

Effects of water on electrical properties of lunar fines

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Abstract—The electrical properties of lunar sample 15301,38 have been measured over a period of 33 months in various vacuums to 2×10^{-8} torr and in 30–50% relative humidity. After normalizing to a constant density of 1 g/cm^3 , it was observed that short exposures (hours) of lunar samples to humid air caused large changes in electrical properties which are reversible to their original values upon remeasurement in vacuum. Exposure to air for 30 months however, produced changes which were only partly reversible in vacuum. The vacuum dielectric constant and loss tangent were irreversibly increased by 14% and 50% respectively (independent of frequency), and the D.C. resistivity decreased by 86%. These irreversible changes in electrical properties are attributed to alteration of the surfaces of the soil grains. Measurement of the magnetic properties before and after 33-month exposure to air found no appreciable change in quantity or state of the iron in the sample.

INTRODUCTION

THE ADDITION OF WATER to a porous insulating material alters the resultant bulk electrical properties by orders of magnitude (see recent reviews in Hasted, 1973; Olhoeft, 1975), particularly so in lunar samples. Strangway *et al.* (1972) and Olhoeft *et al.* (1972, 1973) have demonstrated the effects of short-term exposure (hours) of lunar samples to moisture. They found that water increased the dielectric constant by tens of percent, the loss tangent by a factor of 50, and the D.C. conductivity by a factor of 10^4 . Upon remeasurement in vacuum, the lunar samples were observed to recover to the original values of their electrical properties.

Such short-period exposures of lunar samples to moisture have been found to cause irreversible changes in other properties, such as the specific surface area (Cadenhead and Stetter, 1974; Holmes *et al.*, 1974; and others). Taylor *et al.* (1974) and others have observed the formation of akaganeite (βFeOOH) from iron with one or two days exposure to water vapor and in the presence of lawrencite. It is the intention of this paper to present the long-term exposure effects of moisture on the electrical properties of lunar samples.

EXPERIMENTAL DATA AND PROCEDURE

Lunar sample 15301,38 is a sub-1-mm fines fraction of soil returned from the moon in DB 173 in SRC 2 (LSIC, 1971). The SRC failed to seal properly upon the moon; thus, the sample was exposed to spacecraft and terrestrial atmosphere for several days. The sample was processed in the positive pressure dry-nitrogen (less than 25-ppm water) processing lines of the Lunar Receiving Laboratory and stored in dry nitrogen for 1 yr prior to the initial measurements.

Experimental procedures have been described elsewhere (Olhoeft *et al.*, 1974). The sample was transferred from storage in dry nitrogen to the vacuum chamber while under a positive pressure dry

Table 1. (Continued).

Loss tangent 25°C.										
0.010	—	—	—	—	—	1.16	0.0327	0.0334	0.0326	0.0327
0.020	—	—	—	—	—	0.85	0.0249	0.0268	0.0261	0.0261
0.050	—	—	—	—	—	0.58	0.0201	0.0201	0.0198	0.0206
0.10	0.015	—	0.010	0.059	0.592	0.439	0.0169	0.0168	0.0160	0.0158
0.20	0.012	0.0118	0.0088	0.052	0.487	0.331	0.0127	0.0131	0.0127	0.0127
0.50	0.008	0.0095	0.0071	0.054	0.364	0.219	0.0097	0.0097	0.0097	0.0096
1.0	0.007	0.0076	0.0058	0.061	0.292	0.153	0.0080	0.0080	0.0077	0.0078
2.0	0.0062	0.0062	0.0048	0.056	0.220	0.102	0.0062	0.0066	0.0064	0.0065
5.0	0.0045	0.0048	0.0039	0.038	0.14	0.057	0.0046	0.0051	0.0050	0.0052
10.	0.0040	0.0038	0.0033	0.024	0.092	0.036	0.0041	0.0048	0.0045	0.0043
20.	0.0020	0.0030	0.0026	0.015	0.060	0.024	0.0034	0.0041	0.0039	0.0039
50.	0.0020	0.0018	0.0034	0.0067	0.028	0.015	0.0009	0.0038	(0.0041)	—
100.	0.0010	0.0008	0.0032	0.0032	0.016	0.011	—	(0.0040)	(0.0043)	—
100.	—	0.0008	0.0008	—	0.007	—	—	—	—	—

