The Moon: Biogenic Elements

## E. K. Gibson, Jr. and S. Chang

Among the highest research priorities for life sciences in space is the search for extraterrestrial life and for the fundamental understanding of life's origins. This search, coupled with the investigation of the origin and evolution of the solar system, constitutes the essential element of a quest for a "cosmic perspective" for humankind; a quest that may illuminate our long evolutionary path from elemental origins in the primal fireball, to formation of galaxies, through interstellar dust clouds, solar systems, and planets (inorganic chemical evolution), to the first stirrings of life in the Earth's primitive oceans (organic chemical evolution), and the beginnings of biological evolution. Humanity's explorations of the cosmos are essential steps in the development of this new perspective.

The origin and evolution of life is tied to the conditions of primitive planetary environments. Throughout the history of the space program it has been assumed that there is a connection between evolutions of life and planets. Until humans went to the Moon in 1969, the only extraterrestrial material available for study was the meteorites which fall randomly on the Earth. The early search for direct evidence of life and/or organic chemical
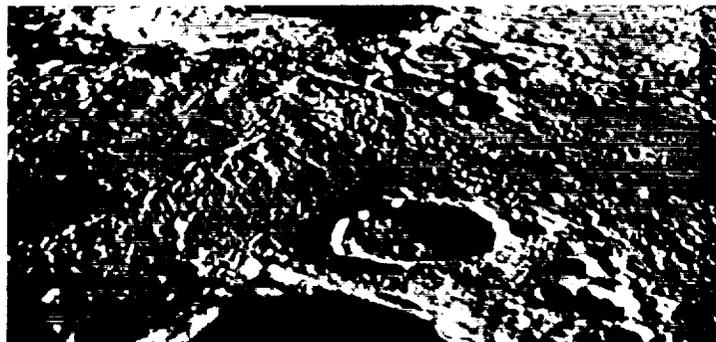
evolution in extraterrestrial bodies was limited to Earth-bound laboratory studies of meteorites; no evidence of extraterrestrial life was detected, and terrestrial contamination confounded any adequate assessment of the real significance of organic compounds isolated from meteorites. Since then, the organic chemical analyses of meteorites and the study of the interstellar medium through radio telescopes have revealed the presence of organic compounds of unambiguous extraterrestrial origin, thereby providing clear evidence that organic chemistry occurred or does occur elsewhere in the solar system and cosmos.

The specific objectives of the organic chemical exploration of the Moon involve the search for molecules of possible biological or prebiological origin. Detailed knowledge of the amount, distribution, and exact structure of organic compounds present on the Moon is extremely important to our understanding of the origin and history of the Moon, and to its relationship to the history of the Earth and solar system. Specifically, such knowledge is essential for determining whether life on the Moon exists, ever did exist, or could develop. In the absence of life or organic matter, it is still essential to determine the abundance, distribution, and
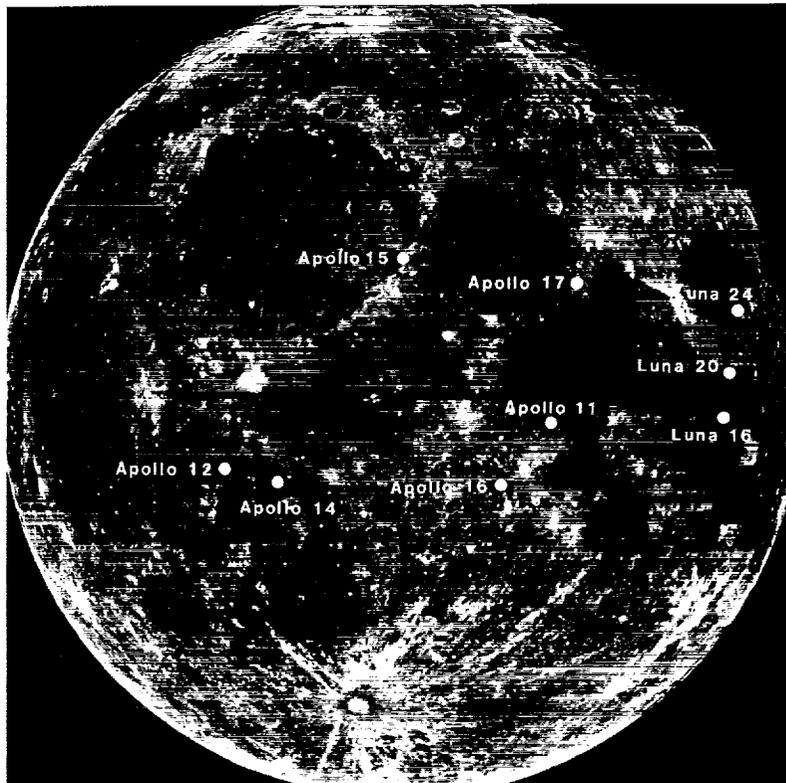

Figure 2-1. Map of the Moon showing the Apollo and Luna landing sites where samples were collected and subsequently returned to Earth for detailed study.

origin of the biogenic elements (e.g., H, C, O, N, S, P) in order to understand how the planetary environment may have influenced the course of chemical evolution.

During the early 1960s various investigators suggested that the lunar surface might contain elevated carbon concentrations and even abundant organic matter. The first direct measurement of a possible carbon abundance for the lunar surface was obtained by the Surveyor missions which soft-landed spacecraft on the lunar surface during 1966-68. On board three of the Surveyor probes were alpha back-scattering instruments which measured between 0.2 and 0.9 ± 0.2% carbon. However, the analytical error in the measurements was so large that a true carbon abundance for the lunar surface remained unknown until the return of samples by the manned Apollo missions.

30

From 1969 through 1976 samples were returned from nine sites on the Moon (fig. 2-1). The six Apollo sites offered samples collected from a wide variety of localities by the twelve astronauts. The Soviet Luna program landed three automatic sample collecting robots which collected soil samples with a drill located at the base of the landers, and subsequently returned the samples to Earth. The six Apollo lunar missions returned 2,196 samples, weighing a total of 381.69 kg (841 pounds). The three Luna missions from the Moon returned three core samples with a combined weight of 300 gms (0.6 pounds). The lunar samples were examined in pristine laboratories prior to release to investigators throughout the world for detailed study (fig. 2-2).

