra to be obtained (Fig. 19), with spectral bandwidths of around 0.1%, revealing the 1.65-μm water ice band on all five satellites, indicative of cold crystalline H₂O ice (Grundy et al. 1999; Bauer et al. 2002). An apparent dip in Miranda’s spectrum near 2.2 μm has been tentatively attributed to ammonia ice (Bauer et al. 2002) but this identification has not yet been confirmed. Repeated observations of the other four satellites have shown no comparable 2.2-μm features, but did reveal the presence of a narrow triplet of CO₂ ice absorptions near 2 μm on Ariel, Umbriel, and Titania, but not Oberon (Grundy et al. 2003, 2006). Interestingly, the strengths of these CO₂ ice absorptions were found to be spatially variable, being strongest on the trailing hemispheres of the satellites, and also on the satellites closer to Uranus (whether or not Miranda fits this pattern remains to be tested). This spatial pattern is consistent with in situ production.

Figure 19. Reflectance spectra of the Uranian satellites showing strong water absorptions and narrow CO₂ absorptions. Note the asymmetric (toward longer wavelengths) 2-μm ice absorption of Oberon indicating the presence of sub-micron ice grains.
of CO$_2$ from local H$_2$O plus carbonaceous materials driven by Uranian magnetosphere charged particle radiolysis, balanced by relatively rapid sublimation loss (Grundy et al. 2006). Water ice absorptions were seen to exhibit the opposite pattern, being deepest on the leading hemispheres of Ariel, Umbriel, and Titania (although perhaps not Oberon; Grundy et al. 2006). This pattern of deeper water ice absorptions on leading hemispheres is also seen in the Jovian and Saturnian satellite systems, but the cause remains uncertain. Possibilities include preferential gardening of icy regoliths by impactors impinging on leading hemispheres (Zahnle et al. 2003), and preferential sputtering removal of H$_2$O ice via magnetospheric charged particle bombardment on trailing hemispheres (e.g., Cheng et al. 1986; Eviatar and Richardson 1986; Pospieszalska and Johnson 1989; Johnson 1990). No ices have been identified to date in spectra of the Uranian rings (e.g., Soifer et al. 1981; Pang and Nicholson 1984; Baines et al. 1998). The low albedos of Uranian satellites and ring particles implies the presence of a darkening agent, which has long been presumed to be carbonaceous in nature, although its precise composition remains unknown.

The Neptune system and beyond

The Neptune system was explored by Voyager 2 in 1989, providing a wealth of physical details. But, as with the Uranus system, almost all compositional information about ices in the Neptune system came from Earth-based observations. Neptune’s largest satellite, Triton, provides particularly interesting and complex examples of outer solar system ice geology. Early Triton results came from a series of near-infrared CVF spectrometer observations (~2% spectral resolution) during the 1970s and 1980s, leading to the discovery of methane, nitrogen, and water ice absorptions (Cruikshank and Silvaggio 1979; Apt et al. 1983; Cruikshank and Apt 1984; Cruikshank et al. 1984, 1988, 1989; Rieke et al. 1985).

The advent of array spectrometers with cryogenic optics resulted in much higher quality spectra (Fig. 20), leading to the discovery of CO, CO$_2$, and C$_2$H$_6$ ices (Cruikshank et al. 1993; Bohn et al. 1994; DeMeo et al. 2010). The higher spectral resolution and signal precision enabled by these instruments revealed subtle wavelength shifts in the methane bands consistent

![Figure 20](image-url) **Figure 20.** Near infrared spectra of Triton and Pluto are compared in this figure. Features arising from CH$_4$, CO, CO$_2$, H$_2$O, and N$_2$ are identified.
with the CH$_4$ molecules being dispersed in nitrogen ice (Cruikshank et al. 1993; Quirico et al. 1999), a situation anticipated from thermodynamic arguments (Lunine and Stephenson 1985). They also revealed the phase of Triton’s water ice to be predominantly crystalline (Cruikshank et al. 2000; Grundy and Young 2004).

A picture of Triton emerged of a solar-powered, active world in which volatile N$_2$, CO, and CH$_4$ ices sublimate and condense in response to seasonal insolation on a substrate of H$_2$O and CO$_2$ ices (which are non-volatile at Triton surface temperatures), leading to an array of bizarre landforms and even jetting of sublimated nitrogen gas out of fissures, with possible aeolian transport of non-volatile H$_2$O and CO$_2$ ice dust (e.g., Brown et al. 1990; Hansen and Paige 1992; Stansberry et al. 1996; Grundy et al. 2002). Evidence for short-term changes in the visible wavelength parts of Triton’s spectrum reinforced the perception of an active Triton (Hicks and Buratti 2004), as did the paucity of impact craters in Voyager images (Schenk and Zahnle 2007).

