

Fig. 1. Rubidium-strontium relations in the total rock fragment.

to the current Massachusetts Institute of Technology (MIT) normal solutions. All analyses of lunar materials are calculated relative to the CIT normal solutions for consistency.

The MIT value of 0.7090 for $^{87}\text{Sr}/^{86}\text{Sr}$ in Sargasso Sea water may be compared with 0.7091 reported by Papanastassiou and Wasserburg (1) and 0.7094 by Gopalan and Wetherill (2) for Pacific seawater. The MIT value for the MIT SrCO_3 standard is 0.7080.

Analyses are listed in Table 2 and plotted in Fig. 1. Reference isochrons for 4.4, 4.5, and 4.6×10^9 years are given in Fig. 1 for comparison, based on $(^{87}\text{Sr}/^{86}\text{Sr})_0 = 0.6990$ found for basaltic achondrites (1) but adjusted by a correction of -0.0001 to allow for the difference in the value for standard seawater.

We believe that the most significant result of this study has been the disclosure that the Tranquillity Base sampling has yielded at least two distinctly different materials. In all the samples analyzed the Rb/Sr ratio is much smaller than that in chondritic meteorites and that estimated for the planetary system as a whole. Two of the five samples analyzed (Nos. 72 and 22) have ratios of Rb/Sr comparable to the estimated average earth value. The remaining three samples (20, 58, and 47) have ratios that are much lower, which causes values for the ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ lower than any found in earth or meteoritic rock materials. The combination of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Rb/Sr ratios indicates that the process which caused this relative loss of Rb must have occurred during or shortly after the accretion of the planetary system.

Thus the lunar material scattered on the surface at the landing site must have

been derived from material that has been heterogeneous since close to the time of origin of the solar system. The material is volcanic in nature, and the heterogeneity has been preserved despite the volcanism. The enrichment of non-volatile but hyperfusible components such as the rare and alkaline earths, and the relative depletion in volatile components such as the alkalis, would require a combination of both chemical enrichment by crystal fractionation and a physical loss of some elements in a hot gaseous environment by selective volatility.

Thus these analyses suggest that the moon is made up of an assortment of materials from different condensation regimes in the solar nebula, some of which materials were greatly depleted in alkalis, and that a subsequent volcanic

Rubidium-Strontium Chronology and Chemistry of Lunar Material

Abstract. *Igneous lunar rocks divide into two chemical types, probably representing two rock units. They form separate close groups on the isochron diagram; no total rock age is valid unless the rocks are cogenetic. Mineral isochrons prove that one type has an age of 3.80 ± 0.11 billion years, equal to the line joining total-rock groups, and the initial ratio of strontium-87 to strontium-86 of both types is close to 0.6994. Soil and breccias chemically resemble a mixture of the two igneous types, with a superimposed variation of mineral components, plus a small transferred component rich in nickel, copper, zinc, and possibly strontium-87.*

We obtained 1- to 5-g specimens of seven igneous rocks, two breccias, and the soil for a combined dating and

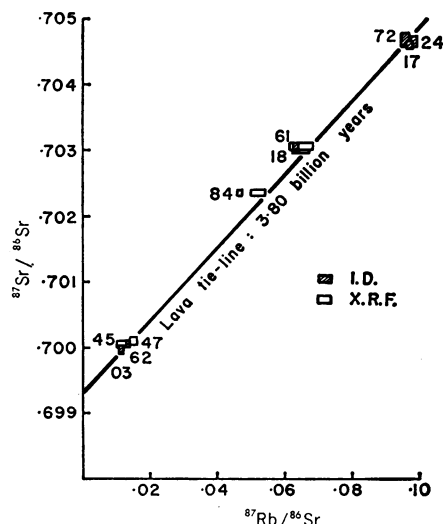


Fig. 1. Isochron diagram showing total-rock analyses of Apollo 11 samples. Sample numbers are identified in Table 1. I. D., isotope dilution analysis; X.R.F., x-ray fluorescence analysis.

or magmatic stage of crystal fractionation must have caused enrichments in some trace elements while still preserving the inherent discrepancy in alkalis. Whether this second stage occurred in the moon, or in earlier bodies which later made up the moon, is not indicated by these measurements.