Within the Lunar Receiving Laboratory (LRL) and other laboratories, over 3,000 tests for viable organisms were carried out with different nutrient media, at various temperatures, and in different atmospheric mixtures of oxygen, carbon dioxide, and nitrogen. No viable life forms were found, not even terrestrial contaminants. Micropaleontological studies of the lunar soils gave no evidence of structures resembling terrestrial microfossils that could be attributed to past biota. In retrospect the noted astronomer, C. Huygens, was correct when he wrote in 1757 that, "the Moon has no air or atmosphere surrounding it as we have, [and I] cannot imagine how any plants or animals whose whole nourishment comes from fluid bodies can thrive in a dry, waterless, parched soil."

Figure 2-2. Lunar Receiving Laboratory scientist examining a large Apollo 14 sample. Extreme care was used in the processing of samples so that minimal contamination was introduced. Stainless steel, aluminum, and teflon were the only materials which came in contact with the samples in a sample processing cabinet filled with purified dry nitrogen. Despite such precautions, contamination by terrestrial carbon and other elements still occurred. When extreme precautions were taken to prevent contamination of the lunar samples, clean samples were delivered to the principal investigators. For example, quantities of carbon as small as 1 microgram were measured in lunar rocks and this work assisted in identifying a spallation carbon component present in lunar materials.
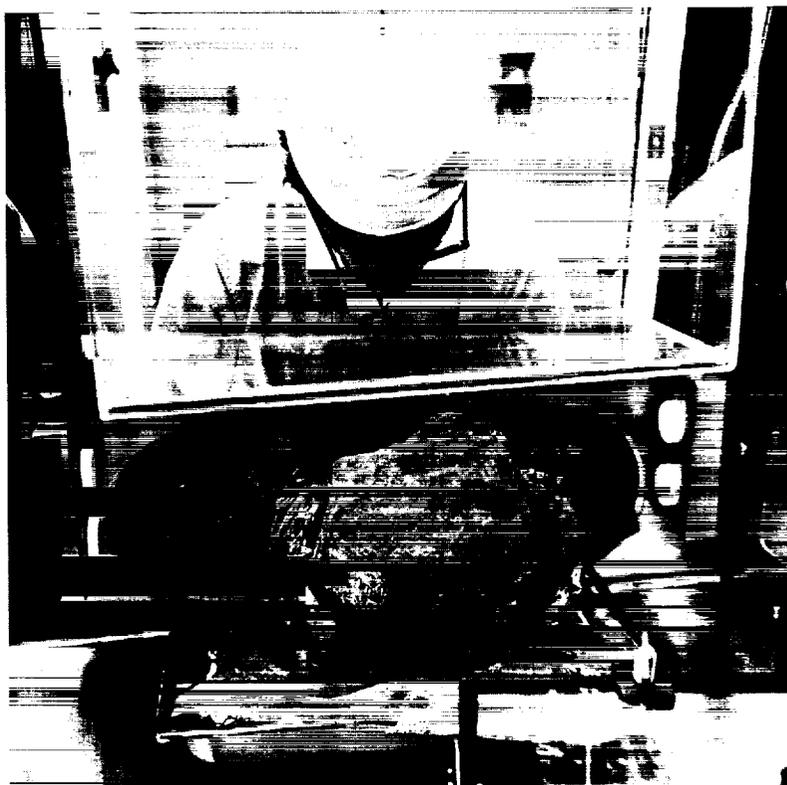
The detailed analysis for organic compounds involved the separation of minute quantities of organic constituents from the inorganic lunar sample matrix, separation of the resulting mixtures by various types of chromatography into classes of compounds such as acidic, basic, and neutral, polar and non-polar, followed by separation of each group into individual components. Instrumental techniques sensitive to the parts per billion (ppb) level were employed to determine the detailed structures and amounts of the resulting compounds.

Extensive studies carried out on returned lunar samples to find complex organic compounds which might be precursors for biochemistry failed to obtain any unequivocal evidence of such species at the ppb level. The parts per million (ppm) amounts of high molecular weight hydrocarbons extracted from lunar soils in several instances were apparently not of lunar origin, but could be accounted for as contaminants introduced during laboratory processing of the samples. Methane and the simple C_2 and C_3 hydrocarbons have been found in trace amounts in lunar soils. The methane, at least, is believed to be of lunar origin (see below). The ppb amounts of amino acids found in lunar soils were not indigenous to the Moon, but

were produced during the analyses from trace amounts of chemical precursors of amino acids. Follow-on tests suggested that these precursors were contaminants present as rocket exhaust products within the lunar soils. These results led to the conclusion that if synthesis of complex organic compounds ever occurred on the Moon, very little evidence remains. Nonetheless, C, H, and N are found in lunar samples, and intensive study of distributions and origins of these elements has shown them to be of extralunar origin.

L unar soils have carbon abundances ranging from 4 to 280 ppm by weight (table 2-1). The average total

carbon for 178 lunar soils from 6 Apollo missions is 115 ppm, while the mean is 78 ppm C for 57 breccias (formed by impact heating and compaction of lunar soils), and 10 crystalline rocks contained on the average less than 2 ppm. The work on crystalline igneous rocks using stepwise oxidation and isotopic measurements (see below) showed that the Moon as a whole is strongly depleted in carbon, as it is in all other volatiles including some metallic elements. Apparently, abundance data for carbon in lunar rocks reported by others, primarily reflected the presence of terrestrial contaminants.

