ORGANICS IN APOLLO LUNAR SAMPLES.

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Introduction: One of many unknowns prior to the Apollo landings concerned the possibility of life, its remains, or its organic precursors on the surface of the Moon. While the existence of lunar organisms was considered highly unlikely, a program of biological quarantine and testing for the astronauts, the Apollo Command Modules, and the lunar rock and soil samples, was instituted in the Lunar Receiving Laboratory (LRL) [1]. No conclusive evidence of lunar organisms, was detected [2-4] and the quarantine program was ended after Apollo 14.

Analyses for organic compounds were also conducted. Considerable effort was expended, during lunar surface operations and in the LRL, to minimize and quantify organic contamination [5]. Post-Apollo curatorial operations and cleaning minimize contamination from particulates, oxygen, and water but no longer specifically address organic contamination. The organic compounds measured in Apollo samples are generally consistent with known sources of contamination.

Lunar Sample Collection and Contamination Control: The lunar rock and soil samples were collected using simple geologic tools including hammers, shovels, rakes, and core tubes. Most samples were placed into pre-cleaned, numbered bags. Some samples, collected for specific high-sensitivity tests, were placed in dedicated metal containers. Upon returning to the Lunar Module the astronauts put most sample bags, containers, core tubes, and loose samples into pre-cleaned aluminum cases. The cases were sealed in the lunar vacuum, and the samples were kept in these sealed cases thru Earth return. The cases were opened under controlled conditions in the LRL [6].

Apollo planners conducted extensive organic contamination monitoring of the containers, tools, and sample handling facilities. Simoneit and Flory [7] summarized the potential sources of organic contamination: 1) surface contamination of the lunar-bound rock box and its contents; 2) surface contamination on the Apollo lunar hand tools used to obtain samples on the lunar surface; 3) exhaust products from the lunar descent engine and reaction control system engines (both using unsymmetrical dimethyl hydrazine and nitrogen tetraoxide); 4) lunar module outgassing; 5) astronaut spacesuit leakage; 6) particulate material abraded from spacesuit or other sources during EVA; 7) venting of lunar module fuel and oxidizer tanks, cabin and waste systems; 8) venting of spacesuit life support back packs; 9) exposure to LRL vacuum or nitrogen processing chambers; 10) surface contamination of sample processing tools and containers; 11) surface contamination of containers sent to investigators. Items 1, 2, 3, 9, 10, and 11 were considered most serious. Simulations, modeling and engineering data were used to estimate the contamination contributed by flight items 3, 4, 5, 7 and 8 [8]. Virtually all rocket exhaust products were low molecular weight and rapidly diffused over large areas. Because of their low concentration, this was not predicted to be a major contaminant. The organic products included acetylene, HCN, ethylene, formaldehyde, and methyl amines.

Apollo-Era Laboratory Contamination Control and Monitoring: Apollo contaminants were greatly reduced by institution of 1) restrictions on materials allowed contact or proximity to samples; 2) isolation of samples in controlled environments; 3) procedures to clean all surfaces in proximity to or contact with samples; and 4) controls on fabrication, processing, and handling of lunar sample hardware.

For laboratory handling operations, measurements of contamination via "monitors" or witness plates were used. Clean coupons of a woven aluminum alloy called York mesh or aluminum foil were processed along with the lunar-bound tools or placed inside the sample cases bound for the Moon. Upon return these coupons were analyzed by solvent extraction and subsequent gas chromatography and mass spectrometry. Aliquots of clean Ottawa sand, exposed inside sample processing cabinets, were analyzed by direct pyrolysis and mass spectrometry. The solvent rinsings from tool, container, and cabinet cleaning were also analyzed. Some of the most frequently encountered contaminants were hydrocarbons from pump oils, and fatty acids. Detected in the vacuum chamber, some of the fatty acids were thought to be from the polishing compound used on the sample cases. Dioctylphthalate, a plasticizer for polyethylene, was ubiquitous in cabinets and bags. Simoneit and Flory [7] provide an extensive list.

York mesh and aluminum foil monitored organic contamination levels of about 1 $\mu g/cm^2$ inside the rock boxes. Bakeout of the Apollo 11 rock box actually added organic contamination, but as a result of the monitoring, cleaning improvements were made which produced flight hardware for Apollo 12 and 13 with only 10-100 ng/cm^2 contamination. With exceptional care, curatorial cleaning procedures during Apollo could produce 1-10 ng/cm^2 contamination ranges for polished, planar surfaces. Simoneit and Flory [7] concluded that organic contamination to lunar samples during Apollo 11 was in the 1 ng/g range, but improved to 0.1 ng/g for Apollo 12.

Long-Term Curation: The lunar sample containers were opened gloveboxes in the LRL, under either vacuum or high purity nitrogen. Splits were removed for preliminary examination and allocation, and the remaining material was sealed in cleaned teflon bags or in metal containers and were stored under nitrogen. Since the construction of the JSC Lunar Sample Laboratory in 1979, all pristine lunar samples have been stored in these containers in positive-pressure nitrogen gloveboxes. All sample processing for allocation to investigators has likewise been conducted in nitrogen-filled gloveboxes. Concentrations of water vapor and oxygen in the gloveboxes are maintained at or below 50 ppm and 20 ppm, respectively. The only materials to come into contact with the samples during processing are teflon and precision-cleaned stainless steel and aluminum. A few samples have been shipped to investigators in polystyrene containers with polyethylene lids. Nylon bags were used briefly as over-bags for a few samples.