P. M. HURLEY

W. H. PINSON, JR.

Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge 02139

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chemical study of Apollo 11 material. Analyses for major and minor elements were made primarily to see which of these rocks might be cogenetic and, hence, which might be validly grouped together on a ^{87}Sr evolution diagram to define a total rock isochron. The Rb-Sr analyses on mineral separates ultimately proved essential for a conclusive result.

The trace elements (Table 1) were determined nondestructively by x-ray fluorescence spectrometry on 1 g of powdered sample using the method of direct measurement of absorption coefficient (1). The recovered powder was used for Na determinations by flame photometry, for the other major elements (Table 1) by x-ray measurements on a fused sample (2), and for the mass spectrometric measurements. Preliminary results for four of the samples have been reported (3). There is good agreement for the major and for many minor elements, although our data indicate lower Mn, Zr, Y, Cr, and Cu and higher Sr and Co.

The igneous rocks divide into two related chemical types, here termed group 1 and group 2. Group 1 (specimens 72, 17, and 24) is particularly uniform and is much higher than group 2 (specimens 03, 45, 47, and 62) in Rb, K, Ba, and Th; higher in Ti, Na, P, S, Zr, Y, and rare earth elements (REE); and lower in Al and Ca. Analyses by the preliminary examination team show that specimens 22 and 57 also belong to group 1, and specimens 20 and 58 belong to group 2. It seems likely that two separate rock units were sampled, including textural variants of both (types A and B as defined by the preliminary examination team). It is unlikely that the strong enrichment of K, Rb, Ba, and Th in group 1 is due to crystal fractionation of a single parent magma, as the two groups have only a restricted variation in major elements (4). Different parent magmas are required, generated either from chemically different source regions or from similar sources but with different degrees of partial melting. For both groups, our data show that the lighter REE resemble Ti, Zr, and Y in

their extreme enrichment relative to terrestrial or cosmic abundances (3).

The breccias resemble the soil very closely in their chemistry (Table 1), which is consistent with their derivation from the soil (3). For most elements the breccia-soil composition is between groups 1 and 2 rocks, which indicates that both groups have contributed to their production and that the soil may be largely of local derivation. The exceptions are Fe and Ti, which are lower in the soil, and Al, which is higher. The differences for Fe and Ti may be explained by removing approximately 6 percent (by weight) of ilmenite from a more primitive soil, which would also account for the slightly higher abundances of Si, Mg, and Ca in the soil. Such removal might well occur by mechanical separation of the denser phase during the gardening processes associated with meteorite impact. However, the Al content remains anomalously high, so that a rock or mineral phase rich in this element must be added. The soil is also enriched in Ni, Cu, and Zn as minor transferred components.

Table 2 lists the mean values for Rb and Sr obtained by isotope-dilution, and mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from both unspiked and spiked mass analyses. Our value of $^{87}\text{Sr}/^{86}\text{Sr}$ for the Eimer and Amend SrCo_3 standard is 0.70810. Our previous practice of determining Rb and Sr in separate aliquots of the dissolved sample was not followed for the lunar samples because representative aliquots in HCl solution could not be taken. The failure to obtain aliquots has been shown by current experiments to be associated with the high ilmenite content of the lunar samples; it is probably due to ionic adsorption onto a Ti colloid. Good reproducibility and agreement with the x-ray spectrometric results were obtained by adding a mixed ^{87}Rb and ^{84}Sr spike solution before dissolution.

The group 1 rocks plot at approximately one point in $^{87}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Rb}/^{86}\text{Sr}$ coordinates, whereas group 2 rocks plot in a narrow range averaging about 8 times lower in $^{87}\text{Rb}/^{86}\text{Sr}$ (Fig. 1). The tie line joining both groups need not have time significance, as each group had a different parent magma,

Table 1. Analyses of major and minor elements in ten lunar samples by x-ray fluorescence spectrometry. All values are expressed as ppm, T.E., trace elements as oxides.

