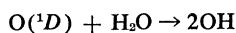


7 and 8. Equation 12 is a somewhat poorer approximation than Eq. 11 for $t > t_{1/2}$ because CO decays faster than NO, and eventually the neglect of the term $k_3[\text{NO}]/k_1[\text{CO}]$ in Eq. 8 becomes unjustified, but by that time nearly all the CO has disappeared anyway.

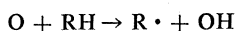
If we accept the ratio $k_4/k_1 \cong 6$, an analysis of Eqs. 9 and 11 indicates that reaction 1 is still essentially the rate-controlling step for CO consumption, because (approximating still further)

$$d \ln[\text{CO}]/dt \approx -2k_1[\text{HO}_x]$$

Thus Weinstock's estimate (6) of the $[\text{OH}]$ required to maintain the global $[\text{CO}]$ at 0.1 part per million (ppm) on the basis of reaction 1 alone would only need to be divided by ~ 2 ; that is, $[\text{HO}_x] \approx 1.5 \times 10^{-9}$ ppm for a CO input rate of 2×10^{14} g/year. The actual $[\text{HO}_x]$ is, of course, an unknown quantity in the atmosphere. Presumably OH is generated in sunlight by such steps as



and



(where RH is any hydrocarbon) and it is likely that the main sinks (at least at night) for OH arise from the reactions



and



both of which have recently been found to be very fast (7). In sunlight the HNO_3 and HNO_2 may be photolyzed to recover OH. If $k_3 \approx k_4$, an analysis of Eqs. 10 and 12 shows that reaction 1 is also rate-controlling for NO consumption, but clearly, if $k_3 \ll k_4$, this is no longer true and we would have

$$d \ln[\text{NO}]/dt \approx -(k_3k_3/k_4)[\text{HO}_x]$$

If we now exclude reaction 4 from the mechanism by letting $k_4 = 0$, the rigorous Eqs. 7 and 8 reduce to

$$\frac{d[\text{CO}]}{dt} = \frac{d[\text{NO}]}{dt} = -[\text{HO}_x] \frac{k_3[\text{NO}]}{1 + k_3[\text{NO}]/k_1[\text{CO}]} \quad (13)$$

If we make the same simplification as before by restricting ourselves to $k_3[\text{NO}]/k_1[\text{CO}] \ll 1$, Eq. 13 may be solved to give

$$\frac{[\text{NO}]}{[\text{NO}]_0} \approx \exp[-k_3[\text{HO}_x]t] \\ (t_{1/2})_{\text{NO}} \approx \frac{0.69}{k_3[\text{HO}_x]} \quad (14)$$

Comparing Eqs. 12 and 14, we see that the effect of including reaction 4 in the mechanism with $k_4 \cong k_3$ is to lengthen (8) the computed lifetime of NO by the factor $(1 + k_4/k_1)$ over that predicted without reaction 4. As discussed above, it is likely (not proven) that $k_4/k_1 \cong 6$, so that the computed $(t_{1/2})_{\text{NO}}$ could be increased by a factor of 7 or more.

On the basis of the sequence of reactions 1 through 3 alone, since

$$d[\text{CO}]/dt = d[\text{NO}]/dt$$

the CO consumption would cease when $[\text{NO}] \rightarrow 0$. The OH would then no longer be regenerated, and the steady-state cycle would be broken. Actually, as noted above, other reactions extraneous to the cycle probably govern $[\text{HO}_x]$ in the real atmosphere.

Thus, in summary, it seems quite likely that reaction 4 is fast—probably faster than reaction 1—and that it would have an appreciable effect on calculated NO lifetimes in polluted atmospheres; that is, the NO lifetime would be considerably longer than the lifetime estimated from the sequence of reactions 1 through 3 alone. The effect of reaction 4 on CO lifetimes is different (NO is not required at all for a quite efficient CO sink to function), since reactions 1, 2, and 4 alone con-

stitute a cyclic system to consume CO. (For appreciable conversion of NO to NO_2 , however, the presence of some CO is required by this mechanism with or without reaction 4.) If $[\text{NO}] = 0$, the rigorous Eq. 7 has an exact solution given the approximate Eq. 11, which implies half the lifetime for CO computed without reaction 4 but with the same constant $[\text{HO}_x]$.

