

MECHANISMS FOR INCORPORATION OF HYDROGEN IN OR ON TERRESTRIAL PLANETARY SURFACES. M. D. Dyar,¹ C. A. Hibbitts², and T. M. Orlando³. ¹Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, mdyar@mtholyoke.edu. ²Johns Hopkins University, Applied Physics Lab, Laurel MD, 20723, Karl.Hibbitts@jhuapl.edu. ³School of Chemistry and Biochemistry and School of Physics, Georgia Institute of Technology, Atlanta, GA, 30332, Thomas.Orlando@chemistry.gatech.edu.

Introduction: Recent reports of a 3 μm band representing OH or H₂O on the lunar surface [1-3] coupled with early reports of the excavation of water ice from within a permanently shadowed crater [press releases and LCROSS website] all support the presence of reservoirs of assessable quantities of “water.” However, the observed 3 μm absorption band, which is due to the stretching motion of the O-H bond, is present for all forms of hydrogen bonded to oxygen including OH, H₂O, and H₃O⁺, and thus is not necessarily indicative of the water molecule. Spectral differences between these are subtle at best and indistinguishable at worst.

Our group is studying the distinctions between molecular water (H₂O) and hydroxyl (OH⁻), with an emphasis on evaluating their thermal stability, possible abundance, and mobility on airless bodies. In this paper, we discuss the many possible mechanisms for sequestering H on or in a planetary surface, and assess the implications that storage mechanisms for H have for understanding the origins of the water, evolutionary processes, and even resource extraction.

Mechanisms: In this paper, we consider these mechanisms (Table 1) under three categories: those involving endogenic (juvenile) H incorporation in the interiors of planetary materials, bulk H on the surface, and results of exogenic alterations of surfaces.

Table 1. Mechanisms for Storage of Water and Possible Magnitudes*

	Mechanism	H ₂ O (ppm)
Internal	Non-structural OH and H ₂ O in nominally-anhydrous minerals	0-1,500
	Structural OH in minerals	0-120,000
	Structural H ₂ O in minerals	0-300,000
	H ₂ O in fluid inclusions	1,000,000
	OH and H ₂ O in glasses	20,000-80,000
Bulk	Liquid H ₂ O (water)	1,000,000
	Frozen H ₂ O (ice)	1,000,000
Surficial	Physisorbed and chemisorbed (H ₂ O)	0-100,000 [†]
	Terminal hydroxyl groups (OH ⁻)	0-16,000 [†]

*estimated values intended to give order-of-magnitude levels of H contents. [†]varies with grain size

1. *Non-structural, OH and H₂O in nominally-anhydrous minerals.* In terrestrial samples, most common rock-forming nominally-anhydrous minerals (NAMs) typically contain hydrogen as OH, including

quartz (<1-40 ppm H₂O), feldspar (0-510 ppm H₂O), clinopyroxene (<5-240 ppm H₂O), orthopyroxene (26-117 ppm H₂O), and olivine (1-200 ppm H₂O) [1-3]. NAMs can also contain significant amounts of H₂O. For example, feldspar may contain H₂O (135-1350 ppm H₂O) and NH₄⁺ (450-1500 ppm H₂O). When present, OH, H₂O, and even NH₄⁺ in NAMs are all indicative of the presence of hydrogen during crystallization. Although the amounts of H may seem small, they can play a “disproportionately important role in the physical, chemical, rheological, electronic, and optical properties” of materials [4]. These minerals are so abundant that they may account for a significant proportion of the water budget in interiors and possibly on surfaces of terrestrial planets.

2. *Structural OH in minerals.* Roughly 1/3 of the >7000 known mineral species have OH in their formulas as a structural constituent. These hydrous minerals include amphiboles and clay minerals, and when they are present, the spectral signatures from OH can dominate reflectance and transmission spectra. From the perspective of planetary science, the spectroscopy of hydrous phases in meteorites has not been well-studied because their ca. 3 μm features have usually been presumed to represent a mixture of structural and adsorbed H bands.

3. *Structural H₂O in minerals.* Hydrated minerals are relatively common on Earth, including minerals such as members of the zeolite group that contain structural H₂O or even both OH and H₂O in the same mineral (biedellite, saponite) and many groups like hydrated salts of sulfates, carbonates, phosphates, and arsenates. These minerals generally form in the presence of liquid water on Earth. Unspecified hydrated non-ice material has been identified on the surfaces of Europa and Ganymede, two of the icy satellites of Jupiter [5]. Hydrated materials have also been reported on Mars and on large outer asteroids such as Ceres [6].

