

CHARACTERIZATION OF WATER IN SURFACE AND NEAR-SURFACE MATERIALS FOR STUDIES OF PLANETARY HISTORY AND RESOURCE PROSPECTING.

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Introduction: Understanding inventories of surface and near-surface volatiles, especially water as ice or structural water in minerals, will be of clear importance for human exploration endeavors and provides important information about the formation and evolution of bodies throughout the solar system.

To date, remote observations, *in situ* analyses and sample return have provided various levels of detail on the nature of water inventories in the near-surface materials on solar system bodies, including the Moon, Mars, asteroids, comets, dwarf planets, and satellites of the outer solar system. In many cases, the most thorough characterization of the nature or abundance of the water or water-bearing phases as inferred from a number of carefully selected returned samples could be performed using the vast analytical capabilities available in terrestrial laboratories which are relatively unconstrained by analysis time, power, mass, volume or other operational requirements. However, to be able to best extrapolate the knowledge gained from specific samples to larger regions of the planetary surfaces, and to select the most scientifically valuable samples in the first place, optimization of *in situ* analyses that enable a large number of operationally constrained, perhaps lower-fidelity, measurements, is needed.

In addition, for many solar system bodies sample return implementations that are expected to maintain the original state of the collected surface materials with respect to their water-bearing phases are not yet fully developed, though the development of these strategies is farther along for some solar system bodies (e.g., Mars) than others. Robust development of this capability, especially for particularly challenging materials such as samples from icy satellites of the outer solar system, would be an important goal over the next few decades. Optimization of approaches that can best characterize water-bearing phases *in situ* will mitigate risks of decreased science return due to post-collection changes in returned samples by establishing the original properties of the samples. These detailed *in situ* analyses and follow-up sample return tasks would likely be first undertaken by robotic missions, and later by crewed missions. A longer term goal, possibly achievable by the 2050s, would be to develop the procedures and technologies to characterize important volatile-bearing surface materials in crewed laboratories direct-

ly on the surface of planetary bodies to levels of detail that rival terrestrial laboratories.

Approaches and Technologies: To fully characterize the nature and distribution of water-bearing phases in planetary materials *in situ*, a variety of approaches and technologies are needed. First, landing areas with the potential for water-bearing phases in the near-surface need to be targeted based on orbital or remote observations. Then, these areas need to be further investigated for indications of hydrated minerals or water ice using techniques that provide reconnaissance over several meters (including to at least several meters depth), such as neutron scattering instruments [1] and thermal [2] or visible/near-IR (e.g., [3]) spectroscopy. Selected areas of interest can then be scouted on sub-meter scales with spot analyzers that can relatively quickly characterize the mineralogy or chemistry of materials in their natural state without sample processing. Examples of these types of technologies include APXS [4] or x-ray fluorescence (XRF), contact x-ray diffraction (XRD) [5], and Raman spectroscopy [6]. An advantage of these techniques is that they are often less mission resource (e.g., time, power, mass) intensive than techniques requiring sample processing. They can also study samples without disturbing the spatial relationships between sample components or disrupting any volatiles present in samples. In addition, they can be used to select the most promising samples for further analyses that are more resource intensive. Finally, samples selected based on the spot analyses can be subjected to techniques that require sample processing. These techniques may be very resource intensive but may provide the highest level of detail on the hydrated minerals or water present in specific carefully chosen samples.

Several of these technologies are being developed for, or have been used by, previous, current or near-term robotic missions, but in many cases there would be significant benefit to continuing refinement or miniaturization to best characterize water-bearing materials on future missions to Mars or other planetary bodies. In addition, because these missions will include both robotic and crewed missions, strategies need to be developed for the use of these technologies as part of robotic missions and by astronauts [e.g., 7].

Examples of enabling technologies under current development: Powder XRD has been successfully carried out on Mars with the Chemistry and Mineralogy (CheMin) instrument on the Mars Science Laboratory (MSL) rover. This approach has yielded more detail on hydrated and/or hydroxylated minerals in martian samples than previously obtained *in situ*, highlighting the strength of XRD for *in situ* studies of volatile-bearing minerals. It does, however, require processing the sample to a powder, which can be mission resource intensive and possibly disruptive to volatiles within samples. Contact XRD is a relatively new area of technology development for planetary instruments (e.g., the Chromatic Mineral Identification and Surface Texture (CMIST) instrument concept [5]). Contact XRD can be used to analyze samples in place without processing them to a powder, resulting in the ability to study phases in their original spatial context and enabling analysis of even very volatile phases such as ices. It is also less resource intensive (analysis time, power, size, etc.) than a powder XRD technique. In addition where robotic or manned mission strategies allow, this contact XRD technology can be used to triage samples for follow-on analysis by powder XRD. *In situ* evolved gas analysis mass spectrometry (EGA-MS), in which samples are heated and any evolved volatiles are detected by a mass spectrometer, has been successfully demonstrated by the Sample Analysis at Mars (SAM) instrument on MSL, which has detected a large variety of volatiles evolved from martian samples including ~1-2 wt% water resulting from adsorbed water and structural H₂O/OH in sample phases [e.g., 8, 9, 10]. *In situ* thermal analysis techniques like EGA-MS necessitate the preparation of a sample powder through scooping, crushing or drilling, as well as pyrolysis ovens coupled to a gas manifold and mass spectrometer. SAM is mission resource intensive, in terms of power, mass, volume and analysis time, but simplified and miniaturized EGA-MS approaches based on SAM are being developed for deployment on the Moon or other planetary bodies (e.g., the Volatile Analysis by Pyrolysis of Regolith (VAPoR) instrument [11, 12]). Instruments like VAPoR would reduce mission resource needs and operations complexity for future use of thermal analysis techniques on robotic missions or by astronauts on crewed missions.

Key in enhancing science return from several of these approaches would be the development of increasingly capable sample acquisition and processing techniques to enable sampling with minimal loss or changes to volatile components and which can robustly sample deeper into the subsurface (e.g., several meters) where volatile-bearing phases may be more abundant.

The further development of sampling and analysis technologies for a variety of mission concepts and planetary environments, building on past and present achievements, is a necessary step to comprehensive characterization of water-bearing materials crucial to studies of planetary formation, evolution or potential habitability.

Knowledge of the nature, abundances, and distributions of water-bearing materials on planetary surfaces and how readily the water is thermally extracted from them would also have important implications for finding and extracting water for use by astronauts.

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