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Trace Elements and Accessory Minerals in Lunar Samples

Abstract. *Halogen contents similar to those in meteorites are reported in Apollo 11 samples. Concentrations of 0.6 to 13 parts mercury, 0.2 to 0.8 part uranium, 1 to 17 parts lithium, and 1 to 800 parts osmium per million and 0.5 to 1 percent chromium oxide by weight have been measured. In contrast to meteorites and terrestrial rocks a large mercury release below 110°C is observed. Some implications of these results are presented. Fluorapatite, quartz, tridymite, fayalite, and iron-rich, manganese-poor pyroxmangite, previously unreported, have been identified. The small amount of fluorapatite found does not account for the fluorine contents.*

Preliminary estimates of the amounts of F, Cl, Br, I, Hg, Os, U, and Li in several types of lunar material are presented. All elements were measured by neutron activation except F, which was measured separately by photon activation (*1*). In contrast to our previous F measurements, the latter irradiations were monitored by polyvinylfluoride foil sandwiches surrounding samples sealed in fused silica vials and rotated in the photon beam (*2*).

Chlorine, Br, I, U, Te, and Li were measured in one 100- to 200-mg portion of a sample; Hg, Os, Ru, Cr, Sc, and F were measured in another. However, most F measurements reported were obtained on still other portions. Uranium and Te were by-products of the I measurements. The production of ^{18}F from neutron irradiation of Li in silicates (*3*) accounts for our Li results. Mercury was volatilized from samples in a closed system. Complete release of Hg is assumed because all the samples were found to be fused after heating to 1200°C.

The samples measured were representative. They consisted of soil, LRL crushed and homogenized medium-grained rocks, vesicular rock, vuggy rock with ilmenite platelets, and microbreccia. The last three were rock chips from which we removed and crushed small fragments. All sample handling was confined to a glove box with a nitrogen atmosphere.

The data from the halogen measurements are summarized in Table 1. In some experiments the samples were leached about 10 minutes with boiling water, and the separate results are indicated. Up to 80 percent of the Cl and Br may be in water-soluble phases. Duplicate measurements were made on the microbreccia and the soil samples. Chlorine, Br, and Li in the former agree within the present estimates of error; Cl, Br, and Li in the two soil aliquots disagree by an almost constant factor. Sample inhomogeneity would seem to be a reasonable explanation.

The average F/Cl ratio is about 22. The vesicular and vuggy rocks have Cl/Br ratios 3.5 times greater than the ratio of about 51 for the other samples.

Measurement of I was compromised by the high-fission I activities derived from the U in the samples. A refinement of the data will be attempted. The parallel trends appearing in most of the F, Cl, and Br results do not hold for I.

The 140- to 340-ppm F concentrations permit estimates of up to 1 percent of apatite if this mineral is the major site of F as it is in terrestrial rocks. The few tenths percent P_2O_5 required has been observed (*4*), but fluorapatite has been observed rarely and only in one of the rock types. Its presence is discussed below.

Mercury data are summarized in Table 2 and Fig. 1. The Hg volatilized from the samples was significantly different from releases observed in meteorites and terrestrial rocks (*5*): a large release at low temperature (⩽ 110°C) is observed, and the maximum in the release at 150°C is shifted to 250°C. We were assured by LRL that no Hg pumps or the like were used in their systems. During isothermal heating at 250°C an initial burst occurs, containing 50 to 80 percent of the Hg eventually evolved. In this respect the release pattern is similar to that noted previously for meteorites and terrestrial samples. The large 110°C fraction might be explained as the release of Hg from low-temperature (⩽ 150°C) traps during thermal cycling on the lunar surface followed by its adsorption on surfaces. The only deviation from the trend noted is in the soil sample 10084-009, which also has the highest relative amount of Hg released above 450°C. Otherwise, the release trends are not inconsistent with the following interpretation. The most degraded material, the soil 10084-019, has the largest low-temperature fraction; it is followed by the microbreccia. The fine-grained rock 10072 has a greater fraction of its Hg in high-temperature traps. The medium-grained igneous rock occupies an intermediate position, possibly because of slower cooling to lower temperatures. The large release ratio for the vesicular rock 10017 can be rationalized as resulting from Hg associated with the vapor phase that formed the vesicules

Table 1. Halogen, lithium, and uranium concentrations in Apollo 11 samples. Except for F, all data on a line are for a single aliquot; subscripts *l* and *s* refer to water extractable and non-extractable portions, respectively.

