samples have not so far been analyzed because of their complex history and their extremely high solar wind content. Figures 1 and 2 summarize the results obtained so far. Without exception, the release patterns are consistent with a recent episode of argon loss having occurred in relatively old rocks, after the fashion described above.

The evidence, in the low-temperature argon release, of regions within each of the samples that are low in radiogenic ^{40}Ar, relative to potassium, makes it possible in principle for one to estimate the time of the event which produced the loss of argon. In practice, with the present samples, it has been possible to place only upper limits on the time of outgassing because in most cases the gas loss was relatively small. These times are included in Table 1 and indicate that the events concerned, possibly the impact events which transported the rocks across the lunar surface, occurred relatively recently. It will be necessary to examine cosmic-ray exposure ages for details of this part of the rocks' history.

In all but two samples (10017,49 and 10024,26) the $^{40}Ar/^{39}Ar$ ratio attains a constant value in the last five or so high-temperature extractions. The average value of these high-temperature ratios is presented in Table 1 together with the root-mean-square deviation of the individual ratios. The ages calculated from these ratios are also included in the table and are a truer indication of the time of origin of the rocks than ages based on the total gas release. The ages based on total gas release are included for comparison and also included is an estimate of the extent of argon loss. This is simply the fractional difference between the high-temperature $^{40}Ar/^{39}Ar$ ratio and the total gas $^{40}Ar/^{39}Ar$ ratio.

Samples 10017,49 and 10024,26 do not show plateaus in the argon release pattern, and it is probable that the "high-temperature" age, calculated on the basis of the last significant argon extraction, represents only a lower limit on the true age of the rock. Likewise the fractional argon losses calculated (48 percent and 45 percent, respectively) can only be regarded as lower limits.

The effect of applying the correction for argon loss is impressive in that the spread of ages is considerably reduced. The ages based on total argon cover a range of 1.4×10^9 years, from 2.30×10^9 years to 3.76×10^9 years. If we take account of the fact that the "high-temperature" ages of samples 10017,49 and 10024,26 are now to be regarded only as lower limits, the significant spread in ages is reduced to 0.4×10^9 years (from 3.53×10^9 years to 3.93×10^9 years).

Once one has been able to largely eliminate the effects of argon loss, the problem of the interpretation of these ages is considerably eased, provided some estimate can be made of the area of the lunar surface represented by the samples. It is probable that most of the regolith is of comparatively local origin. This viewpoint is supported by the relative uniformity of composition of many of the Apollo 11 rocks (*3*), the existence of well-defined color boundaries associated with differences in underlying rock type (*4*), and the relationship of regolith thickness to local cratering density (*5*). Despite the fact that only a limited number of age determinations have been made, we can therefore now say with a fair degree of confidence that much of the vulcanism associated with this region of Mare Tranquillitatis occurred around 3.7×10^9 years ago.

It is impossible at the present time to reach any firm conclusions about the significance of the remaining spread in the measured ages. It is difficult to escape the conclusion that the spread is real and represents different rock-forming events which have occurred in the vicinity of the Apollo 11 site. However, before reading too much into these differences, it will be useful to seek corroboration by a comparison of the ^{40}Ar-^{39}Ar ages with either Rb-Sr or U-Pb ages.

GRENVILLE TURNER
Department of Physics, University of Sheffield, Sheffield, England

References and Notes

1. C. M. Merrihue and G. Turner, *J. Geophys. Res.* **71**, 2852 (1966); G. Turner, *Meteorite Research* (Reidel, Dordrecht, Holland, 1969), p. 407.
2. G. Turner, *Origin and Distribution of the Elements* (Pergamon, London, 1968), p. 387.
3. Lunar Sample Preliminary Examination Team, *Science* **165**, 1211 (1969).
4. E. A. Whitaker, *The Nature of the Lunar Surface* (Johns Hopkins Press, Baltimore, 1966), p. 79.
5. V. R. Oberbeck and W. L. Quaide, *Icarus* **9**, 446 (1968).
6. I thank D. Trotman of AWRE for performing the neutron irradiation and M. Ashworth for invaluable help in writing the computer programs for the reduction of mass spectrometer data. I thank the staff of the University of Sheffield Computing Laboratory for performing the calculations.

4 January 1970

Uranium-Thorium-Lead Isotope Relations in Lunar Materials

Abstract. *The lead isotopic compositions and uranium, thorium, and lead concentrations have been measured on six samples of material from the Sea of Tranquillity. The leads are moderately to very radiogenic; the initial lead concentrations are very low; the uranium and thorium levels are 0.26 to 0.88 and 0.87 to 3.35 parts per million, respectively. The Th/U ratios cluster about a 3.6 value. Apparent ages calculated for four rocks are 4.1 to 4.2 $\times 10^9$ years. Dust and breccia yield apparent ages of 4.60 to 4.63 $\times 10^9$ years. The uranium-lead ages are concordant, or nearly so, in all cases. The lunar surface is an ancient region with an extended record of events in the early history of the solar system. The discrepancy between the rock ages and dust ages poses a fundamental question about rock genesis on the moon.*

Elemental and isotopic abundances of uranium, thorium, and lead have been studied in six samples of lunar materials collected from the Sea of Tranquillity. The initial analytical results contain some fundamental information bearing upon the early history of the moon in matters of genesis, chemical differentiation, and timing. They raise some new questions concerning lunar evolution.

The samples include lunar dust (fines < 1 mm, sample 10084,35) a fine-grained dark breccia, apparently a sample of indurated lunar regolith (10060,-15), and chips of four rocks fairly representative of the textural and compositional ranges encountered in the Apollo 11 collections (10017,34; 10045,30; 10047,34; and 10072,39). The general character and lunar setting of these materials have been described previously (*1*).

