

Chemical evolution of the Moon and the terrestrial planets

Knowledge of the chemical evolution of the Moon, Mercury, Venus, and Mars and the contributions to this knowledge from space missions vary greatly from body to body. Without doubt the Moon is a very special case. The six Apollo missions that landed there returned a total of 381.7 kg of lunar material. The first of these missions was launched on 16 July 1969 and returned to Earth on 24 July 1969. It was followed by Apollo 12, 14, 15, 16, and 17, the last of which was launched on 7 December 1972. Apollo 15, 16, and 17 carried a rover vehicle that extended the range of the astronauts considerably. During the Apollo 17 mission the rover covered a total of 30.5 km. The Russian uncrewed missions Luna 16, Luna 20, and Luna 24 returned about 370 g of lunar material. The robot rover of the Luna 17 mission traveled 10.5 km in 322 days and that of Luna 21 traveled 37 km in 139 days. In addition, 13 lunar meteorites totaling 4.1 kg have been recognized and studied thoroughly.

It should be stressed that with respect to the chemical evolution of a planet the availability of samples increases possible insights both in quantity and quality. Hence, it is no surprise that, except for the Earth, the Moon is the best studied object in the inner Solar System. For the foreseeable future there is no chance that even the most sophisticated instruments flown to anywhere in the Solar System might return as precise and detailed information as that obtainable from investigations of samples in laboratories on Earth.

With respect to our understanding of the subject of this chapter, next to the Moon comes Mars. Viking 1 and 2 returned the first information on the chemical composition of the Martian soil which seems to be well mixed on a global scale by strong storms. Viking 2 was launched ahead

of Viking 1 on 20 August 1975, landed on Mars on 3 September 1976 and transmitted data for 3.5 years. Viking 1 was launched on 9 September 1975, landed on 20 July 1976 and transmitted data for 6.5 years. Between 1962 and 1988, the Russians sent many missions to Mars which mostly failed or achieved only limited success. The exception was Phobos 2, which arrived at Mars orbit on 29 January 1989; it identified water vapor in the Martian atmosphere, returned images of Mars and Phobos as well as visual and infrared spectra, but stopped transmitting data before it was able to deploy surface stations on Phobos. A large increase in our knowledge of the geochemistry of Mars was made by the very successful NASA Pathfinder mission. Its rover Sojourner, traveling a total of 104 m, returned high-quality data on the chemistry of five rocks and six soil samples analyzed by the APX-spectrometer on board the rover in addition to a number of close-up images. The second source of information on the chemical evolution of Mars stems from Martian meteorites, of which 14 with a total weight of 81 kg have been recognized and studied.

Venus is a most difficult planet to study because of the very harsh conditions on its surface. Nevertheless valuable data on the chemical composition of the Venusian surface were obtained by the Soviet Venera and Vega missions, launched between 1972 and 1984, which transmitted data, Venera 13 relaying the first color pictures of the surface. However, the returned data do not allow reliable conclusions to be drawn on the chemical evolution of this planet.

Almost nothing is known of the chemistry of Mercury. This is very unfortunate as Mercury has the highest density of all planets and, hence, this must be reflected in its chemical composition. It is hoped that the missions planned both by ESA and NASA will fill this gap.

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Considering the chemical composition of the Moon and the planets, we have to bear in mind that the Solar System formed from the solar nebula. To show the fractionation process involved it is useful to compare individual bulk compositions of Solar System objects, or parts of them such as individual rocks, to the abundances of elements to solar abundance or even better to C1 (carbonaceous chondrites type 1) abundances which reflect the primordial Solar System abundances of all condensable elements. Data for C1 or solar abundances are given in the classical paper by Suess and Urey (1956) or in later compilations by Cameron (1973), Palme *et al.* (1981), Anders and Ebihara (1982), and Anders and Grevesse (1989).

THE MOON

The pioneer of modern cosmochemistry, Harold Urey (who won the Nobel Prize for Chemistry in 1934 for the discovery of deuterium), suggested the Moon as a possible place of the origin of stone meteorites (Urey 1959). He was, at that time, convinced that the Moon was a “primary” object. To account for the apparent about 10% lower density of the Moon compared with that of ordinary chondrites, he assumed the Moon to contain several percent water and/or graphite. It was his belief in a primitive nature of the Moon formed at low temperature, which made the Moon for him central to the understanding of the formation of the Solar System.