Sample	F (ppm)	Cl (ppm)	Br (ppm)	I (ppb)	Li (ppm)	U (ppm)
Soil 10084,2	144	2.9	0.051		0.19	
10084,2		$9.9_s + 1.8_l$	$.15_s + 0.08_l$	$625_s + 15_l$	7.2*	0.19
Microbreccia						
10061,22	342	9.6	.15		4.0	
10061,22		$6.8_s + 0.7_l$	$.25_s + 0.01_l$			
10019,29		$9.4_s + 6.4_l$	$.24_s + 0.14_l$	$\leqslant 71_s + 3_l$	$13_s + 0.14_l$	
Medium-grained rock 10044,48	202	$2.6_s + 12_l$	$.076_s + 0.14_l$	$1440_s + 12_l$	0.95*	.17
Medium-grained rock 10047,48		$9.6_s + 4.8_l$	$.11_s + 0.22_l$	$\leqslant 4.9_s + 12_l$	$16_s + 12_l$	
Vuggy rock 10072,24	271	14	.079	> 140		.31
Vesicular rock 10017,22	251	15	.080	5.9		.76

*The leach solutions in these experiments were not measured, but little of the Li appears to be water-soluble.

Table 2. Mercury and osmium concentrations (ppb) in Apollo 11 samples.

Sample	Hg		Os
	Total	> 450°C	
Soil 10084,2	5.3	0.060	283
10084,2	0.95	0.22	1.4
Microbreccia 10061,22	1.2	0.042	
Medium-grained rock 10044,48	0.60	0.028	
Vuggy rock 10072,24	5.5	1.1	17
Vesicular rock 10017,22	13	0.09	755

and trapped in the glasslike lining of the voids.

The Hg concentrations range from 0.6 to 13 ppb, the largest being associated with the vesicular rock. These concentrations are significantly lower in general than those in basaltic achondrites (18 to 9000 ppb) (*6*) or in chondrites and approach more nearly the values observed in some terrestrial rocks (*5*).

The Os concentrations (Table 2), as in chondritic and iron meteorites, are in the ppb–ppm range. They are higher than those in a Hawaiian basalt or W-1 and also tend to be higher than the $\sim$ 7.9 ppb reported for the achondrite Nuevo Laredo (*7*).

The Os results could be pertinent to attempts to monitor infall of meteoritic material on the moon by way of the platinum metals (*8*). If these preliminary data are verified, the high value in the igneous rock relative to the soil may imply that the Os is of lunar origin or that the lava flow that produced the rock was associated with the impact and that meteoritic material was incorporated at that time.

Uranium concentrations (Table 1) are in the range indicated by whole-rock counting at LRL (*9*). Two determinations of Cr were made: sample 10084-009 contains 0.54 percent Cr_2O_3 and sample 10017 contains 0.95 percent. These are close to the values reported by LSPET. The Li contents range from 2 to 17 ppm. A value of 13.1 ppm in W-1, not listed in Table 1, was obtained in this work and is in good agreement with literature values (*3*). The Li contents of the samples appear to be similar to or lower than those in achondrites (*3*) and gabbroic rocks. LRL reports similar Li contents (*9*).

Table 3. Electron microprobe analysis of pyroxmangite.

Compound	Average of six grains	Range
SiO_2	46.7	46.3 – 47.1
FeO	46.5	45.9 – 47.7
MgO	0.9	0.3 – 1.2
CaO	5.2	4.7 – 5.6
MnO	0.8	0.6 – 0.9
TiO_2	0.5	0.4 – 0.7
Total	100.6	

Powders of samples 10017, 10072, and 10044 were examined for common rock-forming minerals that are known to contain halogens. In addition, several nonopaque accessory minerals were identified, some of which are reported here. Preliminary identifications based upon optical properties were confirmed by x-ray powder patterns. Chemical analyses were obtained on grain mounts with an electron microprobe.