The Lunar Sample Laboratory was not designed, nor is it operated, to minimize trace-level organic contamination, and several potential sources have been identified. Recent analyses of the nitrogen gas showed concentrations of toluene and C7 hydrocarbons near 1 ng / l. The samples are processed using rubber gloves with teflon overgloves, and offgassing from the rubber has been detected on witness plates in the lunar sample processing cabinets. Heat sealing of nylon bags has been shown to release the plasticizer caprolactam into the glovebox environment, hence, discontinuation of nylon bag usage.

Lunar soils display a small capacity for adsorption of water (approximately 1500 μg / g) and other gases, but essentially no capacity for absorption [9]. Analyses by Des Marais indicated that terrestrial contamination could account for a significant portion of the organic concentration measured on lunar rocks [10].

Early Organic Analyses of Lunar Samples: The analytical results for lunar samples in the early 1970's were consistent with the estimated contamination levels. Burlingame [11] detected systematic organic contamination of about 5 ng/g for Apollo 11 samples. Reports of organic compounds in lunar fines from other investigators included ng level detection of various compounds [12-14] and 0.5 ppm via pyrolysis [15]. Porphyrin-like pigments were detected at the ng to pg level by Kvenvolden [16] and Hodgson [17, 18]. Amino acids were detected at the 50 ng/g level by Hare [19] and Gehrke [20] after aqueous or other processing to the sub-nanogram level.

Recently Clemett *et al.* [21] detected a suite of simple aromatic species at sub-ppm levels in Apollo 16 soil, using dual laser mass spectroscopy. Some of these compounds are clearly contaminants, while the origin of others remains undetermined.

In summary, the analyzes of Apollo rocks and soils indicate the presence of a variety of organic compounds in trace quantities. However, lunar surface operations and laboratory practices are known to produce a variety of contaminants which may account for much or all of the detected organics.

Sources and Possible Sinks: The most likely source of indigenous organics at the lunar surface is the steady influx of micrometeorites, some of which is known to contain large percentages of organic compounds. However, most of these organics are vaporized during hypervelocity impact. Deposition of these vapors on soil grains might be expected, but subsequent micrometeorite impacts as well as diurnal temperature swings in the lunar vacuum would be expected to release much of this material. Analyses of these processes [22] suggest minimal retention of meteoritic organics on lunar soil grains. However, organic compounds could be concentrated in the cold traps within permanently shadowed lunar craters [23]. A likely place to search for organics in lunar samples may well be in craters near the site of a lunar polar outpost.

References: [1] Allton J. H. *et al.* (1998) *Adv. Space Res., 22*, 373-382. [2] Oyama V. *et al* (1970) *Apollo 11 LSC*, 1921-1928. [3] Oyama V. *et al* (1971) *LSC2*, 1931-1938. [4] Taylor G. *et al* (1971) *LSC2*, 1939-1938. [5] Allton J. H. (1998) *LPS XXIX*, Abs. # 1857. [6] Allton J. H. (1989) *Catalog of Apollo Lunar Surface Geological Sampling Tools and Containers*, JSC-23454, NASA JSC, Houston, TX. [7] Simoneit B. and Flory D. (1970) *Apollo 11, 12, & 13 Organic Contamination Monitoring History*, UC Berkeley report to NASA. [8] Aronowitz (1966a,b) *Investigation of Lunar Surface Chemical Contamination by LEM Descent Engine and Associated Equipment*, Grumman RE 237 & 242. [9] Cadenhead D. A. *et al.* (1972) *LSC 3rd*, 2243-2257. [10] DesMarais D. J. (1978) *LPS IX*, 2451-2467. [11] Burlingame A. *et al* (1970) *Apollo 11 LSC*, 1779-1792. [12] Murphy M. *et al* (1970) *Apollo 11 LSC*, 1879-1890. [13] Preti G. *et al* (1971) *LSC2*, 1879-1890. [14] Henderson W. *et al* (1971) *LSC2*, 1901-1912. [15] Oro' J. *et al* (1970) *Apollo 11 LSC*, 1901-1920. [16] Kvenvolden K. *et al* (1970) *Apollo 11 LSC*, 1813-1828. [17] Hodgson G. *et al* (1970) *Apollo 11 LSC*, 1829-1844. [18] Hodgson G. *et al* (1971) *LSC2*, 1865-1874. [19] Hare P. *et al* (1970) *Apollo 11 LSC*, 1799-1804. [20] Gehrke C. *et al* (1970) *Apollo 11 LSC*, 1845-1856. [21] Clemett S. J. *et al.* (2005) METSOC 68^{th}, Abs. # 5300. [22] Thiemens M. H. and Clayton R.N. (1980) *LSC XI*, 1435-1451. [23] Vondrak R. R. and Crider D. H. (2003) *Amer. Sci., 91,* 322-329.