I, being 35 years younger than Urey, have been from early on fascinated by the great old man and his reasoning. In the early 1960s, I had found conclusive evidence for the solar wind origin of the solar-type rare gases observed in several bronzite chondrites (Wänke 1963, 1965; with respect to solar wind implantation in meteorites a number of other papers have to be mentioned: Signer and Suess 1963, Suess *et al.* 1964, Eberhardt *et al.* 1965, Zähringer 1966). To account for this observation, it was a necessity that individual meteorite grains prior to compaction were exposed to solar wind irradiation at the surface of their parent body, which should not have an atmosphere or magnetic field to hinder the solar wind implantation. I thought the Moon would be an ideal body for this implantation and together with some weaker arguments on the distribution of cosmic exposure ages, I published a paper (Wänke 1966). Urey was quite convinced by my arguments and in his letter to me of 10 February 1967 he wrote: “In fact, I think I am probably your most important public relations man in the United States at the present time.” Later on in this letter: “It looks as though I must now begin to caution people not to think that the whole case for meteorites from the moon is completely settled. I keep telling them that only samples from the moon will definitely settle the problem.”

The first chemical data obtained *in situ* on the Moon from Surveyors 5, 6, and 7 by alpha-scattering analyses (Turkevich *et al.* 1970, and references therein), indicated a basaltic composition at the two maria locations and a low-iron, basalt-like composition at the third one for the area near Tycho. They proved that Urey and I were wrong. Urey had just written a paper in which he summarized all arguments for a lunar origin of some meteorites (Urey 1968). On 26 February 1968, he wrote to me with respect to the Surveyor results: “I have the feeling that the data would seem to indicate that no meteorites come from the Moon at all. Moreover, I am led to doubt the Mars origin also.” In my paper “On the lunar origin of the bronzite chondrites” (H-chondrites), I had mentioned that the other major group of ordinary chondrites – the hypersthene chondrites (L-chondrites) – might come from Mars.

The possibility of ejection of rocks from the Moon or Mars was considered to be absolutely impossible by the experts on cratering mechanisms at that time. When the first samples from the Apollo 11 mission were analyzed, I had the satisfaction that at least my proposition that the lunar dust should be loaded with solar wind particles turned out to be correct. Today, meteorites from the Moon – although not of chondritic composition – is a not disputed fact. A Mars origin of a small group of meteorites (the SNC meteorites) is widely accepted.

When NASA asked for proposals for lunar sample investigations my colleagues and I at the Max-Planck-Institute for Chemistry in Mainz, Germany, wrote altogether 12 proposals addressing different areas of research. As result of these proposals, the Mainz laboratory became a major player in the Lunar Sample Analyses Program of NASA. Our laboratory has received the largest amount of lunar material, both in terms of mass and number of sample specimens, of any laboratory outside the USA.

Apart from rare gas measurements, the multi-element analyses of lunar samples at the Mainz laboratory became highly appreciated. All major and minor elements and many geochemically important trace elements (in total up to 54 elements) have been determined in this multi-element analysis program. This turned out to be especially valuable for the investigations of lunar breccias with their considerable heterogeneity. Using this large data set quite a number of element correlations have been observed first or confirmed.

To work with lunar samples was very exciting for all of us involved. Let me describe an incident when we worked on our first lunar sample, a soil sample no. 10084. Most of our analytical work was carried out using neutron activation techniques starting non-destructive by gamma-counting the samples irradiated by thermal neutrons in a nuclear reactor. The reactor, a TRIGA research reactor of the Gutenberg-University of Mainz, was located next to our building. When we applied the first 6 hour irradiation from 9 a.m. to

3 p.m., the sample was in our gamma-ray spectrometer for less than about 30 minutes, and we waited for the first spectra. Our technician, Mr. Bernhard Spettel, came to me highly excited and said: "Very, very strange. I have never seen such a spectrum. There are only three lines, I have to look up the isotope table because I do not know these lines." This was indeed very unusual as Mr. Spettel was a real expert in this field and had most of the gamma-lines in his head. A few minutes later, he said: "You would not believe, the lines indicate only one element, namely indium." I knew that indium, a trace element in rock or soil samples, has a very high cross-section and due to the short half-life of the isotope produced by neutron capture, ^{116}In of only 54 minutes, it would be produced in high quantities even if present only in trace amounts. The short half-life meant that the isotope decayed rapidly, and in the evening of the same day we could see the lines of those elements we actually expected. What had happened? In the overall extraordinarily successful Lunar Sample Analyses Program, NASA had decided to return the samples under vacuum. A sample box was designed into which the astronauts had to put the samples and close the lid, which was supposed to be sealed by an indium gadget between the edges of the lid and box. The whole sealing mechanism did not work properly, and most of the samples returned from the Moon were heavily contaminated with indium. In our sample there must have been a tiny indium grain of about 0.1 mg. In this respect it was an exception, but practically all soil samples showed indium excesses.