Sample 10044 contains fluorapatite as euhedral crystals up to 25 μm long and as irregularly shaped areas up to 100 by 25 μm; the mean refractive index is 1.644. Both habits are present as inclusions in a yellow mineral which is an Fe-rich, Mn-poor variety of pyroxmangite $(Fe,Mn)SiO_3$. The average composition of three selected apatite inclusions is, in percent by weight, as follows: P_2O_5, 39.0; CaO, 52.5; FeO, 1.5; SiO_2, 2.2; F, 3.3; Cl, 0.03. The sum is 98.5; less 1.4 oxygen as F, the sum is 97.1. It is difficult to explain the low summation, for no other elements above atomic number 8 were present in amounts greater than 0.05 percent. Furthermore, it is improbable that much OH was present, because the 3.3 percent F is very close to the maximum of 3.8 percent F for pure fluorapatite. The 2.2 percent SiO_2 in the analysis probably indicates substitution of SiO_4 groups for PO_4 groups and is not due to inclusions of silica minerals which are present within the irregularly shaped areas. The reverse of this type of substitution has been recognized in terrestrial silicates. Although fluorapatite is a common phosphate mineral in terrestrial igneous rocks, it is not known in meteorites (*10*). The bulk of the fluorine in the lunar samples is not located in fluorapatite. This mineral was not found in any of the other rocks examined, even though some of them have higher fluorine contents than the apatite-containing sample 10044. Apatite constitutes approximately 5 percent of the volume of the pyroxmangite grains; thus only 15 of the 202 ppm F in rock 10044 can be accounted for if pyroxmangite constitutes 1 percent of the rock.

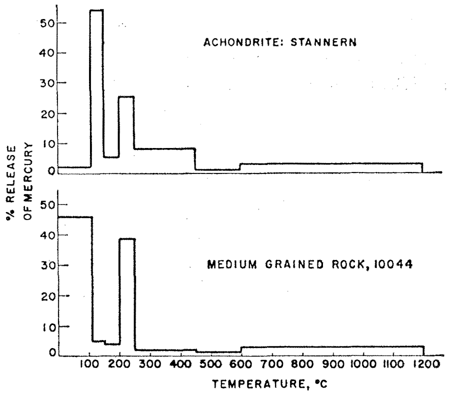

Fig. 1. Mercury release in step-by-step heating of meteoritic and lunar rocks.

The yellow, pyroxmangite-like mineral contains more FeO and less MnO than any known terrestrial mineral. For this reason the lunar occurrence may eventually be designated as a new mineral. The microprobe compositions, corrected for dead time, background, absorption, fluorescence, and atomic number (*11*), are given in Table 3. The formula, based on 18 oxygens, is $(Fe_{4.98}Mg_{0.17}Ca_{0.72}Mn_{0.09}Ti_{0.03})_{5.99}(Si_{5.98}Ti_{0.02})_{6.00}O_{18}$. The optical properties for sodium light are: biaxial (+), $2V = 32 \pm 2°$, $X = 1.745$, $Y = 1.750$, $Z = 1.768$, all values ± 0.003. Weissenberg photographs (Cu radiation) taken on a single cleavage fragment rotated on each of the three crystallographic axes gave these triclinic cell constants: $a = 6.63 \pm 0.01$ Å, $b = 7.58 \pm 0.01$ Å, $c = 17.43 \pm 0.05$ Å, $\alpha = 114.5 \pm 0.2°$, $\beta = 82.6 \pm 0.1°$, $\gamma = 94.4 \pm 0.1°$. A least-squares analysis of 20 indexed reflcetions from a powder photograph (Cr radiation) of several grains gave: $a = 6.62 \pm 0.01$ Å, $b = 7.54 \pm 0.01$ Å, $c = 17.34 \pm 0.02$ Å, $\alpha = 114.26 \pm 0.04°$, $\beta = 82.81 \pm 0.06°$, $\gamma = 94.36 \pm 0.05°$. X-ray density calculated for a unit cell containing 14 molecules of the basic formula $MSiO_3$ is 3.83. The density determined by the volume displacement of 100 μg of grains in a capillary is 3.68 ± 0.05.

Sample 10044 also contains trace amounts of fayalite (Fe_2SiO_4) which form narrow bands between pyroxmangite and ilmenite. The formula derived from the uncorrected probe composition is $(Fe_{1.92}Mg_{0.04}Ca_{0.02}Mn_{0.02}Ti_{0.01})_{2.01}Si_{1.02}O_{4.06}$. Olivine of this composition, Fa_{96}, suggests higher oxidizing conditions of formation than those indicated for the finer-grained rocks 10017 and 10072 in which olivine compositions in the range $Fa_{30\text{-}35}$ were observed.

Three polymorphs of silica were identified. Tridymite occurs with cristobalite in 10044 and quartz with cristobalite in 10072, both as fine-grained intergrowths. Such associations are characteristic of terrestrial lavas where rapid cooling has delayed the sluggish inversions to account for the coexistence of high- and low-temperature forms of silica. Tridymite and cristobalite are seldom, if ever, found in deep-seated rocks. Nonequilibrium conditions are indicated for 10072, in which silica occurs with olivine of composition Fa_{35}, but silica is compatible with fayalite in 10044. Aside from these equilibrium considerations, the presence of tridymite indicates that not all of the Apollo 11 rocks were subjected to shock pressures in excess of 3 kb.