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8. It is not the presence of CO itself that lengthens the NO lifetime. The cycle of reactions 1 through 3 alone would still lead to a faster conversion of NO to NO_2 than when $[\text{CO}] = 0$ (there would then be no NO_2 formation without another step, probably $\text{NO} + \text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$), but reaction 4 decreases the effect, obviously because CO competes with NO for the HO_x . That the presence of CO enhances the conversion of NO to NO_2 has been experimentally confirmed (2).

14 April 1972

Apollo 16 Geochemical X-ray Fluorescence

Experiment: Preliminary Report

Abstract. *The lunar surface was mapped with respect to magnesium, aluminum, and silicon as aluminum/silicon and magnesium/silicon intensity ratios along the projected ground tracks swept out by the orbiting Apollo 16 spacecraft. The results confirm the observations made during the Apollo 15 flight and provide new data for a number of features not covered before. The data are consistent with the idea that the moon has a widespread differentiated crust (the highlands). The aluminum/silicon and magnesium/silicon concentration ratios correspond to those for anorthositic gabbros through gabbroic anorthosites or feldspathic basalts. The x-ray results suggest the occurrence of this premare crust or material similar to it at the Descartes landing site.*

An integrated geochemical package was carried in the Command-Service Module during the Apollo 16 flight to the Descartes highland area. This package, which was identical to the one carried aboard Apollo 15, included the x-ray, gamma-ray, and alpha-particle spectrometers. These experiments were flown to extend our observations to larger areas of the moon and to allow us to extrapolate from the data obtained on the surface to the rest of the moon. Thus, the purpose of the orbital

mapping experiment and, in particular, the x-ray fluorescence experiment was to tie in the information obtained from the analysis of the returned lunar samples from the various sites to the global geochemical picture.

There was some overlap of orbital coverage between the two missions so that the reproducibility of our results could be determined and the results could be compared. The total coverage for the two missions is greater than 20 percent of the total surface of the moon.

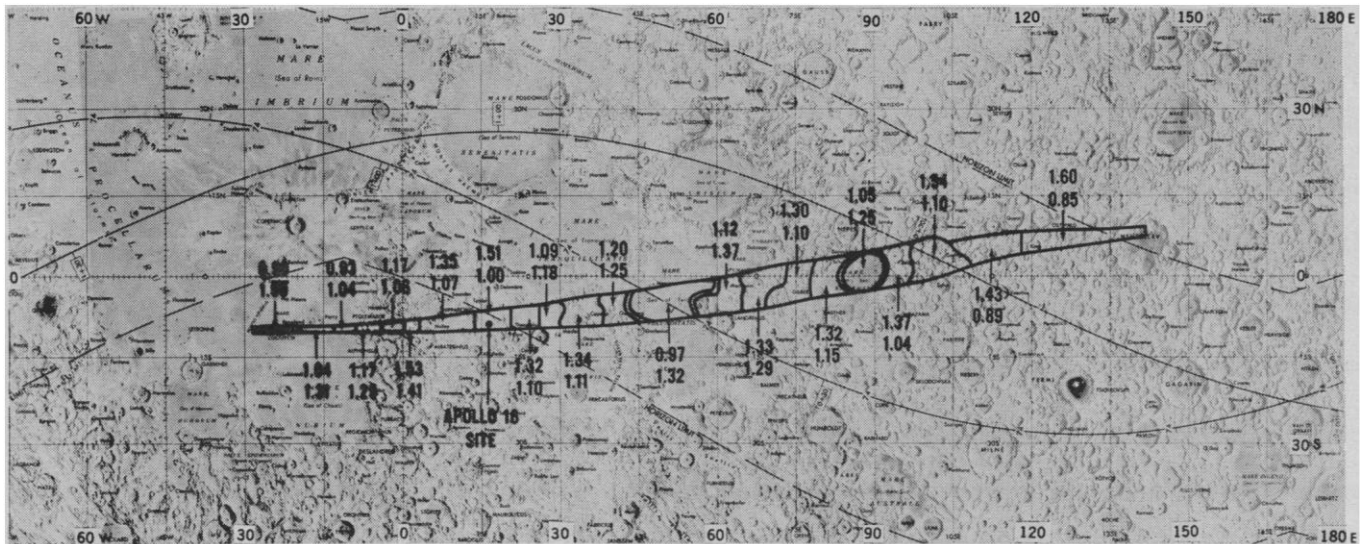


Fig. 1. Aluminum/silicon and magnesium/silicon intensity ratios for specific areas along the Apollo 16 ground tracks. The upper values are Al/Si ratios and the lower values Mg/Si ratios.

