Science-Driven Organic Inventory — Lunar Volatiles

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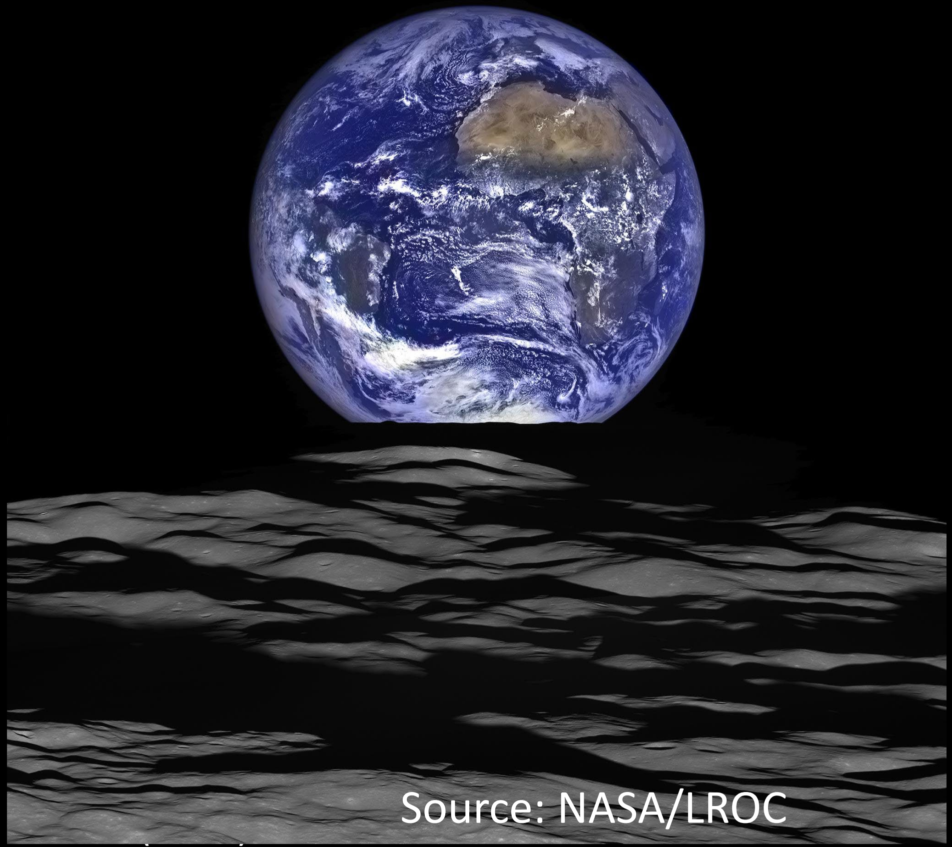
Why do we care about lunar volatiles?

The Moon is a Cornerstone for the history of the solar system

- Impact history for the Earth-Moon system, the terrestrial planets, and the solar system as a whole
- Terrestrial planet formation and interior evolution
- History of volatile delivery to the Earth-Moon system