The Apollo missions

Apollo 11 – Mare Tranquillitatis

Soil samples and soil breccias

As expected (Wänke 1965, 1966), all soil samples contained large amounts of solar wind-implanted rare gases. ^4He concentrations up to $0.5 \text{ cm}^3 \text{ STP g}^{-1}$ have been observed. From the ratios $^4\text{He}/^{20}\text{Ne} = 91$ and $^4\text{He}/^{36}\text{Ar} = 505$ compared with the ratios of more than three times higher found in magnetically separated metal grains, which hold rare gases more strongly, a considerable loss of helium due to diffusion was evident for the bulk samples (Hintenberger *et al.* 1970). The amount of hydrogen in the lunar soil, in soil breccias, was found to exceed that of ^4He by about a factor of six with a D/H ratio of about three times less than the terrestrial ratio. Laboratories worldwide were engaged in the Lunar Sample Analysis Program. With respect to the solar wind-implanted rare gas isotopes, the studies in Bern (Eberhardt *et al.* 1970) were very comprehensive, while Epstein and Taylor (1970) analyzed hydrogen. The findings of these groups were identical to those obtained in Mainz as well as by other laboratories.

The chemical composition of the soil and soil breccias was found to mimic that of the igneous rocks from which they were obviously derived with only small additional components (Wänke *et al.* 1970). From the amount of hydrogen evolved during the treatment of lunar soil with diluted acid under vacuum, the presence of 0.6% metal in sample 10084–18 was calculated. Analyses of metal particles separated from the bulk soil by a hand magnet showed that practically all of the nickel, cobalt, gold, and iridium in the bulk soil resides in the metal particles, indicating a mainly meteoritic origin. An exception was observed for tungsten, for which high concentrations of 24 ppm in these metal particles proved their equilibration with matter from lunar basalts at elevated temperatures. (In Figures 1 and 2, instead of individual mare rocks the soil sample 10084 is used for comparison as in this way small differences from rock to rock are avoided.)

The meteoritic component was extensively studied by Ganapathy *et al.* (1970) who estimated a 1.9% admixture of carbonaceous chondrite-like material, corresponding to an average influx rate of meteoritic and cometary matter of $3.8 \times 10^{-8} \text{ g cm}^{-2} \text{ yr}^{-1}$.

Rock samples

The igneous rocks, the mare basalts from Mare Tranquillitatis (Wänke *et al.* 1970) compositionally reflected highly differentiated material of clearly basaltic nature (Figure 1). In contrast to terrestrial rocks, the high titanium concentration

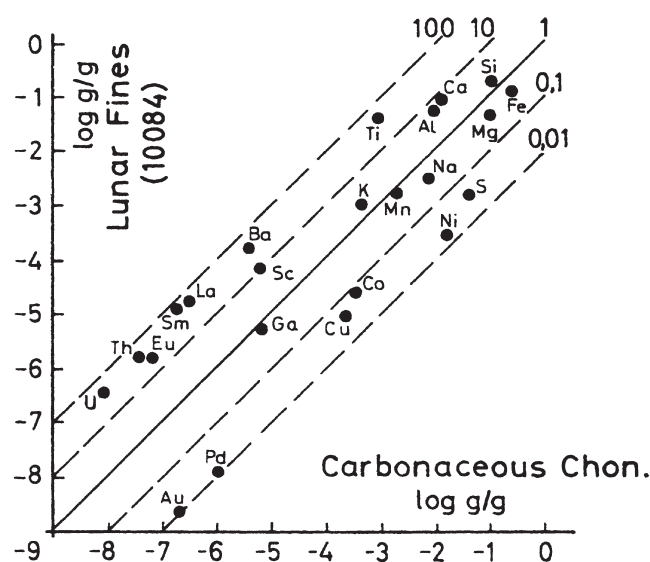


Figure 1 Comparison of the concentrations of various elements in lunar fines and carbonaceous chondrites type 1. The huge compositional differences clearly show that the Moon is not a primitive but a highly differentiated object. Data for lunar fines from Wänke *et al.* (1970). (After Wänke *et al.* 1970, reproduced with permission.)

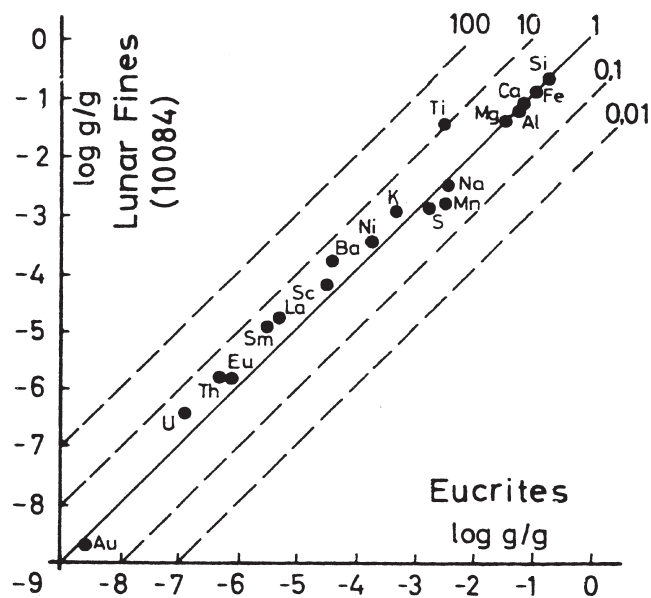


Figure 2 Comparison of the concentrations of various elements in lunar fines and eucrites. The higher differentiation of the Moon compared to the eucrite parent body is evident. (After Wänke *et al.* 1970, reproduced with permission.)