nitrogen tent. Measurements were performed using 3-terminal techniques with a variety of instruments (primarily General Radio 1615 and 1621 bridges). Previous studies of this sample have yielded measurements of electrical properties as functions of frequency, temperature, and short-term exposure to air (Olhoeft *et al.*, 1972, 1974) and as functions of frequency, temperature, density, and vertical stress (Frisillo *et al.*, 1975).

The dielectric constant, loss tangent, and D.C. resistivity at 25°C from Olhoeft *et al.* (1972, 1974) are tabulated in columns A–E of Tables 1 and 2. Column A lists measurements made immediately after initial evacuation to 0.025 torr from the dry-nitrogen tent. Column B has measurements at 1×10^{-7} torr after 24 hr at that vacuum pressure. Column C lists results at 8×10^{-8} torr after several vacuum heating cycles to a maximum temperature of 500°C. Column D shows measurements taken immediately after exposure to 30% RH (relative humidity) atmosphere. Column E has data after 19.5-hr exposure to air. The sample was then re-evacuated to 1×10^{-7} torr with nearly complete recovery of dielectric properties (total recovery was not possible as a heating cycle between C and D to 827°C irreversibly altered the loss tangent, see Olhoeft *et al.*, 1972).

Strangway *et al.* (1972) have demonstrated for lunar soil 14163,131 that brief exposure to 30% RH air and re-evacuation to 1×10^{-7} torr produces electrical properties that are identical with those observed for the sample in vacuum prior to exposure to air.

Columns F–J of Tables 1 and 2 contain measurements made after the sample had been exposed to air for 30 months. Column F lists measurements in 20% RH air after 30-month exposure. Column G shows results in 0.02-torr vacuum. Column H has measurements at 1×10^{-7} torr after 24 hr at that vacuum pressure. Column I shows data at 6×10^{-8} torr after 22 days in vacuum. Column J lists data measured at 2×10^{-8} torr after 89 days in vacuum.

The measurements of A–E are on a separate aliquot from the same 10-g vial as the sample for F–J. The same aliquot was not usable in both cases due to the irreversible change in electrical properties caused by heating to 827°C (see Olhoeft *et al.*, 1974). As the samples are from a sub-1-mm fines fraction, it is unlikely that the differences observed are due to inhomogeneity.

Table 3 lists the results of a study of the magnetic properties of 15301,38 to 18 kG. The changes in the quantity of iron and the state of the iron are negligible (within the experimental error of the measurements) before and after 33-month exposure to air.

DISCUSSION

The two sets of measurements (A–E and F–J) were performed at two different densities, so density normalization must be performed before the effects of the 30-month exposure to air may be observed. Olhoeft and Strangway (1975) have demonstrated by a regression analysis of all of the available measurements of electrical properties of lunar samples at high frequencies (above 10^5 Hz) that the geometric mean mixing formula is applicable. They found, over all measurements,

Table 3. Magnetic properties.

Sample		J_s	$X_p \times 10^6$	J_{rs}/J_s	H_c	Fe^0/Fe^{2+}
15301,38-B1	August 1972	0.997	31.1	0.047	20	0.0320
15301,38-B1	April 1975	0.944	29.0	0.046	20	0.0376
15301,38-B	April 1975	0.974	28.8	0.046	21	0.0338

J_s = saturation magnetization—e.m.u./g.

X_p = paramagnetic susceptibility e.m.u./g.

J_{rs} = saturation remanence.

H_c = coercive force.

that the dielectric constant, k' , at a density of p g/cm³ was given by

$$k' = (1.93 \pm .17)^p$$

and the loss tangent, $\tan d$, at a density of p g/cm³ was given by

$$\tan d = \tan ap$$

which, for loss tangent less than 0.1, may be approximated by

$$\tan d = pA,$$

where A is the loss tangent at 1 g/cm³ (determined by the ilmenite content and frequency, see Olhoeft and Strangway, 1975). Figure 1 illustrates the measurements of dielectric constant of 15301,38 from Olhoeft *et al.* (1972, 1974) (error bar), Frisillo *et al.* (1975) (circles), and this study (triangle). The solid line is the geometric mean of the illustrated data only. It is clearly observable that the triangle (from column J in Table 1) is anomalously high.