	Igneous rocks									
	Group 1			Group 2				Breccias Type C		Soil Type D
	Type A	Type B		Type B				10018	10061	10084
	10072	10017	10024	10003	10045	10047	10062			
SiO_2	40.49	40.69	40.25	39.76	39.04	42.16	39.80	41.81	41.87	41.79
TiO_2	11.99	11.92	11.90	10.50	11.32	9.43	10.74	7.99	7.84	7.55
Al_2O_3	7.74	7.78	8.09	10.43	9.51	9.89	10.22	12.34	12.62	13.44
FeO	19.38	19.49	19.46	19.80	19.40	19.11	19.22	16.46	16.45	15.91
MnO	0.24	0.28	0.24	0.30	0.27	0.28	0.30	0.22	0.22	0.21
MgO	7.45	7.51	7.53	6.69	7.73	5.67	7.08	7.79	7.83	7.66
CaO	10.56	10.76	10.66	11.13	11.28	12.15	11.47	12.00	11.96	12.14
Na_2O	0.50	0.51	0.52	0.40	0.36	0.45	0.41	0.46	0.47	0.43
K_2O	0.29	0.30	0.30	0.06	0.05	0.11	0.08	0.17	0.18	0.14
P_2O_5	0.19	0.18	0.20	0.12	0.10	0.11	0.12	0.15	0.14	0.13
S	0.23	0.23	0.22	0.18	0.15	0.18	0.16	0.15	0.15	0.14
T.E.	0.52	0.56	0.56	0.39	0.39	0.30	0.45	0.45	0.43	0.43
Total	99.58	99.65	99.93	99.37	99.60	99.84	99.60	99.99	100.16	99.97
O = S	0.11	0.11	0.11	0.09	0.07	0.09	0.08	0.07	0.07	0.07
Total	99.47	99.54	99.82	99.28	99.53	99.75	99.52	99.92	100.09	99.90
	<i>Trace elements</i>									
Ba	300		310		10	88		175	128	134
Rb	5.61	5.72	5.96	0.62	0.62	1.11	0.89	3.60	3.68	2.96
Sr	168.4	163.7	178.3	160.9	137.7	209.2	187.8	158.5	161.6	164.8
Pb	3.4	7.1	3.0	6.6	3.3	3.2	6.3	4.2	3.1	2.9
Th	3.5	3.7	4.1	1.1	0.4	0.6	0.9	2.4	2.7	2.5
Zr	497	476	375	309	194	334	319	328	342	318
Nb	25		25		14	23		19	19	18
Y	162	159	168	112	73	134	103	106	108	99
La	43		39		16	20		24	23	21
Ce	94		108		32	48		67	37	58
Pr	16		12		6	13		11	15	10
Nd	49		55		17	36		29	20	33
V	22		37		98	13		51	34	36
Cr	2280		2610		2400	1220		1950	1940	1850
Co	34		32		23	16		35	23	34
Ni	< 20		< 20		< 20	< 20		200	170	230
Cu	22		16		20	16		32	25	33
Zn	34		14		14	13		54	37	37
Ga	4	4	5	3	3	4	3	4	5	4

Table 2. Isotope-dilution analyses for Rb, Sr, and $^{87}\text{Sr}/^{86}\text{Sr}$ of lunar rocks and mineral concentrates. t.r. denotes total-rock; plag., plagioclase; pyrox., pyroxene; and meso., mesostasis.

		Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
<i>Group 1 lavas</i>					
10024,20	t.r.	5.75	169.5	.0980	.70464
10072,30	t.r.	5.60	168.5	.0959	.70467
	plag.	3.87	531.0	.0210	.70063
	pyrox.	1.87	85.9	.0629	.70306
10017,68	t.r.	5.59	167.1	.0966	.70460
	meso. A	19.5	282.7	.1993	.71034
	meso. B	20.9	292.8	.2066	.71058
	plag.	0.92	499.9	.0053	.69970
<i>Group 2 lavas</i>					
10003,20	t.r.	0.63	159.9	.0114	.69996
10062,36	t.r.	0.88	190.0	.0133	.70003
10045,20	t.r.	0.62*	137.7*	.0130*	.70005
	plag.	1.33	299.0	.0129	.69999
	pyrox.	0.65	86.7	.0220	.70036
10047,21	t.r.	1.11*	209.2*	.0153*	.70009
	plag.	0.53	574.6	.00268	.69949
<i>Breccias</i>					
10061,25	t.r.	3.69	166.1	.0631	.70306
10018,20	t.r.	3.64	166.1	.0633	.70299
<i>Soil</i>					
10084,44	t.r.	2.65	164.4	.0466	.70233

* X-ray fluorescence result.