Table 2-1: Lunar Biogenic Element Abundances (in parts per million)			
	Soils	Breccias	Rocks
Hydrogen			
Range	3.2-60	12-48	1.2-3.8
Mean	40	68	2.1
Carbon			
Range	4-280	30-250	0.1-3
Mean	115	78	1.5
Nitrogen			
Range	7-164	16-181	1-6
Mean	82	68	3
Sulfur			
Range	290-1400	20-2250	20-2800
Mean	850	756	1950 basalts 300 anorthosites

The carbon concentration in any soil is dependent upon its exposure history while on the lunar surface. Immature lunar soils (short exposure time) generally have carbon contents below 40 ppm. The unusual and highly immature orange soil from Apollo 17, which has been shown to be a volcanic glass, contains a wide range of carbon (4 to 100 ppm), but the variability probably reflects different amounts of terrestrial contaminants rather than differences in adsorbed carbon from lunar volcanism. Soils characterized as mature by various indices of exposure on the lunar surface such as solar wind argon content, exposure age, and agglutinate content (see below) contain the highest carbon contents.
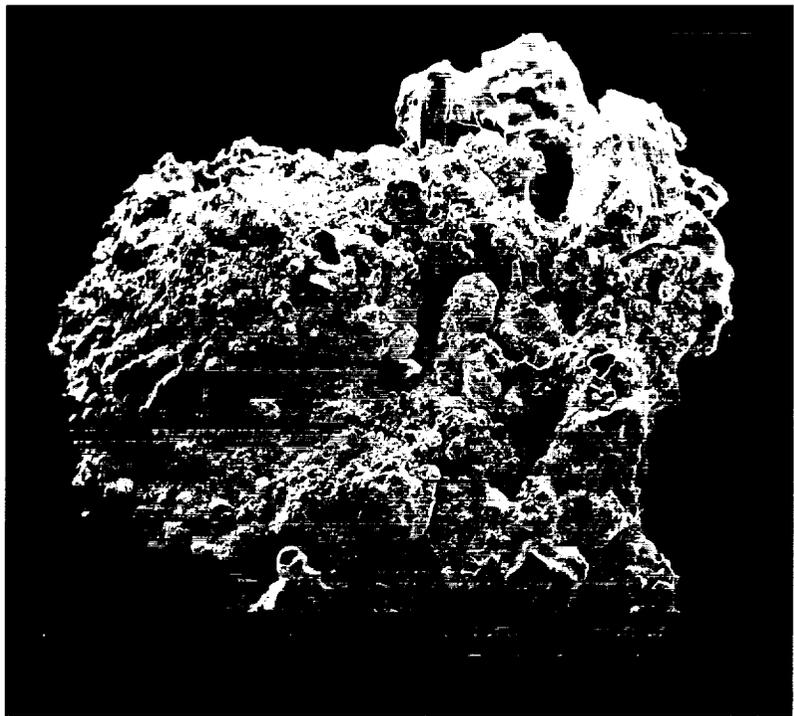

Figure 2-3. Photomicrograph of a lunar agglutinate particle. The agglutinate is a constructional particle produced during micrometeorite and/or meteorite impact on the lunar surface. The particle consists of lithic, mineral, and glassy debris bonded together by an inhomogeneous glass. The particle is approximately 1 mm in size.

Selected lunar soils have been separated into their individual components and studied for their carbon contents. Within a lunar soil, agglutinates (glassy components consisting of fine-grained, comminuted rock, mineral, and glass fragments bonded together with glass) produced during meteorite or micrometeorite impacts (fig. 2-3) contain the highest carbon concentrations. The breccia fragments contain intermediate amounts, while the individual mineral grains contain the least carbon. In soil components separated by grain size, the highest concentrations of carbon occur in the smallest grains, and the concentrations are inversely correlated with grain size indicating that the accumulation of carbon is related to the surface area of the grains.

Carbon at the lunar surface is contained primarily in the fine-grained material of the regolith where layers of dusty ejecta have accreted over time as a result of meteoritic impacts (fig. 2-4). The present distribution of carbon and other volatile elements in the regolith is a consequence of a dynamic equilibrium between addition and loss processes associated with solar radiation and meteorite

bombardment (fig. 2-5). The lunar carbon cycle is governed by these regolith processes, in contrast to the carbon cycle on Earth which is mediated by volcanism, sedimentation, and biological activity. Since crystalline rocks contain only a few ppm carbon at most, and a significant atmosphere cannot have been retained on the Moon, indigenous lunar sources such as volcanism and the attrition of the crystalline rocks cannot have contributed much to the content of the soils. Indeed, the preponderance of data so far (see below) supports the view that carbon is contributed primarily from sources outside the Moon such as the solar wind, meteorites, and comets. Among these sources, the evidence favors the solar wind on the basis of isotopic composition and because hypervelocity ($\geq$11 km/s) impacts of meteorites and comets with the Moon are expected to vaporize the projectile and some of the target with subsequent loss of the gases to space. Possibly the interaction of the solar wind with this pulse of gases may result in charge exchange and reimplantation of a small fraction of the vaporized material into the surface of grains in the regolith. Some estimates place the contribution of meteoritic or cometary carbon to a mature lunar soil at 5 to 10 ppm.

The solar wind is a stream of charged particles (mainly ionized hydrogen with the other elements in their solar abundances) moving outward from the Sun with velocities in the range 300-500 km/sec. For every 7,500 hydrogen nuclei in the solar wind, there is one carbon nucleus. The ionized particles interact
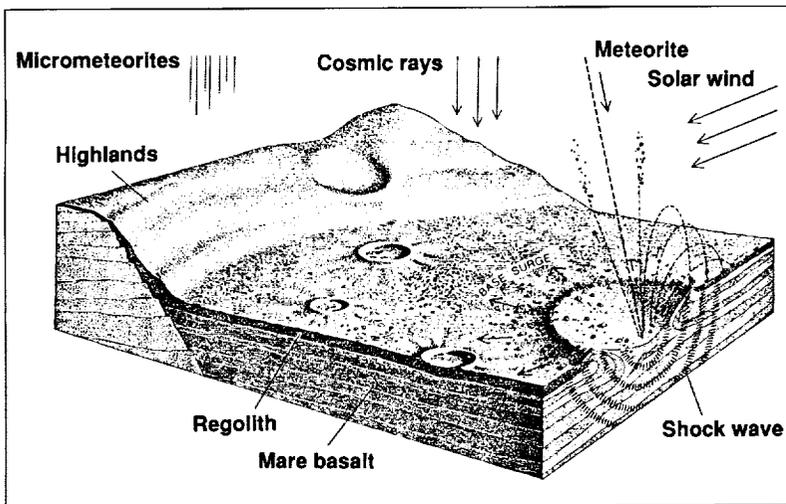
Figure 2-4. Processes of erosion on the surface of the Moon are extremely slow compared with the processes on Earth. Bombardment by micrometeorites is the main cause, removing approximately 1 mm of the surface of the rocks in a million years. A large meteorite strikes the lunar surface very rarely, excavating bedrock and ejecting it over thousands of square kilometers, sometimes as long rays of material radiating from the resulting crater. Much of the meteorite itself is vaporized on impact, and larger fragments of the debris create secondary craters. Such an event at a mare site pulverizes and churns the rubble and dust that form the regolith. Accompanying base surges of hot clouds of dust, gas, and shock waves might compact the dust into breccias. Cosmic rays continuously bombard the surface. During lunar day ions from the solar wind and unshielded solar radiation impinge on the lunar surface. (After Eglinton et al., 1972.)