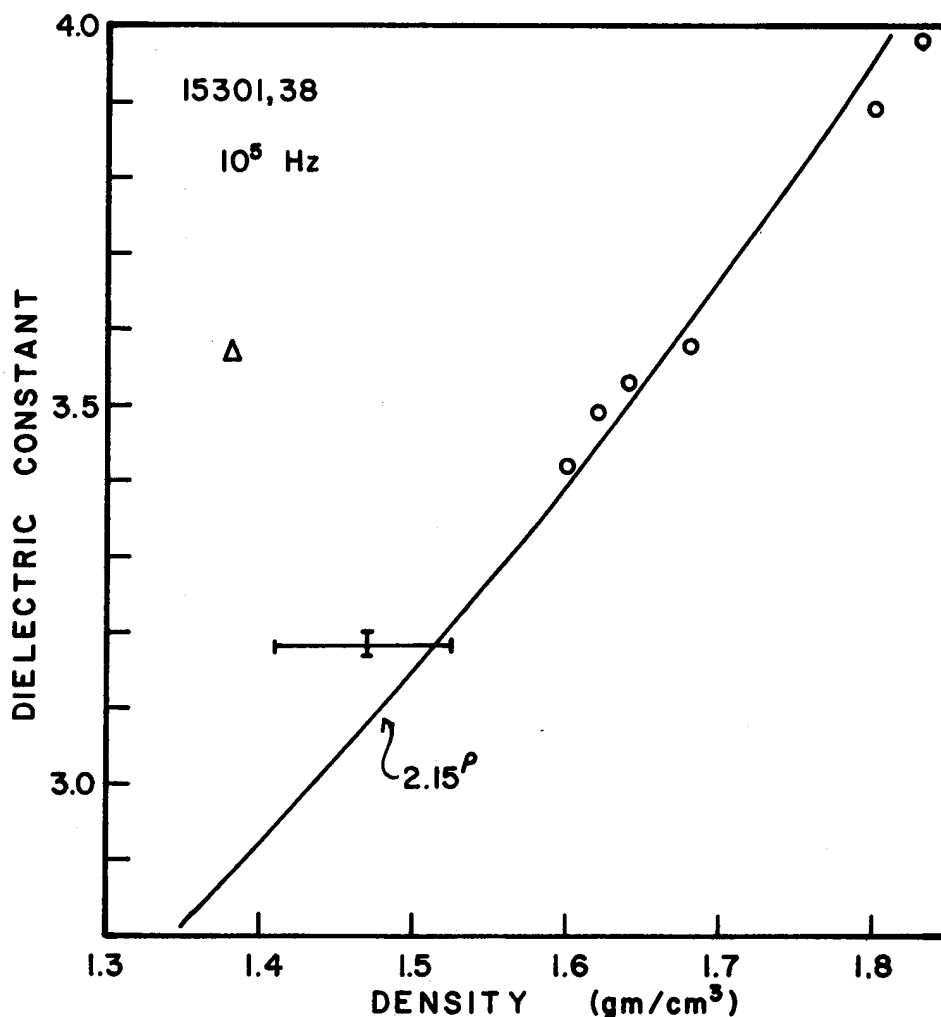


Fig. 1. Dielectric constant versus density for lunar sample 15301,38. Circles are from Frisillo *et al.* (1975), crossed error bar is from column C of Table 1 after Olhoeft *et al.* (1974). Triangle is this work in vacuum from column J of Table 1 (after 30-month exposure to air). Solid line is geometric mean mixing formula fit to the data illustrated excluding the triangle.

