

TOWARDS RANKED IMPURITY INVENTORIES OF WATER RESOURCES ON THE MOON AND

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Introduction: Water is one of the most, if not the most, desired product of in-situ resource utilization (ISRU) in space. Its uses comprise a wide range of applications, including environmental control and life support systems (ECLSS), agriculture and biomass production, propellant production, radiation protection, thermal management, etc. Most applications have stringent purity requirements. Hence, besides the extractive mining of water from accessible deposits, subsequent purification is expected to be required.

The desired degree of the water's purity and the efforts required for purification depend on the water's final application and the robustness of the downstream technologies. As not all impurities are equal, the evaluation and the design of system architectures for purification requires the understanding of the types of impurities and their concentrations expected to be present in the water effluents of the extractive processes. These qualities relate to the associated volatiles and minerals present in the deposits and how the extraction steps would release impurities from them.

Beyond recognizing impurities as potentially critical contaminants, impurities may also constitute valuable commodities to be recovered as by-products of ISRU water production. This also has implications for the selection and design of system architectures for extraction and purification.

In an effort to gain a better understanding of the geological and geochemical baselines of the water occurrences on the Moon and Mars, the European Space Agency (ESA) has tasked ESRIC to evaluate the impurity inventories expected in the raw water products.

We will present first iterations and assessments of which impurities are to be expected and how they might be ranked in criticality for downstream ISRU processes. A parallel evaluation of their potential as recoverable by-products is also conducted.

Approach: Our bottom-up approach is initially agnostic of the scale and accessibility of water occurrences as potential resources, yet it considers their potential to become resources or reserves [1]. Among many factors, the classification hinges on the estimated amount and composition of impurities in the expected raw water streams, as purification efforts, usage constraints on impure water, and recoverable by-products could significantly impact the economics of water mining.

Given the limited geological and geochemical data on extraterrestrial water and hydrogen occurrences, descriptive models alone may not adequately support an evaluation of impurities. For the Moon, there is one data point from the LCROSS mission [2]. For Mars, there is no compositional data available. Hypotheses on the genesis of the water occurrences and genetic models can help constrain which volatiles and compounds might be present. This broadens our approach to include a wider view of volatile processing on the Moon and Mars.

Lunar water occurrences: On the Moon we consider i) the solar and meteoritic volatiles in the global regolith, ii) the adsorbed water at circumpolar latitudes, iii) the ices in the permanently shadowed regions (PSRs), iv) the occurrences of hydrous pyroclastics.

Solar and meteoritic volatiles in the regolith. Exogenic volatiles delivered by the solar wind and impacts of asteroidal/cometary meteoroids are variably bound at the surfaces of mineral grains and may be transferred into impact glasses [3]. The main H species are molecular H₂O, -OH and H₂. Impurities expected in the gas released by thermal processing are noble gases (mainly He, some Ne and Ar), sulfur compounds (possibly H₂S, S₂ and SO₂ under vacuum extraction, SO₂ under oxidative extraction), carbon and nitrogen compounds (CO/CO₂, N₂) [4]. High-temperature processing may mobilize volatile metals and chalcogens (e.g., Na, K, Pb, Cd, Hg, Tl, Te, Se).

Adsorbed water at circumpolar latitudes. Loosely bound exogenic molecular H₂O and -OH may be preferentially retained in or migrate into cold high-latitude regions as indicated by (epi-)thermal neutrons and 3- μ m IR absorption. Species with volatility larger than water are not expected to bind and accumulate strongly [5], and lower temperatures would suffice for extraction (or loss during mining). Volatile metals and chalcogens are not expected in the extracted gases, except maybe Hg. Despite having lower water abundances than expected in the PSRs, the illuminated circumpolar regions are scientifically important to elucidate the migration and trapping of volatiles on the Moon.

Ices in the permanently shadowed regions. Long-term migration and trapping of volatiles within PSRs have led to the most promising water occurrences on the Moon. LCROSS [2,6] has provided critical information on impurities expected upon heating PSR ices,

including CO/CO₂, H₂S, NH₃, SO₂ and simple hydrocarbons. Hg was predicted and detected at mg/g levels. Large uncertainties on the abundances remain, and heterogeneity among and within PSRs is likely. Understanding of volatile delivery, which currently points to exogenic cometary sources [7], may inform about critical trace volatiles, such as HCN and HF.

Hydrous mare pyroclastics. NIR reflectance spectrometry indicates localized pyroclastic mare units with H₂O abundances on the order of 0.1 mg/g [8]. This endogenic water content is unusual for lunar magmatism, in which H₂ rather than H₂O is expected at low f_{O_2} . Associated magmatic volatiles may comprise H₂S, S₂, SO₂, HCl, and HF, besides volatile metals and chalcogens potentially released during high-temperature extraction.

