formation of the earth. Also, since Tilton has shown that tektites contain lead resembling closely the isotopic composition of modern terrestrial lead (6), a lunar origin of these objects can be ruled out unless some lead much more like that found on earth is found elsewhere on the moon.

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## **Rubidium-Strontium Relations in Tranquillity Base Samples**

Abstract. Preliminary total rock analyses disclosed a greatly different rubidium depletion between two groups of these igneous rocks, and ratios of strontium-87 to strontium-86 indicate that the rubidium depletion in these materials must have occurred during or shortly after the accretion of the terrestrial planets.

Five rock samples weighing 0.82 g (No. 22.43), 1.27 g (No. 20.28), 1.14 g (No. 47.25), 2.36 g (No. 72.25), and 1.2 g (No. 58.36) and a 5.16-g sample of fines from the lunar soil (No. 84.39) were available for analysis. This progress report gives analyses on total rock samples only; work on separated minerals and the finedgrained soil material has not been completed. Rubidium, strontium, and the isotopic composition of Sr were determined by mass spectrometric techniques in separate whole pieces of rock ranging upward in size from a few tens of milligrams. These samples were not necessarily assumed to be representative of the rock chips selected by the Lunar Receiving Laboratory, but, by relating the isotopic data from each sample separately and using different whole fragments in repeated analyses, we hoped to obtain additional information on the homogeneity of the rocks, test the assumption of a lack of short range migration of components, and derive meaningful age evaluations and average compositions.

The sample fragments were gently broken in a boron carbide mortar. weighed, and digested in a Parr Industries Teflon-lined bomb at 120° to 140°C. Before acid digestion the samples were spiked with <sup>87</sup>Rb. Minimum amounts of reagents were used: 10 ml of HCl carrying the spike, 3 ml HF and 1 ml HClO<sub>4</sub> per 0.15 g of sample were the approximate amounts. The solution was washed into a Pt dish, covered with a Teflon lid, and heated with a hot plate below and a heat lamp above. After achieving total solution 30 JANUARY 1970

(no visible mineral or chemical residues) the solution was evaporated to get rid of excess HF and SiF4 and diluted with 0.5N HCl to 50 ml in a volumetric flask, and aliquots were taken for Sr spiking and for Rb and Sr isotope dilution and Sr isotope ratio analysis. Element separations were achieved on cation exchange columns

Table 1. Preliminary contamination and spike analyses.

Reagent	Rubidium (10 <sup>-9</sup> g/ml)	Strontium		
HaO	0.003	(20 8/112)		
H <sub>2</sub> O HCl	0.005	0.05		
HNO <sub>3</sub>	0.009	0.05		
HF	0.05			
$HClO_4$	0.15			
Total blank	1.5			
Compari	ison of normal s	olutions		
CIT Sr	14.61 $\times$ 10	-9 mole <sup>88</sup> Sr/g		
MIT Sr	14.70 $\times$ 10	<sup>-9</sup> mole <sup>88</sup> Sr/g		
CIT Rb	$0.440 \times 10$	<sup>-9</sup> mole <sup>87</sup> Rb/g		
MIT Rb	0.449  imes 10	<sup>-9</sup> mole <sup>s7</sup> Rb/g		
Fused silica	Rb, 10 <sup>-9</sup> g/g	Sr, 10 <sup>-9</sup> g/g		
C-17-A	< 9	<190		
F-19-A	<3	<160		

using Dowex 50, 8 percent cross-linked, 350 mesh.

The mass spectrometer used for this work consisted of a 12 inch radius, 60° sector analyzer section (Consolidated Electrodynamics Corporation) with detachable source, in-line valve, and cold finger in source housing using single Ta filament surface ionization, Faraday cup collector, Cary vibrating reed electrometer, and W. Shields design expanded scale system of recording residual voltages (after 70 to 90 percent precise nullification) on a modified Leeds-Northrop Speedomax G recorder. All scale settings on vibrating reed electrometer and expanded scale system were kept the same for all runs, including the calibration and standardization analyses, so that instrumental fixed bias was removed.

In analyses of Sr isotopic ratios the internal consistency of repeated ratio measurements in a single analysis gave a standard deviation of the mean of less than 0.01 percent. Allowing for possible contamination, we believe that the overall error will not exceed a standard deviation of 0.00015.

Mass spectrometer errors in analyses of isotope dilution are generally not more than 1 percent (standard deviation) for Sr and 2 percent for Rb, but in these cases of low Rb content the error due to contamination may outweigh the measurement error. Repeated analyses on separate small rock fragments show also the inhomogeneity of the rock, so that overall errors determined on this basis would reflect this added factor. Because the Rb, Sr, and Sr isotope analyses are performed on each piece separately, the inhomogeneity does not affect the age relationship. The uncertainty in the error at this stage of the investigation has resulted in an assignment of a larger error than is probably necessary.

Analyses of the California Institute of Technology (CIT) Rb and Sr normal solutions are given in Table 1, relative

Table	2.	Tranquillity	Base	samples :	total	rock	fragments.
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Sample	Rubidium (10 <sup>-6</sup> g/g)	Strontium (10 <sup>-6</sup> g/g)	<sup>87</sup> Rb/ <sup>86</sup> Sr Atomic ratio	<sup>87</sup> Sr/ <sup>86</sup> Sr Normalized*
22.43	6.0†	174†	0.099	0.7051‡
72.25	5.4	168	0.093	0.7051
20.28	0.77	152	0.0146	0.7000
58.36	0.62	173	0.0103	0.6998
47.24	1.18	189	0.0181	0.6996
Sargasso Sea	a water			0.7090

\* Normalized to  ${}^{86}Sr/{}^{88}Sr = 0.1194$ . † Preliminary values only; errors not yet established by replicate analyses to ascertain inhomogeneity between fragments. # Error in replicate ratio measurements in single analysis  $\sigma_m = 0.0001$ 



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  ${}^{87}$ Sr/  ${}^{86}$ 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<sub>3</sub> standard is 0.7080.

Analyses are listed in Table 2 and plotted in Fig. 1. Reference isochrons for 4.4, 4.5, and  $4.6 \times 10^9$  years are given in Fig. 1 for comparison, based on  $({}^{87}Sr/{}^{86}Sr)_0 = 0.6990$  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 <sup>87</sup>Sr/<sup>86</sup>Sr lower than any found in earth or meteoritic rock materials. The combination of 87Sr/86Sr 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 nonvolatile but hyperfusible components such as the rare and alkaline earths, and the relative depletion in volatile components such as the alkalies, 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 alkalies, 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  $3.80 \pm 0.11$  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 totalrock analyses of Apollo 11 samples. Sample numbers are identified in Table 1. I. D., isotope dilution analysis; X.R.F., xray flourescence analysis.

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 <sup>87</sup>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.

SCIENCE, VOL. 167

## References and Notes

or magmatic stage of crystal fractiona-

tion must have caused enrichments in

some trace elements while still preserv-

ing the inherent discrepancy in alkalies.

Whether this second stage occurred in

the moon, or in earlier bodies which

later made up the moon, is not indicated

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