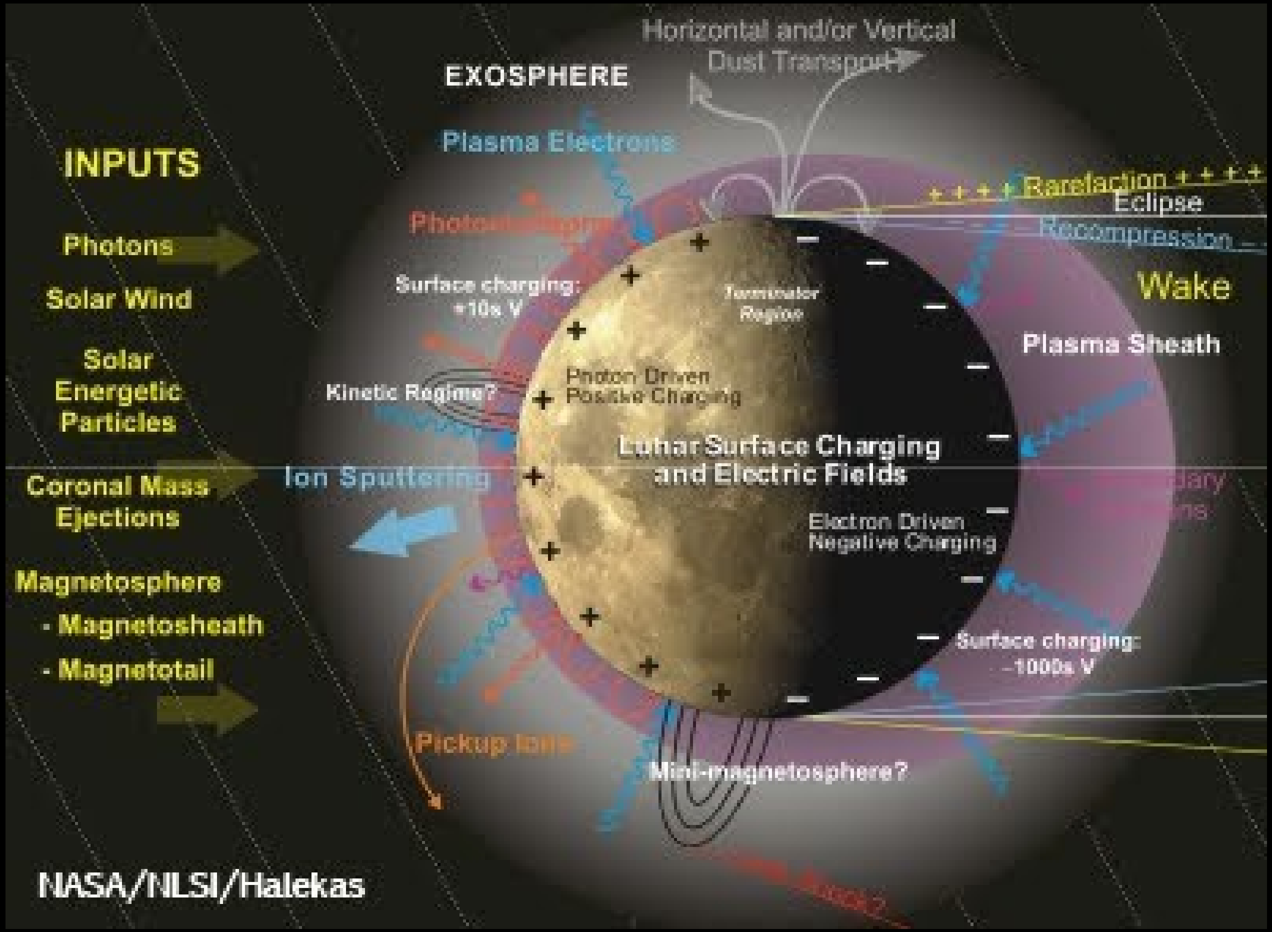


As we begin to explore and make use of volatile reservoirs on the Moon, it is essential to recognize their scientific value and fully characterize their composition.

Slide credit: Kathy Mandt

The Moon's atmosphere is an Exosphere

- Studied remotely through a variety of methods
- First in situ observations: Apollo mass spectrometers
- Orbital with LADEE
- The Moon's exosphere is where volatiles enter and exit from the Moon system.



Slide credit: Kathy Mandt

Which lunar volatiles are of interest?

- Measurements from LCROSS

Compound	Molecules cm^{-2}	% Relative to $H_2O(g)$*
H_2O	5.1(1.4)E19	100.00%
H_2S	8.5(0.9)E18	16.75%
NH_3	3.1(1.5)E18	6.03%
SO_2	1.6(0.4)E18	3.19%
C_2H_4	1.6(1.7)E18	3.12%
CO_2	1.1(1.0)E18	2.17%
CH_3OH	7.8(42)E17	1.55%
CH_4	3.3(3.0)E17	0.65%
OH	1.7(0.4)E16	0.03%

Colaprete et al. (2010)

- Small organic molecules (e.g., methylamine, formaldehyde) detected in returned regolith samples (ANGSA program)
- Other volatiles that could be preserved in PSRs, such as noble gases

Some driving science questions

- What volatiles are outgassing from the Moon itself, and what does that tell us about internal lunar processes and materials that formed the Moon?

Compounds outgassing from the Moon

- What is the inventory of endogenous organics?
  - Noble gases (Xe, Ar, Kr)
  - Carbon, nitrogen, and sulfur-bearing species
- Desirable to measure exosphere as a function of time in area near where outgassing is happening
- Simultaneous measurements of multiple compounds would allow for relative abundance calculations
- **Preserving the exosphere is critical to understanding endogenous outgassing**; sensitive to contamination

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- What volatiles are delivered exogenously, from solar wind or impactors?