Normalizing the dielectric constant by taking it to the power of the reciprocal density, Table 1 becomes Table 4. Comparing columns C and J in Table 4, the dielectric constant measured in vacuum has increased by $14 \pm 7\%$ due to the 30-month exposure to air. Similarly, normalizing the loss tangent by dividing by the density, the loss tangent (Table 5) is seen to have increased by $49 \pm 7\%$ due to the 30-month exposure to air. The ± 7 point uncertainty in the percentage increases is due to measurement errors and uncertainties from the density normalization. It should be clear, however, that the observed increases are significant.

There is no obvious way to normalize the D.C. resistivity to density, so the measurements must be compared at face value. The D.C. resistivity decreased by $86 \pm 22\%$. As the density between measurements decreased from 1.47 to 1.38 g/cm^3 and therefore grain-grain contacts would be expected to become poorer, the D.C. resistivity would be expected to increase, if any change were to be expected. As the opposite occurred, the D.C. resistivity was also altered by the 30-month exposure to air.

Olhoeft and Strangway (1975) have observed that plots of density normalized dielectric constant versus ilmenite content show no clear trends or clustering. They also observed, however, that the density normalized loss tangent plotted against ilmenite content clearly illustrated a dependence of loss tangent upon both the ilmenite content and upon a grouping of Apollo 11, 12, and 14 samples versus Apollo 15–17. Between Apollo 14 and 15 the lunar sample handling and processing procedures were changed from a negative pressure quarantine to a positive pressure isolation. Thus, the Apollo 11, 12, and 14 samples were more likely to be contaminated by water vapor over long periods of time than were samples from the later missions. This is demonstrated by the consistently higher loss tangents reported for samples from Apollos 11, 12 and 14 compared to those measured from Apollos 15–17.

The mechanism of sample alteration which is producing the observed changes in electrical properties upon long-term exposure to air is uncertain. As is shown in Table 3, the iron content and the state of the iron has not been significantly altered by the 33-month exposure to air; thus, the "rusting" mechanism to akaganeite of Taylor *et al.* (1974) is unlikely. This is not altogether unexpected due to the high-glass content of 15301, and the likelihood of the iron being imbedded in and protected by the glass (see Pearce *et al.*, 1972; Housley *et al.*, 1973a,b). The observed changes in electrical properties are unlikely to be caused by adsorbed water remaining after sample exposure and re-evacuation. Such adsorbed water only alters electrical properties in quantities greater than a single adsorbed monolayer (see Olhoeft, 1975; McCafferty and Zettlemyer, 1971; Baldwin, 1958; and others), and such quantities of water are easily removable by evacuation without heating (see above references). The sub-monolayer adsorbed quantities of water that remain do not alter the dielectric constant or loss tangent, but may alter the D.C. resistivity (Olhoeft, 1975), so part of the observed 86% decrease in the D.C. resistivity may be due to such sub-monolayer quantities of water.

It is more likely that the observed changes in electrical properties are due to

Table 4. Dielectric constant normalized to 1 g/cm³.

15301,38-0											
15301,38-1											
Date	7/27/72	7/28/72	8/4/72	8/15/72	8/16/72	1/11/75	1/11/75	1/12/75	2/3/75	4/10/75	
Torr	0.025	1×10^{-7}	8×10^{-6}	Air	Air	Air	0.020	1×10^{-7}	6×10^{-8}	2×10^{-8}	
Freq. (kHz)	A	B	C	D	E	F	G	H	I	J	
0.010	—	—	—	—	—	4.82	2.60	2.62	2.61	2.60	
0.020	—	—	—	—	—	4.22	2.58	2.59	2.58	2.58	
0.050	—	—	—	—	—	3.63	2.56	2.56	2.56	2.56	
0.10	2.28	—	2.22	2.47	3.75	3.29	2.55	2.56	2.55	2.55	
0.20	2.25	2.22	2.22	2.44	3.30	2.84	2.54	2.54	2.54	2.54	
0.50	2.25	2.25	2.21	2.39	2.88	2.80	2.53	2.53	2.53	2.53	
1.0	2.25	2.21	2.21	2.35	2.64	2.69	2.52	2.52	2.52	2.52	
2.0	2.25	2.21	2.20	2.29	2.56	2.62	2.51	2.52	2.52	2.52	
5.0	2.23	2.20	2.20	2.24	2.38	2.58	2.52	2.51	2.51	2.51	
10.	2.23	2.20	2.20	2.22	2.30	2.54	2.50	2.51	2.51	2.51	
20.	2.23	2.20	2.19	2.21	2.26	2.52	2.50	2.51	2.51	2.50	
50.	2.22	2.20	2.19	2.21	2.23	2.52	2.50	2.51	2.50	2.50	
100.	2.23	2.20	2.19	2.21	2.22	2.53	—	2.51	2.51	—	
1000.	—	2.20	2.19	—	2.24	—	—	—	—	—	