which need not have the same age or the same primary $^{87}\text{Sr}/^{86}\text{Sr}$. Nor can precise total-rock isochrons be defined within each group, as the internal dispersion in Rb/Sr is too low. Analyses of separated minerals were thus essential. Nevertheless, assuming that both groups are precisely the same in age and initial $^{87}\text{Sr}/^{86}\text{Sr}$, we obtain a total-rock age of 3.80 ± 0.12 billion years and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.69935 ± 0.00012 . Using the x-ray spectrometric values alone for $^{87}\text{Rb}/^{86}\text{Sr}$, these parameters become 3.77 ± 0.20 billion years and 0.69934 ± 0.00017 . In both cases, the scatter of points slightly exceeds their assigned experimental errors, and the lines were fitted by assigning greater y variance.

By heavy liquid and magnetic separation, mineral concentrates that ranged from 50 to 200 mg in weight were made from two samples of each group (Table 2); sample 47 of plagioclase was handpicked. Data for plagioclase, pyroxene, and total-rock from sample 72 are well correlated, which suggests an age of crystallization of 3.8 ± 0.3 billion years. The same age is given by the mineral data for sample 17: 3.80 ± 0.11 billion years with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.6994 ± 0.0002 . Most of the Rb in the rock is located in the glassy mesostasis (Table 2), and the big difference in $^{87}\text{Rb}/^{86}\text{Sr}$ between this phase and the plagioclase produces a precise result. The age of the group 2 rocks is comparatively poorly defined as there is much less spread in $^{87}\text{Rb}/^{86}\text{Sr}$ between the mineral concentrates. Both groups were included in the

seven specimens dated by the preliminary examination team as 3.0 ± 0.7 billion years (3), which also implies a single value of age for both.

Equality in initial $^{87}\text{Sr}/^{86}\text{Sr}$ for both groups is consistent with their cogenesis. In general, it now seems likely that the lava tie line of Fig. 1 does have time significance and that both groups have the same age and the same source region. Combining all rock and mineral

Rubidium-Strontium Age and Elemental and Isotopic Abundances of Some Trace Elements in Lunar Samples

Abstract. Data on six lunar crystalline rocks give an apparent Rb-Sr isochron age of $4.42 \pm 0.24 \times 10^9$ years (95 percent confidence limits) and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio similar to that in a basaltic achondrite. Relationships between K, Rb, Sr, and Ba and depletion of Eu in these samples point to plagioclase separation from the melts that produced these rocks. The abundance of ^{157}Gd in the three lunar samples is similar to terrestrial abundance within <0.2 percent, thus setting a limit of $<6 \times 10^{15}$ neutrons per square centimeter for the integrated thermal neutron flux difference between lunar and terrestrial materials.

This paper deals with the abundance and distribution of K, Rb, Sr, and Ba and the isotopic composition of strontium and the rare earth elements Sm, Eu, and Gd in Apollo 11 lunar samples. Six crystalline rocks of types A and B (I), a breccia, and the lunar soil sample were analyzed for K, Rb, Sr, and Ba abundances by stable isotope dilution methods. We measured the isotopic composition of Sr to a precision of 0.6 to 2.6 parts in 10^4 by the use of a digital data acquisition system in conjunction with programmed magnetic-field switching

data on this model, we obtain 3.81 ± 0.07 billion years as our best present estimate for this age, with initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.69936 ± 0.00008 .

The data for the soil and breccias (Fig. 1) are displaced from the rock isochron toward lower $^{87}\text{Rb}/^{86}\text{Sr}$. This might be due to loss of a few percent of original Rb during the production of glass in the soil or to the presence of a transferred Sr component having a higher $^{87}\text{Sr}/^{86}\text{Sr}$.

WILLIAM COMPSTON
PIETER A. ARRIENS
MICHAEL J. VERNON

*Department of Geophysics
and Geochemistry, Australian
National University, Canberra*

BRUCE W. CHAPPELL

*Department of Geology,
Australian National University*

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with a field-sensitive device in a 60° solid source mass spectrometer of 30.5-cm radius. Repeat analyses of two lunar samples and multiple analyses of the Eimer and Amend standard reagent (Table 1) show that a reproducibility of about 2 parts in 10^4 has been achieved. The abundances of the rare earth elements were determined by neutron activation analyses, and their isotopic composition was determined in a manner similar to that used in Sr-isotopic analyses.

The data for the abundances of K,