Exogenous delivery

- Solar wind is a steady source of ions (e.g., H, C, N, O) that can recombine to form new compounds in the lunar environment

- Impactors such as meteorites and comets can deliver a range of organic compounds and volatiles

- How do these volatile organics contribute to the lunar organic inventory?

Some driving science questions

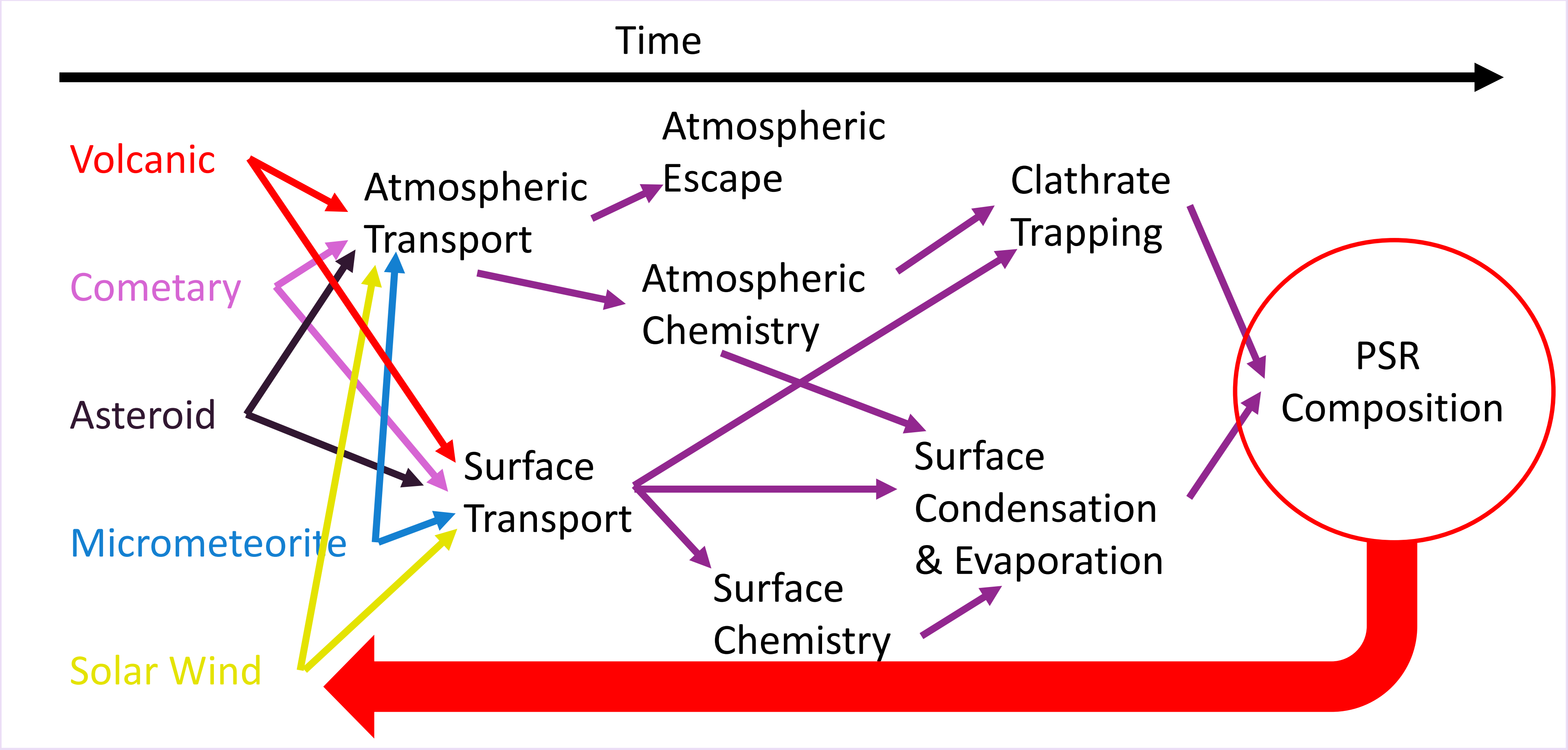
- What volatiles are outgassing from the Moon itself, and what does that tell us about internal lunar processes and materials that formed the Moon?
- What volatiles are delivered exogenously, from solar wind or impactors?
- What is the origin of the volatiles in the lunar polar regions?
    - A3 SDT report Science Objective: “Understanding the character and origin of lunar polar volatiles”
- What are the processes that transport volatiles through the lunar exosphere or regolith?
    - If there's a comet impact at the equator, how much ends up in PSRs/polar regions?