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Gallium, Germanium, Indium, and Iridium in Lunar Samples

Abstract. *Neutron activation analyses of gallium, germanium, indium, and iridium in eight lunar samples and in meteorites and rocks (including four calcium-rich achondrites and five terrestrial basalts) with similar bulk compositions are reported. Lunar gallium concentrations are remarkably constant at about 5 parts per million, three times higher and four times lower than those in eucritic (calcium-rich) achondrites and terrestrial basalts, respectively. Lunar germanium concentrations range from* ≤ 0.04 *to 0.4 part per million. Basaltic achondrites have similar germanium concentrations, whereas those in terrestrial basalts are uniformly higher at about 1.4 parts per million. Concentrations of indium in lunar samples range from 3 to 60 parts per billion, whereas those in terrestrial basalts are 80 to 100 parts per billion, and those in basaltic achondrites 0.4 to 3 parts per billion. Lunar iridium concentrations appear to be in the 0.1 to 10 parts per billion range. The Tranquillitatis samples are distinctly different from calcium-rich achondrites and terrestrial basalts.*

In meteorites containing reduced Ni-Fe, Ge and Ir are heavily concentrated in such phases, Ga is slightly concentrated in the metal relative to the silicate fraction, and In is enriched in the sulfide and silicate phases (*1*). The samples from Mare Tranquillitatis are of basaltic composition, with negligible amounts of reduced Ni-Fe (*2*). Relative to Si, Ga and In abundances in basaltic terrestrial rocks are similar to those in type 1 carbonaceous chondrites. Germanium and Ir are severely depleted in basalts relative to the chondrites. Reasonably good information is available regarding the geochemical behavior of Ga in basalts; Prinz (*3*) indicates that Ga concentrates in the plagioclase and that Ga shows no correlation with the crystallization index, which is an indication of the degree of magmatic fractionation. Very little is known about the geochemical behavior of Ge, In, and Ir in basaltic rocks and magmas, mainly because the concentrations of these elements are at or below the detection limits of emission spectrographic analysis. Thus, to provide a meaningful basis for the interpretation of our analyses of the lunar materials, we initiated studies of the basaltic geochemistry of the elements included in our investigations. We report here concentrations of Ga, Ge, and In in eight Apollo 11 samples and initial investigations of these three elements in terrestrial and meteoritic rocks of basaltic composition. Our Ir data need further refinement and are not tabulated.

The elements Ga, Ge, In, and Ir were determined by a neutron activation scheme involving their sequential radiochemical separation. Gold was also determined in the sequence, but will be discussed elsewhere. The techniques are those outlined previously, with minor changes. After the samples were subjected to radiochemical separation, γ spectra were recorded with NaI scintillation detectors [or occasionally a Ge (Li) ionization detector] in conjunction with a multichannel analyzer.

The precision limits of the method at 68 percent confidence when applied to the analysis of L-group chondrites has been given (*4*) as ± 3.5, 30, 18, and 8 percent for the elements Ga, Ge, In, and Ir. We have not adequately retested the precision during these analyses, but estimate that our Ga (all values), In (values

Table 1. The Ga, Ge, and In concentrations in lunar surface materials.

Sample	Petrolog. class	Ga (ppm)		Ge (ppm)		In (ppb)	
		Replicates	Mean	Replicates	Mean	Replicates	Mean
10084	Fines	4.4, 4.9	4.6	0.34, 0.35	0.34	681, 677	679
10021	Brec	5.7, 5.3	5.5	0.46, 0.31	0.38	14, 30	22 ± 8
10046	Brec	5.6, 5.2	5.4	0.38, 0.34	0.36	25, 6	16 ± 9
10048	Brec	5.1, 5.4	5.2	0.35, 0.29	0.32	56, 65	60
10056	Brec	5.0, 5.1	5.0	0.02, $\leq$0.04	$\leq$0.04	2.4, 3.5	3.0
10057	CrysA	5.0, 4.9	4.9	0.22, $\leq$0.08	$\leq$0.2	3.0, 2.9	3.0
10060*	Brec	4.9, 5.5	5.2	0.20, 0.24	0.22	1150, 911	1030 ± 150
10072	CrysA	4.8, 5.1	4.9	0.026, 0.085	$\leq$0.08	49, 54	52

*Ground and split at Manned Spacecraft Center.