in the lunar basalts was striking. Comparing the major and trace element abundances, it was shown that the lunar mare basalts are compositionally close to basaltic achondrites, the eucrite meteorites (Figure 2), although certain element ratios differ considerably excluding a lunar origin of eucrites. Striking were also the fractionated rare earth element (REE) patterns with a large negative europium anomaly (Figure 3), reflecting a lower oxygen fugacity on the Moon as compared to the Earth. As in the case of rare gases, the major and trace element compositions were also studied by many groups. The REEs, for example, were studied by Wakita *et al.* (1970). The paper by Gast *et al.* (1970) should also be mentioned in this respect. It contains, apart from data on REEs and some other trace elements, suggestions on the petrogenesis of the Apollo 11 basalts. In all cases the Mainz data agreed very well with those from other investigators.

One of the proposals for our investigations on lunar samples to be carried out at Mainz was the determination of radioactive isotopes produced by the interaction of cosmic-ray particles. For this work sample masses of about 100 g were required. It was necessary to decompose chemically the sample in order to extract the various radioisotopes to be studied. The first step in this procedure was reduction and pulverization of the sample. Because of the high value of the sample, my colleague, Prof. Friedrich Begemann, and I had decided to do this step ourselves. For the pulverization we used a steel mortar that we had put inside a small plastic tent so that particles thrown out of the mortar or the sieves could

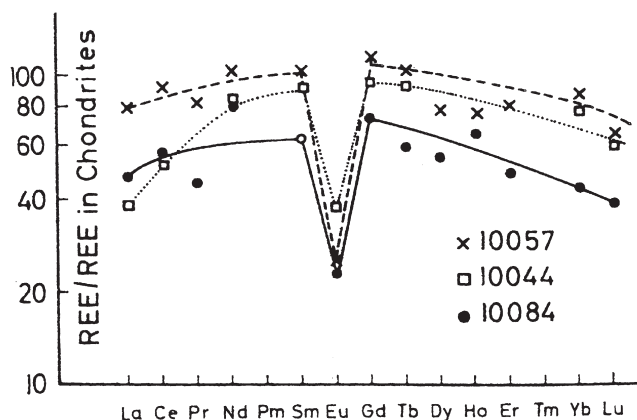


Figure 3 Rare earth concentrations in lunar rocks 10057 and 10044 and lunar fines 10084, normalized to chondritic values. Data for chondrites from Schmitt *et al.* (1963, 1964); data for lunar samples from Wänke *et al.* (1970). The negative Eu anomaly reflects the low oxygen fugacity of the Moon where Eu becomes divalent and does not fractionate with the other REEs that remain trivalent, but enters feldspar. The Eu anomaly has been reported by various authors (Gast and Hubbard 1970, Haskin *et al.* 1970, Philpotts and Schnetzler, 1970, Schmitt *et al.* 1970). (After Wänke *et al.* 1970, reproduced with permission.)

be caught. We started our work around 8 p.m. When we finished around 11 p.m., I walked back to my office on this rather cold but very clear late evening with the Moon high up in the sky. Suddenly I noticed an irritation in my nose and got out my handkerchief. When I put down the handkerchief I noticed two black dots on it, which obviously were due to some fine dust liberated during the sample preparation in spite of the plastic tent. I looked up to the Moon on which Mare Tranquillitatis was easily visible with the naked eye, thinking that a rock is missing from it now and a tiny, tiny fraction of it I have just removed from my nose. This was the most touching moment of my life.

Apollo 12 – Oceanus Procellarum

Soil and rock samples

Both the soil and the rock samples returned by the Apollo 12 mission showed larger variations in chemical composition than those from Apollo 11, which may just reflect the fact that all the Apollo 11 samples were collected much closer to the landing module.

Apollo 12 landed within 200 m of the Surveyor 3 spacecraft. Some distant ejecta rays from the large crater Copernicus, located 400 km to the north, crossed the site. However, none of the returned samples could be proven to contain material originating from Copernicus.

With respect to their major-element chemistry, the mare basalts from Oceanus Procellarum were divided into two



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The Century of Space Science

Bleeker, J.A.; Geiss, J.; Huber, M. (Eds.)

2001, XLIX, 1846 p., Hardcover

ISBN: 978-0-7923-7196-0