Where did the volatiles in PSRs come from?

Volatile sources have varied over time and each source has unique composition characteristics

Slide credit: Kathy Mandt

Can volatile composition in the PSRs be traced back to their sources?



Many processes change the molecular composition between source and storage. How do we untangle this to trace volatile composition back to the source?

Slide credit: Kathy Mandt

The Moon's exosphere is a place where volatiles travel from one place to another

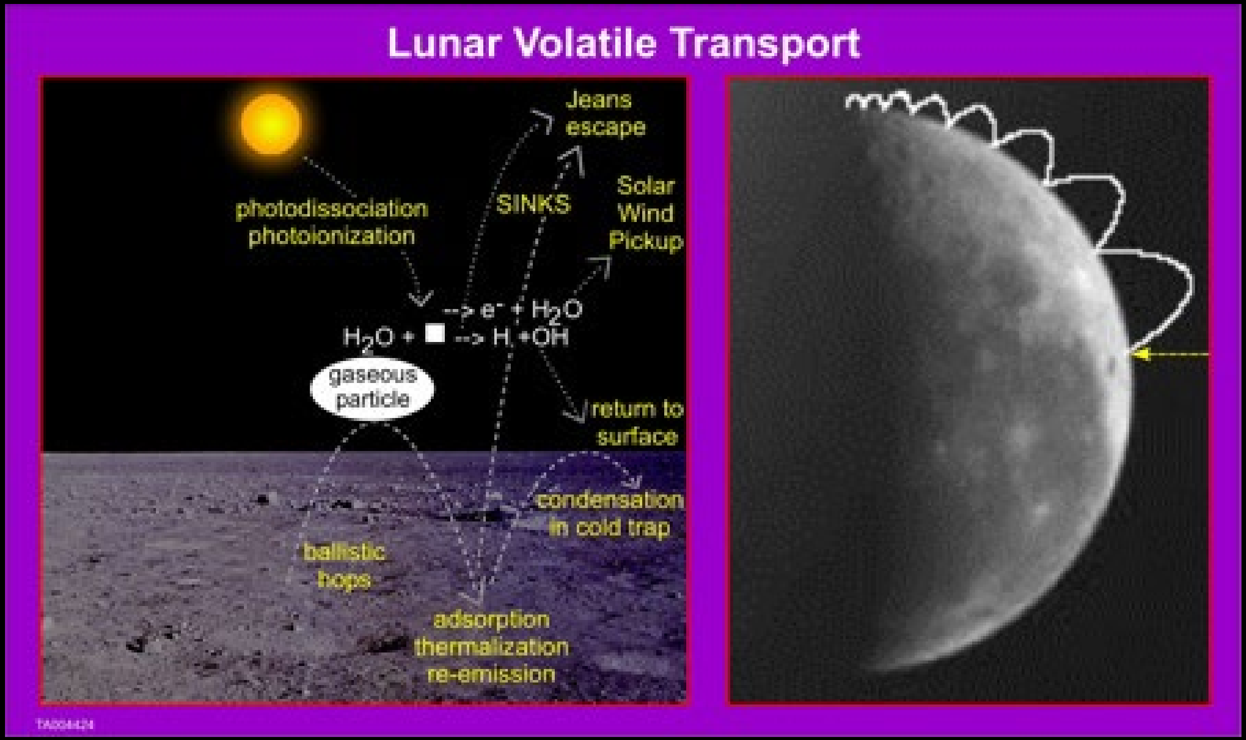


Image source: https://www.boulder.swri.edu/lamp/water.html

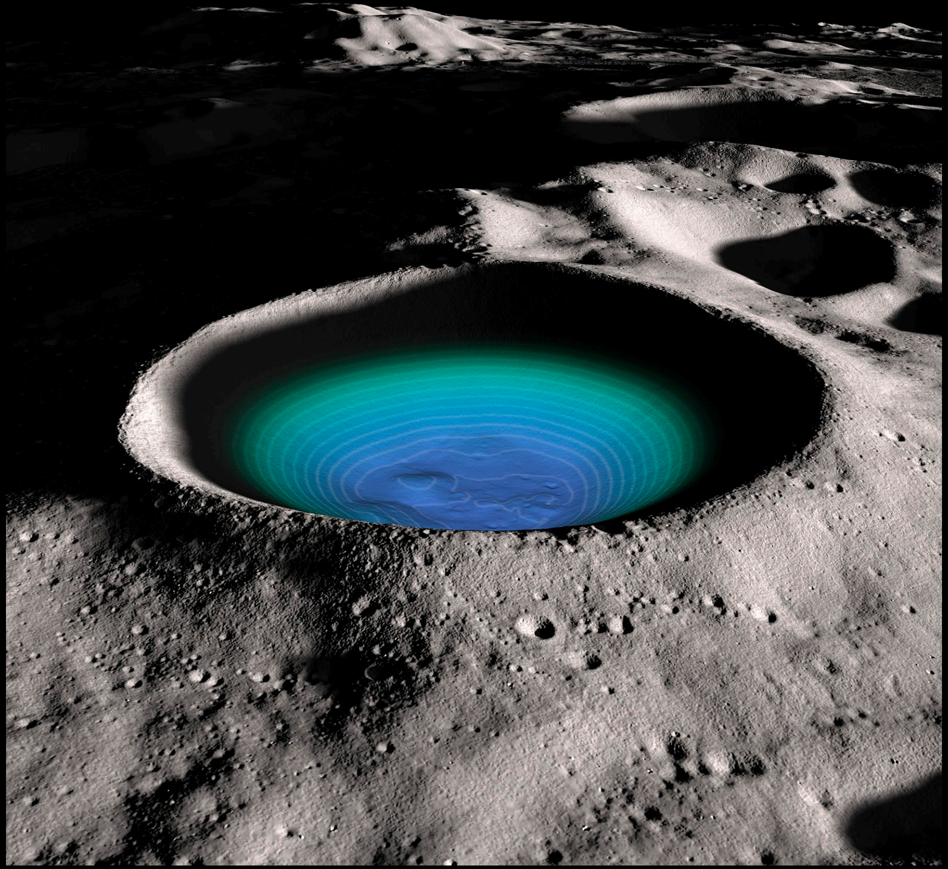


Image source: NASA Goddard/SSERVI

Slide credit: Kathy Mandt

Determining origin of PSR volatiles

- Measuring of volatile abundances, composition, and isotopes in samples from PSRs could help distinguish between origins

- Core samples could provide insight into long-term history of the Moon
  - Don't fully understand transportation processes, so unclear how deep contamination from landing activities would reach

- How important are processes such as pumping, evaporation, and condensation in transporting volatiles to polar regions and PSRs?

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Key measurements required

- Identity of volatiles
- Abundances (absolute and relative)
- Spatial and depth distributions
- Isotopes

Measurements possible in-situ and through sample return, curation, and analysis in laboratories on Earth

Key measurements required

- Composition of volatiles
- Abundances
- Spatial and depth distributions
- Isotopes