Impact of comets and meteorites | Solar wind | Loss to space

Atmosphere — Incorporation — Volatilization — Implantation — Erosion — Volcanic gases (?) — Sputtering — Reimplantation (?) — Regolith

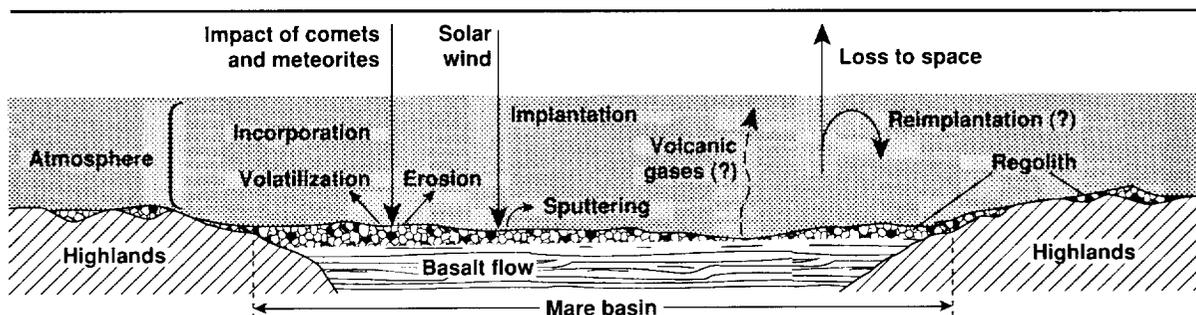Highlands — Basalt flow — Highlands

|← Mare basin →|

Figure 2-5. Biogenic elements at the lunar surface are contained primarily in the regolith of the maria and in the lunar highlands where layers of dust have slowly accreted. It is not expected that layers of coarse ejecta contain much carbon or biogenic elements, and the crystalline igneous and highlands anorthositic rocks contain only a few parts per million of the biogenic elements. The present distribution of carbon and other biogenic elements in the regolith is a consequence of a dynamic equilibrium. Hydrogen, carbon, and nitrogen are contributed from sources outside the Moon such as the solar wind, meteorites, and comets, and from lunar sources such as volcanism and the attrition (wearing down) of the crystalline rocks. Possibly some of the carbon released into the tenuous lunar atmosphere produced by sputtering or volatilization of impacting projectiles is reimplanted. The biogenic elements hydrogen, carbon and possibly nitrogen are lost to the atmosphere by diffusion, erosion and volatilization. They are constantly lost from the Moon to space, sometimes very rapidly, as during the impact of a meteorite. The volatile element abundances of the lunar soils measured now represent the end result of more than three billion years of these processes. The dust of the lunar maria may be regarded as both the reservoir and the reaction site for the biogenic elements at the surface of the Moon. (After Eglinton et al., 1972.)

directly with the lunar surface and are imbedded into the outer portions (i.e., 500 angstroms thickness) of lunar soil components and rocks which are exposed to the Sun. Solar wind irradiation of planetary surfaces occurs only if the planetary body does not have a magnetic field of sufficient strength to deflect the charged particles and its atmosphere is too thin to stop the ions. (Earth's magnetic field is sufficient to deflect the solar wind.) Interaction of the solar wind with the lunar soils and rocks has enriched the surfaces of these materials in carbon, nitrogen, and hydro-

gen (fig. 2-6), and some mature soils may have attained an apparent solar wind carbon saturation level of about 200 ppm C. Conclusions regarding the role of solar wind are based only in part on the evidence cited above, namely, the direct correlation of the abundances of these biogenic elements in lunar soils with the surface area of the soils, their exposure histories, and with solar wind implanted rare gas abundances.

Data on the range of isotopic compositions for carbon in lunar samples (table 2-2) reflect several sources of the element, including terrestrial contamination. Values of $\delta^{13}C$ that fall within the range for terrestrial organic matter, −35 to −10 per mil, are highly suspect and indicative of major contributions from terrestrial contamination. Note, however, that bulk carbon isotopic compositions of meteorites lie typically in the range −25 to −5 per mil, making it difficult to distinguish isotopically between a

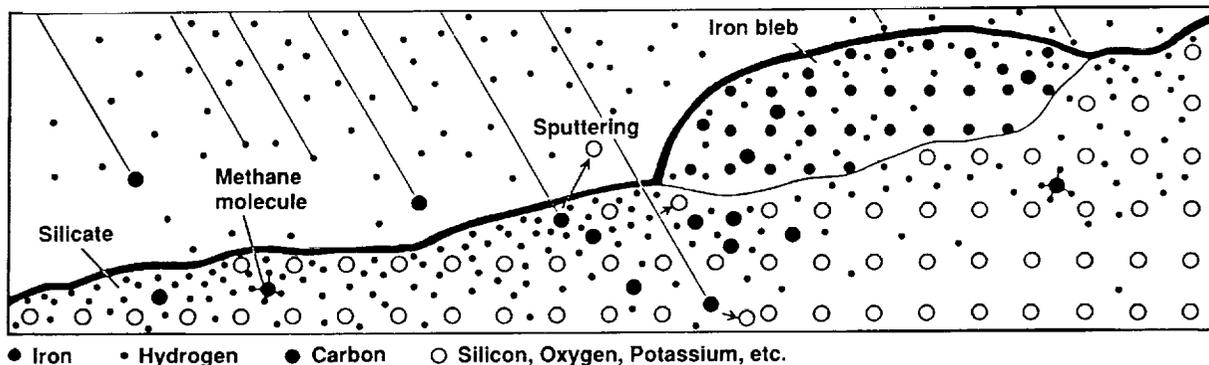● Iron　● Hydrogen　● Carbon　○ Silicon, Oxygen, Potassium, etc.