To explain the large optical path-lengths required by the observed 2.15-μm N$_2$ absorption band, Triton’s N$_2$ ice could have an unusually compacted texture, perhaps more like a sintered slab than the usual particulate soils encountered on planetary surfaces (e.g., Eluszkiewicz 1991; Grundy and Stansberry 2000). Based on seasonal models, latitudinal heterogeneity in the spatial distribution of Triton’s ices is expected, but time-resolved spectroscopy reveals a longitudinal heterogeneity as well (Grundy et al. 2010). The N$_2$ and CO ices seem to co-occur, and to be much more abundant on Triton’s Neptune-facing hemisphere. Despite being mostly dissolved in N$_2$ ice, Triton’s CH$_4$ shows a very different longitudinal pattern, with its strongest absorption seen on Triton’s trailing hemisphere. The H$_2$O and CO$_2$ ice absorptions show little or no longitudinal variation, as if they are globally distributed, perhaps as wind-blown dust.

To date, H$_2$O ice has only been detected on one other body in the Neptune system, the satellite Nereid (Brown et al. 1998, 1999). Little is known beyond photometric colors regarding compositions of Neptune’s other satellites and rings (e.g., Dumas et al. 2002).

Objects at Neptune’s heliocentric distance and beyond (the transneptunian region, also known as the Kuiper Belt) have surface temperatures sufficiently low (<~50 K) for multiple ices to condense on their surfaces. The equilibrium temperature, $T_{eq}$, of a solid body is a function of both the heliocentric distance ($a$) of the objects and their albedos, ($q$), following the relation $T_{eq} = 280 \text{K} \left(\frac{1-q}{a^2}\right)^{1/4}$. For an object at 30 Astronomical Units (AU) with an albedo of 0.04 this gives $T_{eq} = 50.6 \text{K}$. Larger heliocentric distances, $a$, and/or higher geometric albedos, $q$, lead to even lower temperatures. For objects near condensation thresholds, there is a positive feedback favoring the stability of icy surfaces once the threshold for formation is met. The stability of ices is also a function of surface gravity and the ability of a body to limit atmospheric escape. Schaller and Brown (2007) have calculated the expected stability for CH$_4$, N$_2$ and CO ices in outer solar system bodies and find that objects with diameters below 1000-1500 km are not expected to have retained significant amounts of these ices on their surfaces. The handful of larger objects in the Kuiper Belt can retain these materials, and apparently have.

Methane ice was first detected as a solid in the solar system in an infrared spectrum of Pluto (Cruikshank et al. 1976). More recently, solid CH$_4$ has been identified in the large Kuiper Belt Objects (KBO) Eris (Brown et al. 2005b), Sedna (Barucci et al. 2005), and Makemake (Licandro et al. 2006), as reviewed by de Bergh et al. (2013). The signal-to-noise ratio and wavelength coverage of spectra of small outer solar system objects have steadily improved.

For Pluto in particular, high signal-to-noise ratio spectra show that it shares many spectral features with Triton (Fig. 20) including multiple discrete features of CH$_4$, although the two clusters of features due to CO$_2$ ice in Triton’s spectrum are absent from Pluto’s spectrum. The quality and detail of the spectra allow for detailed analyses comparing band strengths and positions to constrain the detailed physical state of the ices on the surface. As with Triton, the beta N$_2$ 2-0 absorption is interpreted as arising from optical path lengths in beta N$_2$ ice of the order
of many centimeters, implying unusually coarse particle sizes or perhaps a sintered glaze of N₂ ice, as noted above (e.g., Eluszkiewicz 1991; Grundy and Stansberry 2000). The existence of the ~2.16-μm side band in spectra of both Pluto and Triton has been used to place upper limits on the temperature of N₂ ice on those bodies (Grundy et al. 1993; Tryka et al. 1993, 1994).

Even without directly detecting its absorption bands, it may be possible to infer the presence of N₂ ice from its effect on absorptions from other species. For instance, when CH₄ is dispersed in N₂ ice, the much stronger CH₄ bands are shifted to slightly shorter wavelengths (Quirico and Schmitt 1997a), an effect which has been reported in spectra of Eris and Makemake, in addition to Pluto and Triton. Unfortunately, details of how the distinct CH₄ bands shift depend on the relative concentrations of N₂ and CH₄ are not yet fully understood (e.g., Brunetto et al. 2008; Cornelison et al. 2008), and the uniqueness of N₂ in its ability to shift CH₄ absorption bands has yet to be established. For instance, Tegler et al. (2010) report that dilution of CH₄ in argon ice produces similar shifts.

Pluto shows evidence for time-varying albedo features on its surface (Buie et al. 2010). Seasonal effects are expected to result in redistribution of surface ices over time. Grundy et al. (2013) have recently shown what appears to be seasonal evolution of features on Pluto over a decade of observation. Differing longitudinal variations of CH₄ and N₂ ices suggest that these two ices may be physically segregated on the surface. In contrast, CO and N₂ vary together with longitude, implying they are intimately mixed. Ethane ice has also been reported in spectra of Pluto, notably using bands at 2.27, 2.405, 2.457, and 2.461 μm (DeMeo et al. 2010), where it presumably forms through radiolysis and or photolysis of CH₄ (Moore and Hudson 2003).