Martian water occurrences: On Mars we consider i) water vapor in the martian atmosphere, ii) ices at polar and middle to low latitudes, iii) phyllosilicate-bearing lithologies, iv) sulfate-bearing lithologies, v) the eolian regolith. The last three are related and individual deposits may have been combined in different proportions.

Martian atmosphere. Due to extremely low H₂O abundances, the harvesting of atmospheric water on Mars has been assessed infeasible under reasonable circumstances (e.g., M-WIP [9]). However, the complex oxidizing atmospheric chemistry (strong UV irradiation, dust load) may be relevant to other ISRU processes and may inform hypotheses about critical impurities in ice deposits, which may have originated via atmospheric exchange. These impurities may include H₂O₂, Cl-O compounds, and possibly (ancient) volcanic volatiles such as H₂SO₄, HCl and HF.

Polar and mid-/low-latitude ices. Grouped together for impurity assessment, these ice occurrences differ in silicate overburden, ranging from zero at the poles to 10s or 100s of m at near-equatorial latitudes [10]. Ices may be very pure or with admixtures of dust, carrying sulfate, perchlorate/chlorate and nitrate salts. The extraction pathway (liquid or gas) will determine their concentrations in the extraction effluent. Perchlorates are mostly benign contaminants with respect to corrosion but chemotoxic to organisms. The timing of ice deposition in relation to changing atmospheric chemistry and volcanism may determine the abundances of impurities originating from atmospheric exchange.

Phyllosilicate-bearing lithologies. Warm and wet climate on early Mars has produced sedimentary units rich in smectitic clays and other hydrous silicates with dominantly structural -OH. These mostly consolidated sediments require calcination to free water. Impurities released into the gas are mainly expected to be SO₂ (sulfide oxidation), CO₂ (atmosphere, organics, and carbonates) and some H₂ (sulfide oxidation, organics)[11]. Overprinting with sulfate mineralogies and infiltration

of perchlorate may alter the release patterns significantly. Organo-sulfur and organo-chlorine compounds may be present at relevant trace levels in the gas.

Sulfate-bearing lithologies. Polyhydrated Mg and Ca sulfates and hydroxylated jarosite have formed during the transition of Mars to colder and dryer climate. They occur in clastic sedimentary units and may have infiltrated older sedimentary strata, possibly along with variable amounts of perchlorate from changed atmospheric chemistry. Calcination is expected to produce additional SO₂, as well as O₂, HCl, and NO from perchlorate and nitrate decomposition [12]. Soluble Cr(VI) may not be widespread but is of high concern.

Eolian regolith. The water content of unconsolidated windblown soil strongly depends on particle size distribution. The finest, globally distributed fraction is more hydrous and contains more oxidant salts. The less mobile, coarser fraction may more closely represent local bedrock compositions with variable igneous (hydrous basaltic glass) and sedimentary (clay, sulfate) components [13]. Calcination is expected to produce less H₂O yield, higher proportions of CO₂, and lesser SO₂, H₂, and O₂ depending on the mixing ratios.

Conclusions: The conceptualization and evaluation of extraction-purification system architectures requires a ranking of the expected impurities by concentrations and their uncertainties, by their impact on downstream applications and the environment (if disposed), and by their possible synergistic recovery. Purification approaches should be tunable to multiple use cases and robust to natural variations. Optimization may attempt to align extraction and purification to tune impurity profiles for best processing. Note also that understanding the nature of impurities in water sources on the Moon and Mars will yield important science data as well as informing ISRU processes.

References: [1] Neal C. R. et al. (2024) *Acta Astron.*, 214, 737. [2] Colaprete et al. (2010) *Science* 330, 463. [3] Lucey P. G. et al. (2021) *Geochemistry*, 82, 125858 [4] Gibson E. K. & Moore G. W. (1972) *Proc. LPSC*, 3, 2029. [5] Schorghofer N. & Aharonson O. (2014) *ApJ*, 788, 169. [6] Colaprete A. et al. (2012) *Space Sci. Rev.*, 167, 3. [7] Mandt K. E. et al. (2022) *Nat. Comm.*, 13, 642. [8] Milliken R. E. & Li S. (2017) *Nat. Geo.*, 10, 561. [9] Abbud-Madrid A. et al. (2016) *mepag.jpl.nasa.gov*. [10] Putzig et al. (2023) *Handb. of Space Resources*, p. 583. [11] Sutter B. et al. (2017) *JGR*, 122, 2574. [12] McAdam A. C. et al. (2022) *JGR*, 127, e2022JE007179. [13] Stern J. C. et al. (2018) *GRL*, 45, 10240.

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