Figure 2-6. Solar wind plays an important role in the carbon chemistry of the lunar surface. An area of lunar soil is enlarged some 10^8 times to show a silicate grain with an iron bleb adhering to it. Carbon atoms implanted by the solar wind could be converted to methane by the vast excess of hydrogen in the solar wind. Damage to the crystalline structure of the silicate creates defects and voids that accommodate the gas and allow some compounds to escape by diffusion. Hydrocarbons containing two carbon atoms are probably generated as well with decreased efficiency. Carbon ions implanted into the iron bleb might react chemically to form the carbide-like species in lunar soils which on treatment with deuterated mineral acids yield deuterated hydrocarbons. Other elements in the solar wind, such as nitrogen, oxygen, and rare gases, are simultaneously implanted to a depth of a few hundred angstroms. (After Eglinton et al., 1972.)

meteoritic and terrestrial source. Positive values for soils, however, appear to reflect a non-terrestrial, non-meteoritic component of probable solar wind origin. The several ppm methane observed in lunar soils and believed to have been produced in soils by solar wind irradiation (see below) exhibited positive $\delta^{13}C$, including the highest (+46 per mil) found thus far in a naturally occurring organic compound. The very high positive $\delta^{13}C$ values in rocks coupled with their extremely low abundances reflect the production of carbon in their interiors by cosmic ray spallation reactions.

In conjunction with analyses of lunar samples, solar wind simulation experiments involving ion irradiation of lunar materials and terrestrial analogues were carried out. These simulation experiments together with sample analyses provide persuasive evidence of the role of solar wind in the chemistry of the biogenic elements on the Moon. Some experiments were designed to determine the molecular forms in which isotopically labeled ions (e.g., D^+, $^{13}C^+$, $^{15}N^+$) injected into samples at

solar wind energies would be extracted and the temperatures over which such extraction occurred during vacuum pyrolysis. These experiments showed that carbon was evolved predominantly as ^{13}CO with minor amounts of $^{13}CO_2$, and nitrogen was evolved as $^{15}N_2$. Each of these labeled species exhibited essentially the same pattern of gas release over the 400-1300°C range as did the respective unlabelled gas that was derived from the indigenous carbon and nitrogen in the lunar soils. When extracted by vacuum pyrolysis, CO, CO_2, and N_2 accounted for all but a few percent of the total carbon

and nitrogen in a lunar soil, a finding that is at least consistent with a solar wind source for most if not all of these elements.

In other experiments, serial irradiations with $^{13}C^+$ and D^+ ions led to production of ppm amounts of multiply labeled methane whose pattern of release from the

artificially irradiated samples by heating under vacuum was the same as that of both the unlabeled methane extracted from lunar soils and the solar wind implanted noble gases. Apparently, solar wind irradiation can result not only in the retention of chemically bound species of carbon and nitrogen in the mineral matrix, but also the synthesis and trapping of the simplest of organic compounds, thus accounting for the methane and possibly other low molecular weight hydrocarbons found in lunar soils.

The nature of the chemically bound carbon in the soils is not entirely understood. About 5 to 30% of this carbon can be released by deuterated mineral acids in the form of simple C_1 to C_3 hydrocarbons containing deuterium. This behavior is similar to that exhibited by some carbide minerals and by carbon dissolved in metallic iron. In these experiments with deuterated acids, the trapped solar wind synthesized methane is released in undeuterated form. The carbon of the deuterated hydrocarbons is typically enriched in ^{13}C relative to average terrestrial and meteoritic carbon and is characterized by positive $\delta^{13}C$ values

Table 2-2: Isotopic Compositions of Lunar Soils and Rocks(δ- Values in per mil)*		
	Soils	Rocks
Hydrogen		
Range	-115 to -807	-10 to -97
Carbon		
Range	-35 to +46	-35 to +64
Nitrogen		
Range	-90 to +96	0 to +62
Sulfur		
Range	+6 to +11	-2 to +2.5

*For hydrogen,

$$\delta D = \frac{(D/H)_{sample} - (D/H)_{standard}}{(D/H)_{standard}} \times 10^3$$

Standard = standard mean ocean water

*For carbon,

$$\delta C = \frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}}{(^{13}C/^{12}C)_{standard}} \times 10^3$$

Standard = Peedee belemite limestone

*For nitrogen,

$$\delta N = \frac{(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{standard}}{(^{15}N/^{14}N)_{standard}} \times 10^3$$

Standard = air

*For sulfur,

$$\delta S = \frac{(^{34}S/^{32}S)_{sample} - (^{34}S/^{32}S)_{standard}}{(^{34}S/^{32}S)_{standard}} \times 10^3$$

Standard = Canyon Diablo meteorite troilite

(+5 to +20 per mil) comparable to those of the uncontaminated bulk soils. This non-volatile, carbide-like carbon, like the bulk of the remaining uncharacterized carbon, is converted by pyrolysis (see above) to CO (predominantly) and CO_2 with isotopic compositions in the same range. The similarity in isotopic composition of the trapped gas, the carbide-like species and the remaining carbon, which may be trapped interstitially in minerallic, metallic, or glassy phases, argues strongly for a predominant contribution from a common source, that is, the solar wind.

The release of carbon mostly as CO rather than CO_2 during pyrolysis probably reflects the highly chemically reduced nature of the lunar soils due to the presence of metallic iron (fig. 2-6). Unlike terrestrial basalts, lunar basalts also contain metallic iron and are, therefore, highly reduced. If any carbon-containing magmatic gases accompanied the lavas that flowed across the Moon's surface, they too would have been dominated by CO. In contrast, CO_2 is predominant in terrestrial volcanism. If the Moon ever had a thick atmosphere produced by global outgassing, the reduced chemical composition of the atmosphere would have been conducive to the synthesis of organic matter. This conclusion is based on the highly successful results of Miller-Urey type experiments designed to simulate chemical evolution in Earth's prebiotic atmosphere. No evidence of such synthesis has been found in lunar samples.

Instead, any organic chemical synthesis or high pressure hydrogenation reaction that occurs on the Moon results from ion-molecule chemistry driven by the interaction of solar wind ions with mineral grains, and only simple hydrocarbons are produced within a thin surface layer of the grains. Such synthesis could also occur on the surfaces of bodies in the asteroid belt and satellites of the outer planets. A related process could also be operating in the upper atmosphere of Titan where solar wind interactions with gases could lead to synthesis of organic compounds. Moreover, the organic chemistry of interstellar clouds is thought to arise from ion-molecule reactions driven by cosmic ray interactions with gas and dust. Thus, the limited organic synthesis occurring on the Moon is but one manifestation of a type of physical-chemical process that occurs throughout the cosmos.