Water ice has been detected on numerous Kuiper belt objects and Centaurs, both small and large (e.g., Dotto et al. 2003; Barkume et al. 2008; Guilbert et al. 2009). However, it seems to be absent from some of them. For most of the smaller objects, the bands are fairly shallow, consistent with their low albedos. Systematic changes in albedo and color from the Kuiper belt through the inner solar system could be linked to the sublimation loss of H₂O ice (Grundy 2009; Lamy and Toth 2009). Reports of weak absorptions at 2.2 μm in spectra of Kuiper belt objects have been tentatively attributed to ammonia or ammoniated species (e.g., Delsanti et al. 2010) and an absorption at 2.27 μm in spectra of several objects has been interpreted as resulting from methanol ice (Cruikshank et al. 1998b; Merlin et al. 2012).

The dwarf planet Haumea along with its largest satellite Hi’iaka are noteworthy for their particularly deep water ice bands (e.g., Barkume et al. 2006; Trujillo et al. 2007; Pinilla-Alonso et al. 2009). Several members of the Haumea collisional family also have similar water-rich spectral characteristics, suggesting they could be fragments of the icy mantle of a differentiated target body (Brown et al. 2007; Leinhardt et al. 2010).

A similar catastrophic impact scenario may apply in the Pluto system (Canup 2005, 2011). Unlike Pluto, the largest satellite Charon has a water ice dominated surface (Buie et al. 1987). Additionally, Charon’s spectrum shows strong evidence for NH₃ ice (Cook et al. 2007). Charon may represent a sample of Pluto’s mantle material which was too small to retain the more volatile CH₄, N₂, and CO ices which mask Pluto’s own mantle from view. The compositions of Pluto’s small satellites remain unknown.

**SUMMARY**

Minerals and ices are ubiquitous in the solar system. From the Earth and farther from the Sun, water ice and other more volatile ices are common. As our observational technology has improved, we have found more minerals and other solid compounds in more locations. If water ice in the poles of Mercury can be confirmed, water ice would be found throughout the solar system on every planet and/or their moons with the exception of Venus.
The Earth displays the greatest mineralogic diversity in the Solar System, due to two primary factors. First and foremost, the active volcanism, plate tectonics, and weather in a relatively warm environment provide the conditions for many chemical processes, leading to diverse compositions. Second, because we live on the Earth, we can study it in far greater detail than any other moon or planet.

But as we explore other worlds, we are finding they too have diverse mineralogy. On Mars, for example, it was difficult to prove a case for any clay minerals on the surface as recently as a decade or so ago. But now with orbiting imaging spectrometers with spatial resolutions as low as about 20 m, smaller outcrops are being found to contain diverse mineralogy indicative of a more complex geologic history.

There are outstanding issues. Some small absorptions seen in spectra of outer solar system objects have yet to be identified. For example, possible \( \text{SO}_2 \) absorptions on the outer three icy Galilean satellites need confirmation. A 2.42-\( \mu \text{m} \) absorption seen in spectra of Saturn’s satellites, identified as trapped \( \text{H}_2 \), needs confirmation, and a 5.01-\( \mu \text{m} \) absorption seen in spectra of Titan remains unidentified. Some absorptions seen in CRISM spectra of Mars are also still unidentified or poorly understood. This implies a continuing need for improving spectral libraries of reference compounds.

Water ice dominates most icy objects in the outer solar system. But why is the ice so pure in Saturn’s rings and most satellites, yet Titan is covered in organics? Similarly, Pluto is covered in organics yet its moon Charon displays a relatively pure water ice surface. What drives most surfaces to show such pure water surfaces with few other ices is unknown. Where are the expected signatures of ammonia or ammonia-water mixtures? If methane is so abundant on Pluto, Triton, Eris, Makemake, and Titan, why is it not abundant on other objects?

Why are some objects very high in albedo with relatively pure ice surfaces while others are very dark (e.g., Phoebe, the two faces of Iapetus, brighter Hyperion, dark Callisto versus brighter Ganymede and Europa)? Some of the answers certainly relate to resurfacing (e.g., Europa and Enceladus), whereas others display ancient heavily cratered surfaces that are still bright (e.g., Rhea) and still other ancient surfaces are dark (e.g., Phoebe). The mechanisms leading to these diverse surface compositions are not completely understood, although there is a trend in the Jupiter and Saturn systems for increasing darkening on moons farther from the planet, implying that dark dust preferentially coats the outer moons, probably from sources external to the system.

How are molecules complexed with one another, as in the case of \( \text{CO}_2 \) and \( \text{CH}_4 \) enclathrated in \( \text{H}_2\text{O} \), and what are the spectroscopic and physical-chemical implications of the processes that lead to complexing?

If water condenses below 135 K, it is expected to be amorphous. Yet the spectra of water ice throughout the solar system is dominated by crystalline ice (where our spectra are of sufficient quality to distinguish between amorphous versus crystalline water ice), with the exception of icy satellites orbiting within Jupiter’s inner magnetosphere where intense radiation can destroy the ice crystal structure. Even in the outer solar system beyond Saturn, where temperatures are well below 90 K, observed water ices are at least partially crystalline. Why we do not observe more amorphous ice is a mystery.

Spectroscopy and imaging spectroscopy have played major roles in exploring the solar system, and will continue to do so into the future.

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