4. *Fluid inclusions.* Fluid inclusions are found in a large range of different rock types in terrestrial rocks, and are used for applications such as understanding paleoclimates and elucidating the petrogenesis of crustal and crust-mantle boundary fluids. The contents of a fluid inclusion are presumed to represent the liquid from which the mineral crystallized, and have great geological utility. Minerals that crystallize in water-rich environments may contain fluid inclusions that are at least partly H₂O.

5. *Dissolved OH and/or H₂O in glasses.* OH and/or H₂O may be dissolved in silicate glasses with variable speciation depending on crystallization history and composition. This mechanism is distinct from nominally-anhydrous minerals because the amounts of H in glasses can be quite large; most terrestrial glasses should be considered hydrous.

6. *Liquid water (H₂O).* For the sake of completeness, we must mention that liquid water (H₂O) occurs at present only on the surface of Earth, where it is of course a very stable mechanism for storage of H on the planet. There is also at least a possibility of subsurface liquid water on Mars, Ceres [6] one or more of the icy Galilean satellites [7] and Enceladus [8].

7. *Ice (H₂O)* Also for completeness, we include ice (H₂O) that occurs on the surfaces of many terrestrial planets as an example of H storage. The formation of low temperature ice has been the subject of a number of investigations. At adsorption temperatures below 100 K, monomers may be present at very low coverages. These water molecules tend to cluster at temperatures below 130K forming amorphous solid water (ASW). Crystalline ice (CI) forms at even greater temperatures (140-150K in ultrahigh vacuum).

8. *Physisorbed and chemisorbed water (H₂O).* Water that is weakly bound (bond energy <0.35 eV) is referred to as physisorbed. However, because this molecular water is typically bound only by weak van der Waals electrostatic attractions, i.e. induced dipole-dipole interactions, it exists only at low temperatures. The physisorption of gases is inversely dependent on temperature and proportional to the gas overpressure. Physisorption is also proportional to grain surface area and porosity [9]. Molecular water can bind more strongly (bond energy >0.35 eV) to surfaces in a process often termed chemisorption. Because water bound to charged surfaces or surface defects has a higher binding energy than physisorbed water it can persist at temperatures above 150 K.

9. *Terminal hydroxyl groups (OH).* Depending upon the nature of the surface sites and defects, water may dissociatively adsorb forming terminal hydroxyl groups due to covalent bonding with the surface. These terminal OH can also form via implantation of hydrogen ions/atoms, such as from the solar wind. As water continues to accumulate, the sites for chemisorption will become saturated, and water will no longer dissociate but will form traditional water-water hydrogen bonds such as those present in liquid water or ice.

Discussion: Interpretation of a 3- μ m band from a remote-sensed reflectance spectrum is affected by a number of intrinsic factors, including:

- The grain size and surface roughness of the surface material (the effective grain size),

- The H content of the interior of the surface materials and any adsorbed water or OH,
- Uncertainties regarding the optical constant of the H in the materials being studied, and
- The use of reference library spectra in which there is ubiquitously adsorbed surface water and in which the 3- μ m bands therefore represent contributions from adsorbed water and from internal water.

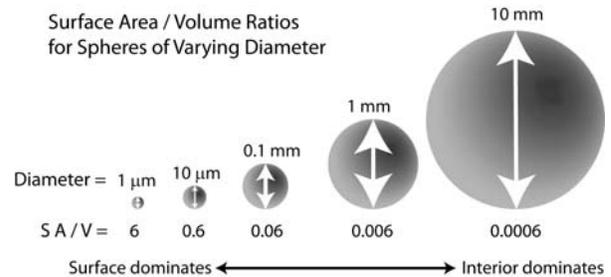


Figure 1. Graphical depiction of the relationship between grain size and surface area in mineral grains. If grain size is large, then a reflectance spectrum will be dominated by the signal of H from the interior of the sample. In contrast, small grain sizes (e.g., dust-sized μ m particles) have large surface areas relative to their volumes, and so their reflectance signals may be dominated by surface effects.

Some of these possibilities are represented in Figure 1, which shows the ratio between surface area and grain size (expressed in terms of diameter and volume) for some likely grain sizes found on planetary surfaces. In a 1- μ m (dust-size) particle, a monolayer of water on the surface would dominate a spectrum, even if the interior of the grain was hydrous. At the other extreme, a monolayer of water on a >10 mm pebble would store only a tiny molar volume of water relative to the volume of the entire pebble, so the H contents of the interior would dominate. Such calculations raise cautions about appropriate interpretations of 3- μ m band.

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