Although the effects of another widely occurring process, bombardment of planetary surfaces by meteorites and comets, have not left a clearly discernible imprint in carbon and other biogenic elements on the Moon (see below for sulfur and phosphorus), there are several reports of lunar samples containing small amounts of water and other volatiles which might be interpreted as vestiges of impacting objects. For example, several rocks from Apollo 16 contained the minerals goethite and lawrencite typically associated with rust. The formation of these minerals from water in terrestrial laboratories was also possible. One of the immature soils collected from the rim of Flag crater at the Apollo 16 site and sieved in the LRL to remove coarser than mm-sized particles was found to contain an unusual amount (up to 100 ppm) of HCN, CH_4, and H_2O. It was suggested that the soil contains the remnants of volatiles associated with a cometary impact. Such high abundances of volatiles, however,

were not found in an unsieved sample of the same soil. These findings leave unresolved the question of direct evidence for cometary volatiles in lunar soils, but they do raise another interesting question. The time interval of cosmic ray exposure of the soils at the Apollo 16 site, where the putative "cometary components" were found, is similar in age to that of the K-T boundary on the Earth. Could this possibly suggest that on the Moon a record of cometary impacts might be found to correlate with those hypothesized to have been responsible for the extinction of the dinosaurs and other biota 65 million years ago?

The average nitrogen content found in 85 lunar soils was 82 ppm with a range of 7 to 164 ppm; immature soils contain less than 40 ppm N (table 2-1). Lunar breccias have an average of 68 ppm N with a range of values between 16 and 181 ppm N. Lunar rocks averaged 3 ppm N and ranged between 1 and 6 ppm. Early workers suggested that nitrogen abundances for lunar rocks were a factor of 10 greater but it has since been shown that the higher abundances resulted from terrestrial contamination of the samples, despite the precautions taken. Nitrogen contents of lunar soils are proportional to the carbon contents of the same soil. As for carbon, the data for nitrogen indicate that most of the nitrogen in lunar soils originated in the solar wind. The total nitrogen content of lunar soils was found to be proportional to the solar wind ^{36}Ar and H. It was shown that the grain size separates of lunar fines indicate that the highest concentrations of nitrogen reside in the particles with the greatest total surface area (per unit mass) or smallest grain sizes. Because the retention of solar wind nitrogen in lunar materials was found to be highest of any solar wind component, the nitrogen content has become a useful indicator of soil maturity.

J ohn Kerridge of the University of California at Los Angeles showed that the solar wind nitrogen, implanted in lunar soils, exhibits isotopic variations that are related to the time, although not to the duration, of implantation, with earlier samples characterized by lower ratios of ^{15}N to ^{14}N (table 2-2). The increase in the solar ^{15}N content of lunar materials during the lifetime of the lunar regolith was probably caused by spallation of ^{16}O in the surface of the Sun (fig. 2-7). From the study of the isotopic composition of the nitrogen present within the lunar regolith, the early history of the Sun might be tracked.

The hydrogen distributions in lunar materials are similar to those of carbon and nitrogen, and are predominantly attributable to a solar wind origin. The isotopic composition of the hydrogen (table 2-2) shows a depletion of deuterium in the lunar materials consistent with a solar source. The finite abundance of deuterium, however, must be attributed to terrestrial contamination or a meteoritic contribution; the solar wind is free from deuterium and thus would not contribute to its abundance. Hydrogen abundances are directly related to length of time of surface exposure to the solar wind. The greatest hydrogen abundances are found in the finest grain size fractions of the soils. For example, the sub-45 micrometer grain size fraction of a mature lunar soil contains between 40 and 145 ppm hydrogen. Hydrogen concentrations for bulk lunar soils range from 3.2 to 60 ppm. Mature lunar soils typically contain greater than 50 ppm H. The lowest hydrogen concentrations are found for immature lunar soils. The hydrogen abundances are correlated with the soil maturity index, I_s/FeO (an indicator of the fine-grained
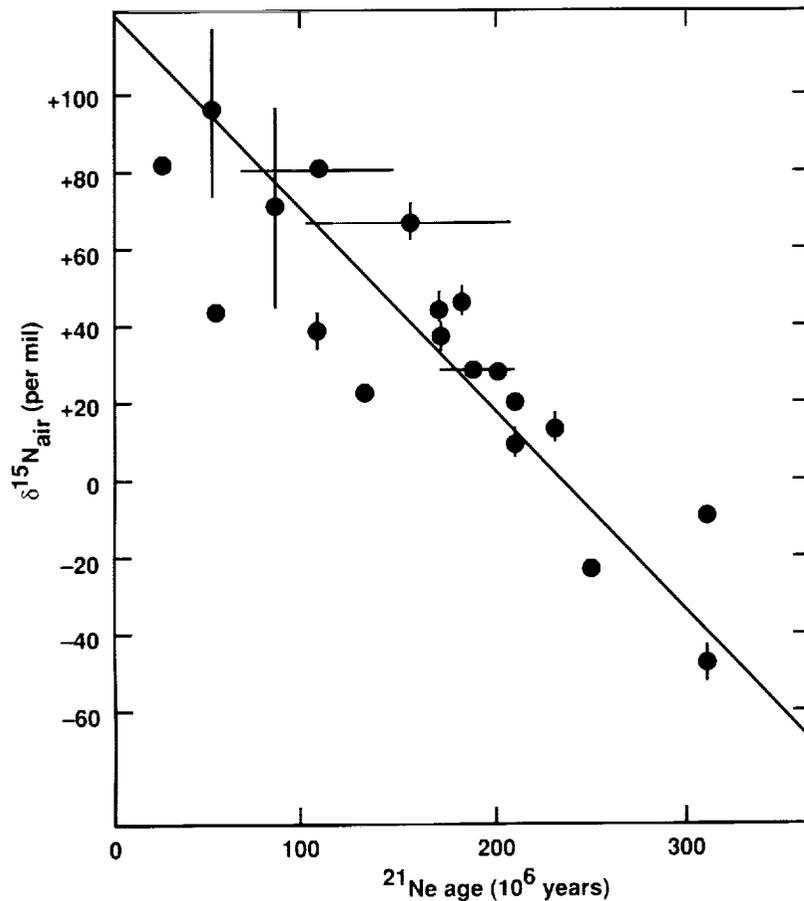
Figure 2-7. The isotopic ratio of ^{15}N to ^{14}N (represented by $\delta^{15}N$) values for Apollo 16 soil samples show a strong negative correlation with the cosmic-ray exposure ages. Kerridge has suggested that the solar abundance of ^{15}N has increased during the history of the Sun. In the solar interior ^{15}N is burned before ^{14}N. The observation that the abundance of ^{15}N has increased with time in the surface of the Sun shows that convective mixing involving the deep interior of the Sun has been insignificant. In addition, the apparent lack of lunar fractionation in nitrogen is consistent with highly efficient retention of this element on the lunar surface.