Table 5. Loss tangent normalized to 1 g/cm³.

Date	7/27/72	7/28/72	8/4/72	8/15/72	8/16/72	1/11/75	1/11/75	1/12/75	2/3/75	4/10/75
Torr	0.025	1×10^{-7}	8×10^{-8}	Air	Air	Air	0.020	1×10^{-7}	6×10^{-8}	2×10^{-8}
Freq. (kHz)	A	B	C	D	E	F	G	H	I	J
0.10	—	—	—	—	—	0.718	0.0237	0.0242	0.0236	0.0237
0.020	—	—	—	—	—	0.560	0.0180	0.0194	0.0189	0.0189
0.050	—	—	—	—	—	0.400	0.0146	0.0146	0.0143	0.0149
0.10	0.0102	—	0.0068	0.040	0.38	0.309	0.0122	0.0122	0.0116	0.0114
0.20	0.0082	0.0080	0.0060	0.035	0.32	0.236	0.0092	0.0095	0.0092	0.0092
0.50	0.0054	0.0065	0.0048	0.037	0.24	0.158	0.0070	0.0070	0.0070	0.0070
1.0	0.0048	0.0052	0.0039	0.041	0.20	0.110	0.0058	0.0058	0.0056	0.0056
2.0	0.0042	0.0042	0.0033	0.038	0.15	0.074	0.0045	0.0048	0.0046	0.0047
5.0	0.0031	0.0033	0.0026	0.026	0.095	0.041	0.0033	0.0037	0.0036	0.0038
10.	0.0027	0.0026	0.0022	0.016	0.062	0.026	0.0030	0.0035	0.0036	0.0038
20.	0.0014	0.0020	0.0018	0.010	0.041	0.017	0.0025	0.0030	0.0028	0.0028
50.	0.0014	0.0012	0.0023	0.0045	0.019	0.011	0.0006	0.0028	0.0030	0.0022
100.	0.0007	0.0005	0.0022	0.0022	0.011	0.008	—	0.0029	0.0031	—
1000.	—	0.0005	0.0005	—	0.005	—	—	—	—	—

alteration of the surface states of the soil particles by the water. Maurette and Price (1975) suggest that the surface amorphous layer of grains is very chemically active. Olhoeft *et al.* (1974) have correlated a change in loss tangent upon heating above 800°C to annealing of radiation damage within this surface amorphous region. Over long exposure to moisture, a similar process may occur due to the hydrolytic action of water as has been observed by Cadenhead and Mikhail (1975) for the aging of surface properties. This process might also be similar to the formation of the akaganeite noted by Taylor *et al.* (1974), but involving material other than iron.

CONCLUSIONS

The vacuum dielectric constant of lunar sample 15301,38 increased by 14% after a 30-month exposure to air. Similarly, the loss tangent increased by 50%, and the D.C. resistivity decreased by 86%. Before and after measurements of the magnetic properties of 15301,38 found negligible changes in the quantity and state of the iron in the sample due to the exposure to moisture. The long exposures of Apollo 11, 12, and 14 samples to likely moisture contamination accounts for the high values of loss tangent measured in those samples. Short-term contamination by atmosphere for hours to a few days (such as in the spacecraft between the lunar surface and the Lunar Receiving Laboratory) is apparently reversible, so most measurements of electrical properties on Apollo 15, 16, and 17 samples in vacuum should be representative of lunar electrical properties.

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