The Apollo 16 mission provided data for a number of features not previously covered, for example, Mare Cognitum, Mare Nubium, Ptolemaeus, the Descartes area, and Mendeleev, as well as other areas. Many data points were obtained in the x-ray experiment over the Descartes landing site (see Fig. 1 and Table 1) while the astronauts were gathering samples on the surface. It is hoped that our results will show how representative these samples were of the Descartes area.

Unlike the high-inclination orbit of Apollo 15, the Apollo 16 flight path was nearly equatorial (9° inclination) so that the projected areas covered were somewhat smaller than during the Apollo 15 flight. Although the original flight plan called for a change of plane, the exigencies of the mission did not permit this, and consequently some of the ground coverage was lost.

The details of the x-ray experiment have already been described (1). The solar monitor on Apollo 16 had an additional beryllium filter in front of the detector window to enable us to look at the high fluxes of solar x-rays without observing the detector gain shifts experienced on the Apollo 15 flight.

The x-ray experiment was turned on initially at 80 hours into the mission and operated for about 12 hours in elliptical orbit (approximately 111 by 18 km). It was turned on again at 106 hours into the mission, with the spacecraft then flying in a circular orbit about 111 km above the lunar surface. As in the Apollo 15 flight, the estimated field of view for each data point in this report is about 111 by 148 km. The data were

reduced during the mission (1); thus, it was possible to draw conclusions about the Descartes site and to report these to the crew while they were on the surface.

The region of overlap between the Apollo 15 and Apollo 16 tracks was mainly between 50° and 100° E longitude and covered such areas as Mare Fecunditatis, Mare Smythii, Langrenus, and the highlands west of Smythii. For these areas, the Al/Si and Mg/Si concentration ratios for both flights agreed to better than 10 percent. This agreement makes it encouraging to draw comparisons between the two flights. It also demonstrates that the sun's x-ray spectral distribution, which produces the lunar fluorescent x-rays, was about the same on both missions. This, in fact, has been confirmed by examination of the Solrad data available for those periods (2).

Figure 1 shows the variation of Al/Si and Mg/Si intensity ratios plotted along the projected Apollo 16 ground tracks. These tracks have been divided into areas based in part on obvious geologic features and in part on intensity contours. Because of the relatively low inclination of the orbit and the repetitive ground tracks there is a high density of data points plotted along the ground tracks. Thus, the values shown represent the averages of a substantial number of points. The results are tabulated in considerable detail in Table 1. A brief summary of our observations follows.

1) Our early reports of very high Al/Si ratios in the Descartes area, which were given while the mission was

in progress, have been confirmed by the analysis of some of the returned lunar samples (3). According to members of the preliminary analysis team (3), "analysis of the Descartes soils shows a surprisingly high concentration of aluminum oxide compared with samples returned from other sites visited by other Apollo missions." The value reported, 26.5 percent aluminum oxide, agrees well with our own estimates. It appears reasonable from Fig. 1 that some of the material sampled at Descartes is similar in composition to the eastern limb and farside highlands. This conclusion is further justified by the fact that the Mg/Si concentration ratio for some of the returned materials is about 0.18, close to our value of 0.19 ± 0.05 . The Mg/Si ratios for the eastern limb and farside highlands, as shown in Table 1, are about 0.16 to 0.21.

2) The observations made after the Apollo 15 flight of high Al and low Mg concentrations in the highlands and the reverse in the mare areas is confirmed by the Apollo 16 data. However, there are exceptions, for example, Ptolemaeus has both high Al/Si and high Mg/Si values.

3) In both missions, the Al and Mg concentrations are for the most part inversely related, although this is not true everywhere, as noted in 2 above.

The following preliminary interpretation of the x-ray fluorescence data is proposed, subject to further detailed analysis of the intensity readings, study of the returned lunar samples, and photointerpretations of areas below the flight path. The major geologic result of

the experiment is further support for the existence of a global lunar crust representing early geochemical differentiation of the moon. This support comes from the high Al/Si ratios measured at many highland areas on the far and near sides of the moon. Although the x-ray fluorescence experiment has covered less than a quarter of the moon's surface, the consistency of these

data (including the Apollo 15 data) over nearly 230 degrees of longitude and over 50 degrees of latitude provide strong support for the global nature of the crust.