metallic iron present in the soil which results from micrometeorite impact processes). Supposedly, the heat released during impacts causes the solar wind hydrogen in the soil to reduce small amounts of ferrous iron in the minerals to metallic iron.

nderstanding the hydrogen abundances and distributions in lunar materials is important if hydrogen is to be used as a consumable or propellant at a future lunar base (fig. 2-8). Hydrogen is also required for the ilmenite

(FeTiO$_3$) reduction process proposed for the production of oxygen at a lunar base. Water, the by-product of the reduction process, can be electrolyzed to produce both oxygen for use in the habitats and hydrogen for use again to reduce additional ilmenite.

Total sulfur abundance measurements along with isotopic ratio measurements of lunar soils have shown significant variations between lunar soils, breccias, and rocks. Lunar soils from Apollo 11, 12, 15, and 17 are depleted in their total sulfur content relative to the mare basalts found at each landing site. The dominant form of sulfur in lunar materials is the mineral troilite, FeS, although trace quantities of other metal sulfides have been reported. The total sulfur content of lunar soils from all of the Apollo missions has been accounted for by mixing models based upon the sulfur contribution from individual components found in the lunar fines at a particular sample site. Addition of sulfur to the lunar regolith from meteorite infall is not needed to account for the observed sulfur abundances. Carbonaceous chondrite meteorites (Type I) contain up to 6% total sulfur. For any lunar mixing model, large amounts of sulfur cannot have been

added to the lunar surface from meteorites (or the total sulfur content of the soils would be too much to be accounted for by the mixing models) unless some major loss mechanism for sulfur has operated.

The average total sulfur content of lunar soils is 850 ppm (192 samples analyzed) with a range of between 290-1400 ppm. Lunar highland soils have the lowest total sulfur abundances (between 290 and 600 ppm). The isotopic composition of the sulfur (table 2-2) associated with lunar soils is isotopically heavy (ranging from +6 to +11 per mil) relative to the meteorite troilite standard. The enrichment has been attributed to the loss of the isotopically light sulfur phases present in the surface materials during reaction with the solar wind hydrogen to form H_2S during micrometeorite bombardment and surface cratering processes. The mean sulfur content of 96 lunar breccias is 756 ppm with a range of 20 to 2250 ppm. Lunar crystalline rocks range in sulfur content between 20 and 2800 ppm (92 samples) with a mean value of 1085 ppm. Anorthosite samples from the lunar highlands or early lunar crust contain the least amounts of sulfur (below 300 ppm) while the mare basalts from Apollo 11 and 17 contain the greatest amounts of sulfur (mean values of 2033 and 1860 ppm, respectively). The sulfur contents of the lunar basalts

Figure 2-8. Surface operations at a lunar base. Two future lunar astronauts are shown overlooking the lunar base habitat and surface mining operations. (NASA-JSC Photograph S86-27256, Artwork by Dennis Davidson.)

are almost 10 times greater than values seen from terrestrial subaerial basalts. A comparison of the sulfur abundances of lunar basalts with submarine basalts shows that lunar samples are enriched two to four times those of terrestrial basalts which contain the greatest amounts of sulfur. This suggests that the source regions where the lunar basalts were formed contained greater amounts of sulfur than those of terrestrial basalts. The isotopic composition of the sulfur associated with lunar crystalline rocks is remarkably constant (ranging from –2 to +2.5 per mil) and similar to the reference meteoritic troilite standard (table 2-2) in contrast to other objects within our solar system.

Phosphorus is present in all lunar samples in trace amounts. For most lunar basalts the range of P contents is quite limited, being about 200 to 900 ppm. The major phosphorous-bearing phase is apatite, $Ca_5(PO_4)_3(F,Cl)$,

although whitlockite, $Ca_3(PO_4)_2$, is also present along with traces of meteoritic schreibersite $(Fe,Ni)_3P$. Lunar highland samples may contain the phosphorous-bearing KREEP (potassium, rare Earth elements, and phosphorous) glass which contains a relatively high phosphorous content of around 0.33% by weight.

The experience with lunar samples has shown clearly the great scientific insight that can be gained by making high-precision measurements on Earth of material returned from other solar system bodies. The variety of techniques which can be used for sample preparation and analysis has increased immensely, and studies in terrestrial laboratories offer the maximum flexibility for designing new experiments or modifying sample preparation to clarify ambiguous results and optimize scientific return. Moreover, as was the case for lunar samples, new analytical techniques developed after the return of extraterrestrial samples can be brought into play. Clearly, study of samples from Mars or comets in terrestrial laboratories will afford data far superior in quality and quantity to that obtainable by any remote analysis on a distant planet.

After nearly two decades of studying the lunar samples some major questions remain which are related to the history and evolution of the biogenic elements during lunar history. Briefly, some of the important questions are: Can the severe depletion of biogenic elements and other volatiles in the Moon be accounted for by an impact origin for the Moon? What is the exact composition of the volcanic gases and volatiles, if any were associated with the lunar magmas which poured out onto the lunar basins? What are the volatiles associated with the young volcanic vents observed in several regions of the lunar maria basins? Are there sinks for the lunar volatiles at the poles and permanently shadowed regions of the Moon? What are the concentrations of OH^-, H_2O, and methane associated with the surfaces of lunar grains resulting from the solar wind irradiation of the lunar surface? What are the production and loss rates of the simple molecules such as methane produced by solar wind irradiation? Are there regions on the lunar surface where the remnants of cometary impacts can be

observed and studied? Is there a record of periodic bombardment of the lunar surface by comets or asteroids that might be correlated with similar processes on Earth? How can the lunar regolith or soil be converted to a medium which will support plant growth or other food production processes in association with a lunar base? Many of these questions may best be addressed by further exploration of the Moon, including the return of materials from previously unsampled regions and the conduct of experiments on the lunar surface.