These measurements are sensitive to contamination that could add terrestrial contributions to lunar inventory and potentially:

Change the measured abundances of lunar volatiles
Introduce new volatiles to the measured inventory
Modify the isotopic values of measured compounds

Contamination concerns

- Sources
  - Outgassing from spacecraft and other materials
  - Venting (e.g. airlock)
  - Exhaust plumes from landing and ascent activities
  - Collection/transportation/curation activities (for sample return)
  - Unknowns – what aren't we considering?


Space > Moon and Mars

Scientists Think We've Officially Entered the 'Lunar Anthropocene'

Welcome to a new moon epoch, y'all.

BY TIM NEWCOMB PUBLISHED: DEC 28, 2023 9:00 AM EST

SAVE ARTICLE

Michael Dunning // Getty Images

Popular Mechanics, 12/28/23
Discussing Holcomb et al., 2023

Effects of exploration

A3 SDT Goal 2f: Understand the impact of exploration on the lunar volatile record across the surface

- “Activity on the lunar surface (both robotic and human) will inevitably alter the current natural state of the surrounding region”
- “Exploration-induced effects should be measured in terms of character and modification of volatile composition, form, and distribution on the lunar surface.”
- “In addition to characterizing the human-induced variations, scientific questions to be addressed by these measurements include determining the broader nature of volatile adsorption in polar regolith, constraining the rate of sublimation of cold-trapped volatiles, and measuring the spatial and temporal variability of exospheric and surface adsorbed volatiles.”