The dominant materials represented by the Apollo 15 x-ray fluorescence data were thought (1) to fall chemically in the range of anorthositic gabbros to gabbroic anorthosites, with probable oc-

currences of anorthosite, felsite, and KREEP (a material rich in potassium, rare-earth elements, and phosphorus). The Apollo 16 data appear to be consistent with this interpretation and with the other lines of evidence concerning highland composition, summarized by Lowman (4). Detailed study of the rock and soil samples collected at the Descartes landing site by the crew will pro-

Table 1. Concentration ratios of Al/Si and Mg/Si; *N*, number of individual data points used to determine the average Al/Si and Mg/Si values (± 1 standard deviation).

Feature	N	Concentration ratios	
		Al/Si	Mg/Si
For lunar features overflown during Apollo 16 geochemical mapping experiment			
Known Sea (19°–29°W)	8	0.38 ± 0.11	0.40 ± 0.29
Upper part of Sea of Clouds (9°–13°W)	8	.39 ± .12	.20 ± .05
Mare Fecunditatis (42°–57°E)	80	.41 ± .05	.26 ± .05
South of Fra Mauro (13°–19°W)	9	.45 ± .07	.26 ± .04
Mare Smythii (82°–92.5°E)	24	.45 ± .08	.25 ± .05
South edge of Mare Tranquillitatis, Torricelli area (26°–30°E)	21	.47 ± .09	.23 ± .05
East edge of Fecunditatis Langrenus (57°–64°E)	44	.48 ± .07	.27 ± .06
Ptolemaeus (4°W–0.5°E)	17	.51 ± .07	.21 ± .04
Highlands west of Ptolemaeus to Sea of Clouds (4°–9°W)	16	.51 ± .11	.25 ± .12
Highlands west of Mare Fecunditatis (37.5°–42°E)	29	.52 ± .07	.24 ± .05
Highlands west of Smythii (72°–77°E)	35	.57 ± .07	.21 ± .03
West border of Smythii (77°–82°E)	33	.58 ± .08	.22 ± .04
Highland east of Descartes (20.5°–26°E)	23	.58 ± .07	.21 ± .04
South of Sea of Foaming (64°–72°E)	45	.58 ± .07	.25 ± .04
Isidorus and Capella (30°–37.5°E)	38	.59 ± .11	.21 ± .05
Highland west of Descartes (3°–14°E)	44	.59 ± .11	.21 ± .05
East Border of Mare Smythii (92.5°–97.5°E)	17	.61 ± .09	.20 ± .06
Farside highlands (106°–118°E)	29	.63 ± .08	.16 ± .05
Descartes area, highland, Apollo 16 site (14°–20.5°E)	30	.67 ± .11	.19 ± .05
East of Ptolemaeus (0.5°–3°E)	12	.68 ± .14	.28 ± .09
Highlands (97.5°–106°E)	31	.68 ± .11	.21 ± .05
Farside highlands, west of Mendeleev (118°–141°E)	30	.71 ± .11	.16 ± .04
For selected returned lunar samples			
Apollo 12, Oceanus Procellarum, type AB rocks, average (6)		0.22	0.22
Apollo 15, Hadley-Apennines, rocks, average (7)		.22	.27
Apollo 12, Oceanus Procellarum, type B rocks, average (6)		.22	.37
Apollo 11, Mare Tranquillitatis, potassium-rich rocks, average (8)		.23	.24
Apollo 12, Oceanus Procellarum, type A rocks, average (6)		.24	.31
Rock 12013 (6)		.24–.30	.20
Apollo 11, Mare Tranquillitatis, low-potassium rocks, average (8)		.29	.23
Dark of rock 12013 (9)		.33	.22
Apollo 12, Oceanus Procellarum, soils, average (6)		.33	.29
Surveyor 6, Sinus Medii, regolith (10, 11)		.34	.20
Apollo 15, Hadley-Apennines, soils (7)		.34	.30
Surveyor 5, Mare Tranquillitatis, regolith (11, 12)		.35	
Luna 16, Mare Fecunditatis, rocks (13)		.35	.21
Apollo 11, Mare Tranquillitatis, bulk soils, average (8)		.37	.24
Apollo 14, Fra Mauro, rocks, average (14)		.38	.26
Kreep, average (9)		.39	.21
Apollo 14, Fra Mauro, soils (14)		.41	.26
Norite material, average (15)		.42	.20
Luna 16, Mare Fecunditatis, bulk soils (13)		.42	.27
Surveyor 7, rim of Tycho, regolith (11, 16)		.55	.20
Luna 20, Apollonius highlands		.58	.26
Apollo 11 and Apollo 12, anorthositic gabbros (15)		.64	.21
Apollo 15, rock 15418, gabbroic anorthosite (7)		.67	.15
Apollo 11 and Apollo 12, gabbroic anorthosites (15)		.82	.074
Apollo 11 and Apollo 12, anorthosites (15)		.89	.038
Apollo 15, rock 15415, anorthosite Genesis Rock (7)		.91	.003