The miniscule amount of organic matter in lunar surface materials and the absence of any life forms are consistent with findings that the lunar surface has undergone melting events and eons of solar and cosmic radiation and meteorite impacts under conditions of high vacuum. These processes appear to have obliterated all traces of any primitive organic synthesis on the lunar surface. Yet, carbon and carbon-containing compounds indeed are found in the samples. They signify that chemical evolution, though severely constrained by the lack of atmosphere and the depletion of volatiles on the moon, has in fact proceeded to a very limited extent and is due virtually entirely to solar wind interactions with the lunar surface. Thus, the Apollo and Luna missions have afforded unique oppoprtunities to study aspects of the chemistry of carbon and the other biogenic elements which have no natural counterparts on Earth. The analyses of lunar samples by organic and analytical chemists became not only searches for compounds related to terrestrial biochemicals, but also primarily studies of lunar chemical evolution and fundamental aspects of the cosmo-chemistry of the biogenic elements. This is only fitting if one realizes that the Sun has been the dominant factor affecting the chemistry of the biogenic elements on the Moon and that in the Sun hydrogen is the most abundant element while carbon and nitrogen are the fourth and fifth most abundant elements.

Additional Reading

DesMarais, D. J.: Light Element Geochemistry and Spallogenesis in Lunar Rocks. Geochimica et Cosmochimica acta, vol. 47, 1983, p. 1769.

Eglinton, G.; Maxwell, J. R.; and Pillinger, C. T.: The Carbon Chemistry of the Moon. Scientific American, vol. 227, 1972, p. 80.

Gibson, E. K., Jr.: Volatile Elements Carbon, Nitrogen, Sulfur, Sodium, Potassium and Rubidium in the Lunar Regolith. Physics and Chemistry of the Earth, vol. 1, 1976, p. 1.

Taylor, S. R.: Planetary Science: A Lunar Perspective. Lunar and Planetary Institute, Houston, TX, 1982.
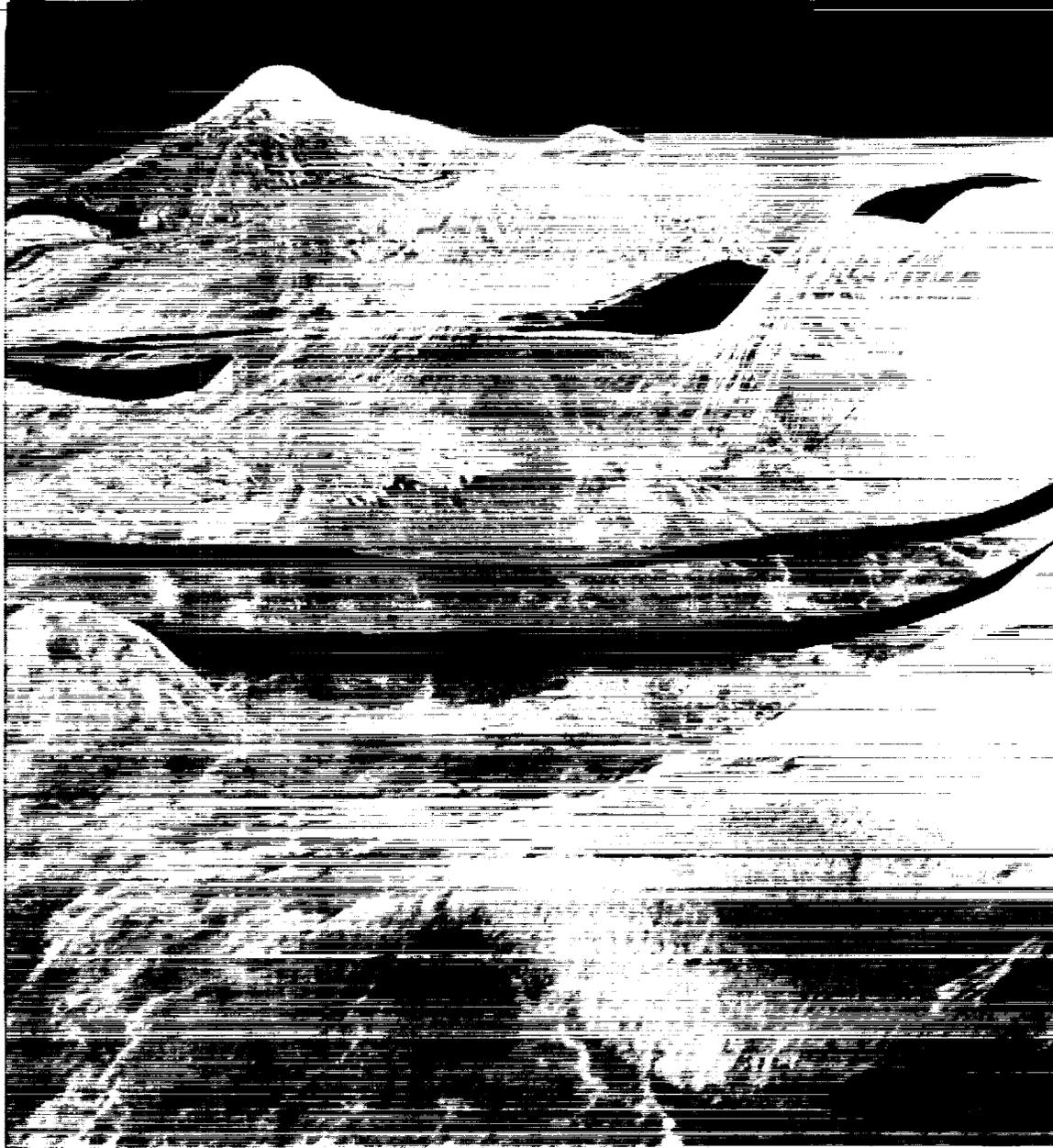
ORIGINAL PAGE
COLOR PHOTOGRAPH