Contamination concerns

- Sources
  - Outgassing from spacecraft and other materials
  - Venting (e.g. airlock)
  - Exhaust plumes from landing
  - Collection/transportation/curation activities (for sample return)
  - Unknowns – what aren't we considering?
- Other concerns
  - Transportation and cold trapping
  - Unknown levels of contamination from Apollo and other activities

It is impossible not to contaminate – need to consider contamination knowledge and mitigation

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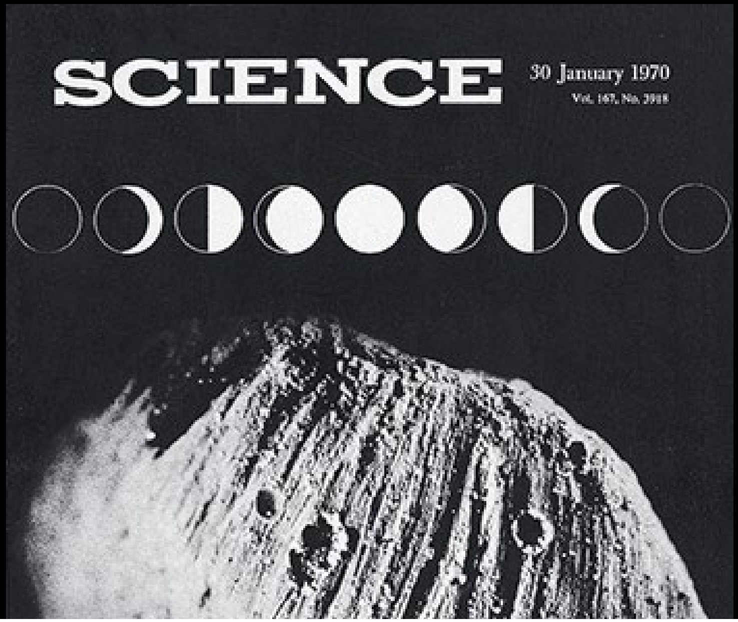
How to understand contamination?

- Contamination Knowledge efforts as part of each mission
- Material archives
- Witness materials
- Measurements
  - Measurements should be made at varying distances from human activities and over varying timescales
- Experiments and research
  - Terrestrial experiments to understand loss and transfer of materials
  - Understanding volatile transport processes

Case study – amino acids in Apollo samples

- Apollo samples were eagerly studied for organic content
- Amino acids were a focus
  - essential to life
  - detected in carbonaceous meteorites
- Amino acids were detected, but there was no consensus on origins in Apollo era
- Analyses of other organics were limited due to analytical and instrumental capabilities



Organic Compounds in Lunar Samples: Pyrolysis Products, Hydrocarbons, Amino Acids

Abstract. *Lunar fines and a chip from inside a rock pyrolyzed in helium at 700°C gave methane, other gases, and aromatic hydrocarbons. Benzene/methanol extracts of fines yielded traces of high molecular weight alkanes and sulfur. Traces of glycine, alanine, ethanolamine, and urea were found in aqueous extracts. Biological controls and a terrestrial rock, dunite, subjected to exhaust from the lunar module descent engine showed a different amino acid distribution. Interpretation of the origin of the carbon compounds requires extreme care, because of possible contamination acquired during initial sample processing.*

Nagy, et al.

Lunar amino acids and potential sources

- Potential sources considered for lunar amino acids
  - Exogenous delivery
  - Solar wind implantation of precursors
  - Terrestrial contamination
- Distinguishable by:
  - structural distribution
  - variations between samples
  - isotopic signature
- **Re-examination possible because of sample return and curation**