vide invaluable ground truth that should permit more specific petrologic interpretation of the x-ray data at a later date.

One specific point of petrologic interpretation can be brought out here. The high Al/Si intensity readings (1.5) over the Descartes site (Fig. 1) are close to those over the farside highlands, which presumably represent premare crust. Although the Apollo 16 surface traverses were on Cayley and Descartes formations (both post-Imbrium basin), there should be abundant fragments of this old, aluminum-rich crustal rock in the regolith samples.

An investigation of the widespread Cayley formation was one of the major objectives of the Apollo 16 mission. It is therefore of interest to note the x-ray intensities (Fig. 1) over the crater Ptolemaeus, whose floor has been mapped by Howard and Masursky (5) as Cayley formation. The Al/Si ratios measured over this crater appear to be intermediate between those typical of highlands and maria. If allowance is made for contamination of the crater floor with aluminum-rich material brought from the surrounding area by mass wasting and ballistic transport, the x-ray results seem to be consistent with the interpretation of the Cayley formation, in at least this area, as volcanic rock (probably feldspathic basalt). If confirmed by detailed data analysis, this would provide further support for major volcanism on the moon in the mare basin-mare filling interval, demonstrating the more or less continuous nature of lunar volcanic activity in the first 1.5×10^9 years of the moon's history.

The x-ray experiment of the Apollo 16 mission has provided additional evidence for the existence of a global, differentiated lunar crust. The x-ray results indicate that this premare crust occurs near the Descartes landing site. Further analysis of the data, comparison with samples returned from the Descartes site, albedo-composition correlations, and photointerpretation are in progress.

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Kom Ombo: Preliminary Report on the Fauna of Late Paleolithic Sites in Upper Egypt

Abstract. *A Late Pleistocene fauna comprising 3 fish, 1 reptile, 22 birds, and 14 mammals is identified from sites containing Sebilian, Sebekian, Silsilian, Menchian, and Halfan industries. It is remarkable for its variety, especially of birds, and gives evidence for year-round occupation of these sites.*

The fauna reported here was identified from specimens collected between October 1962 and April 1963 by the Canadian Prehistoric Expedition to Nubia, under the direction of the second author (1). The specimens were prepared in either the department of zoology, University of Toronto, or the department of vertebrate paleontology, Royal Ontario Museum, and are deposited in that museum.

The plain of Kom Ombo lies in the valley of the Nile River in Upper Egypt and is centered about the town of Kom Ombo (Fig. 1). The town is located at latitude $24^{\circ}46'N$ and longitude $32^{\circ}57'E$, about 40 km north of Aswan and 600 km south of Cairo. The plain lies mainly on the right or east bank of the Nile River, is about 400 km² in area, and is roughly oval or trapezoid in outline. The surface of the plain is composed of Late Pleistocene sediments deposited by the Nile or by the wadis to the east.

The Kom Ombo archeological sites lie along or are associated with abandoned channels of earlier stages of the Nile River and are all associated or contained within the interbedded sands and silts of the Gebel Silsila Formation (Younger Channel Silts), which have been dated by radiocarbon analysis at between 15,000 and 10,500 B.C., approximately (2). Major concentrations of the archeological sites lie near the village of Sebil on the abandoned channel of the same name, about 4 km north of Kom Ombo, and near Gebel Silsila, at the junction of the abandoned Fatira and Manshiya channels at the northern end of the plain, about 2 km east of the village of Fatira. Other sites are near Silsila Station at Khor el-Sil, Fatira Village; near Mata'na Qibli, about 4 km northwest of Kom Ombo; and at Bayara, about 2 km west of Kom Ombo.

The archeological sites include those identified as containing artifacts of