Case study – amino acids in Apollo samples

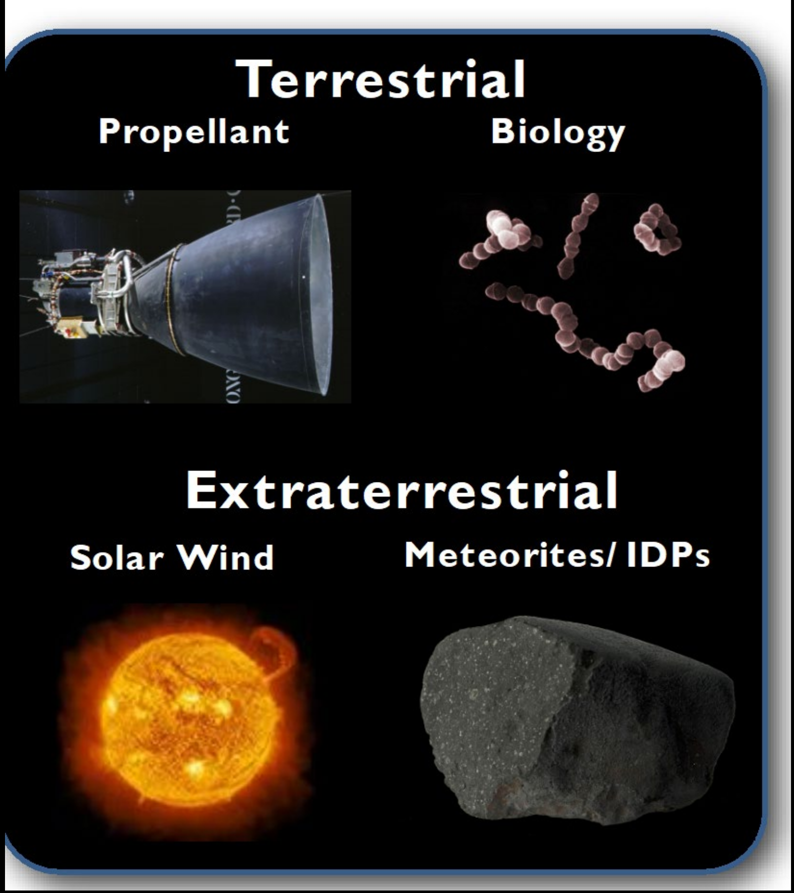
- Samples analyzed:
  - Apollo 16 and 17 samples from JSC curation
  - Apollo 15, 16, and 17 samples stored in a non-curation laboratory for decades
- Contamination Knowledge
  - Apollo-era literature describing contamination tests and mitigations
    - List of materials permitted to contact or "see" the samples
    - Cleaning procedures
  - Two samples of dunite used to test contamination from exposure to lunar module exhaust (stored in non-curation lab)
    - Previous reports of many organic compounds in the exhaust: acetylene, hydrogen cyanide, ethylene, formaldehyde, methyl amines, acetaldenhyde …

Lunar Amino Acid Analysis Results

- Concluded that amino acids detected in lunar samples were **primarily from terrestrial contamination**, with some contribution possible from **meteoritic infall**

- Significant portion of amino acids formed from **precursors** during laboratory hydrolysis

- Samples that had been stored in a non-curation laboratory for an extended amount of time showed significant **organic contamination**



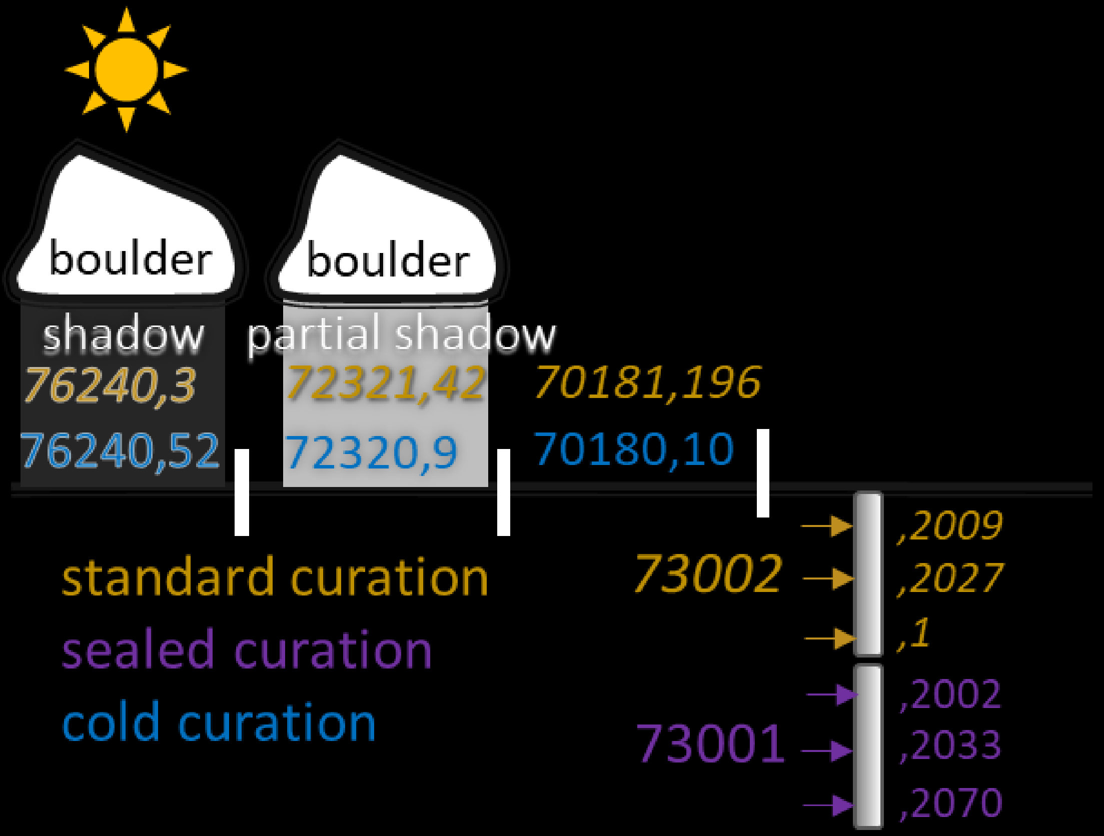
Elsila et al. (2016) *Geochim. Cosmochim. Acta* **172**, 357-369

Lessons learned

- Sample return and long-term curation enabled science not possible at the time of the mission
- Despite thoughtful and careful contamination control and curation efforts, trace organics could be overwhelmed by terrestrial sources
- Contamination knowledge critical to understanding the unavoidable contamination

Case study: ANGSA organics analysis

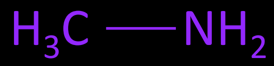
- Building off of the previous study, aiming to examine volatile precursors of amino acids
  - Amines, aldehydes, HCN, carboxylic acids, ketones
- Specially curated Apollo 17 samples
  - Vacuum sealed
  - Frozen
- Witness foils placed in curation processing cabinet during sample allocation

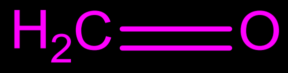


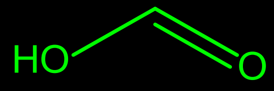
ANGSA organics results

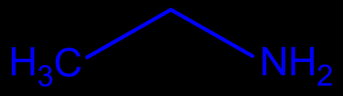
- Volatile organics present in low abundances on the lunar surface
  - Identified C_1 and C_2 compounds not previously reported in lunar samples (methylamine, ethylamine, formaldehyde, acetaldehyde, formic acid, acetic acid)

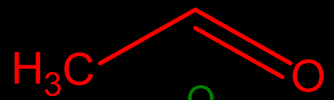
- Potential evidence for cold trapping
  - Higher abundances of amines in the shadowed sample than in the sunlit sample

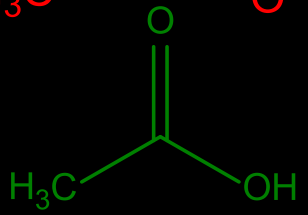












Elsila et al. (in review) *JGR-Planets*

ANGSA Curation/Contamination Lessons

- Nylon **contamination** from curation/handling
  - Identified as primary source of amino acids in the non-core samples
- Sealed curation may preserve volatiles better than standard curation
  - Volatile organics found in the sealed half of double drive tube, but not the unsealed half
- Cold curation does not show substantial enhancement of volatile organics compared to room temperature curation, but may show less contamination

Contamination take-aways

- Publication of contamination control efforts is essential for future researchers
- Contamination Knowledge efforts, including material archiving and witness materials, are needed
- Impossible to list all volatiles of interest or set generic “acceptable levels” of contamination; these depend on specific research questions and evolve over time
- Experiments and research
  - Terrestrial experiments to understand loss and transfer of materials
  - Experiments to understand components of exhaust
  - Modeling efforts to examine transfer and cold trapping

Potential mitigation and concerns

It is impossible to eliminate contamination, but effects can be mitigated!

- Accountability and expectations
  - Lists of volatile compounds used in spacecraft
  - Focus on materials that may have a path to returned samples or to exosphere/regolith
  - Even small amounts of certain materials may be of concern, depending on location
- Contamination knowledge and materials archives (accessible to researchers)
- Research to understand transport and adsorption processes
- How do we mitigate the unknown/uncontrollable contamination from non-NASA or non-Artemis accord missions?