The rocks are basaltic or gabbroic in composition and texture. Rocks 10072 and 10045 are fine-grained, vesicular to vuggy, and olivine-bearing. Rock 10017 has not been definitely identified as containing olivine and is a microgabbro in texture, with striking spherical vesicles. Rock 10047 is a medium-grained, cristobalite-bearing gabbro. The microbreccia, 10060, is very dark and fine-grained with a few scattered glass spherules suggesting its affinity to the dust sample.

The analytical techniques consisted of chemical decomposition with HF and $HClO_4$, extraction of Pb, U, and Th from the residue with concentrated HNO_3 and various procedures of coprecipitation and organic solvent extraction

Table 1. U-Th-Pb isotope data for some Apollo 11 materials.

Sample	Type	Pb Composition						Concentration (ppm)*				
		Observed			Corrected for blank†			U	Th	Th/U	Pb total	Initial lead limits‡
		206/204	207/204	208/204	206/204	207/204	208/204					
10084,35	D Fines	141.18	92.80	153.79	171.22	111.16	181.74	0.56_2	2.17_2	3.86	1.46_5	0.15_7
10060,15	C Breccia	77.77	51.97	82.31	83.18	55.29	86.53	0.60_6	1.46_6	2.42	1.78_5	0.40_0
10017,34	A Rock	206.9	99.8	225.6	257.0	122.1	290.0	0.73_5	2.72_4	3.71	1.65_2	0.13_2
10072,39	A Rock	242.2	115.8	266.7	563.3	259.0	594.1	0.88_4	3.3_5	3.79	1.58_6	0.06_1
10045,30	A Rock	83.20	45.46	102.0	117.81	61.24	135.90			Incomplete		
10047,34	B Rock	67.79	39.25	82.25	79.03	44.41	92.14	0.25_9	0.86_9	3.36	0.74_1	0.18_2
Averages (for 3 rocks)								0.62_6	2.31_3	3.62	1.32_6	

* General concentration error limits, ±3 percent; a few are larger. †Individual blanks determined in all cases where available; general blank for samples 10060,15 and 10045,30. ‡Maximum values, nonradiogenic lead.

for each element. The $Ba(NO_3)_2$ coprecipitation method for lead of Tatsumoto (*2*) was particularly useful.

Concentrations of the elements were determined by isotope dilution and mass spectrometry. Replicate sample analyses show reproducibility within 2 to 3 percent, with greatest uncertainty derived from application of blank corrections. Blank analyses have been run in parallel with all samples, but not all have been completed and specifically applied at this time. Lead blanks vary with the size of the sample analyzed and range from 0.04 to 0.12 μg per analysis. Lead in the sample ranged from 0.75 to 2.0 μg. The size and composition of the lead blanks make them significant corrections in treating the analytical results. Some general blank corrections have been applied which will be refined as the study continues. Uranium and thorium blanks are consistently at the level of 0.002 ± 0.001 μg and in no case have affected the observed data by as much as 1 percent.

Isotopic analyses were performed on a 12-inch (30.5-cm) solid-source mass spectrometer with digital data output. The precision of the analyses were generally better than 1 percent. Small corrections for observed mass-dependent fractionation (0.2 percent per mass unit) have been applied to the lead data. They do not influence the results significantly.

The analytical results are presented in Table 1. The observed lead isotopic compositions are shown along with composition ratios corrected for a common lead blank. The correction lead has values $^{206}Pb/^{204}Pb$, 18.2; $^{207}Pb/^{204}Pb$, 15.6; $^{208}Pb/^{204}Pb$, 38.0; values were measured directly. The uranium, thorium, and lead concentrations have all been corrected for blanks. The lead is reported as total lead and includes both radiogenic and nonradiogenic components. Limiting values for initial nonradiogenic lead, based upon model compositions compatible with the apparent ages of the samples and assuming no extralunar contamination, have been calculated. These must be considered as maximum values. The Th/U ratio has also been calculated on a weight ratio basis.

The observed lead isotopic compositions are strikingly radiogenic, from 75 to more than 95 percent. Comparable enrichments have not been reported for terrestrial basaltic materials. The enrichment reflects (i) very low concentrations of initial or original lead relative to uranium and thorium and (ii) very great ages for these materials.

Pure initial leads have not yet been extracted from the samples. To estimate the quantities, model lead compositions based upon earth and meteorite lead evolution data have been assumed. Because the blank corrections apply only to contamination in our laboratory procedures, previous contaminations are possible and uncorrected. The calculated original lead values are probably maximum limits. The values range from 0.06 to 0.40 ppm and are lower than concentrations found in primitive oceanic tholeites (*2*).

The uranium and thorium concentrations of the three rocks average about 0.63 ppm and 2.31 ppm, respectively; these values are similar to those found in oceanic alkali basalts and are enriched 5 to 10 times compared to oceanic tholeites (*3*). The Th/U ratios also resemble those found in alkali basalts, while contrasting with the oceanic tholeites.

The concentration averages for the limited number of rock samples closely approximate the concentration values for the mixed debris of the lunar regolith represented by the fines and the breccia. This suggests that most of the sources of these fine-grained fragmental aggregates may be comparatively local and related to the source of the rocks. Many other compositional similarities which support this possibility can also be noted in the preliminary data (*1*). Thus, this relatively limited sampling probably has significance for the U-Th-Pb characteristics of some of the Sea of Tranquillity region but may not represent the entire moon.

With this cautionary statement on the sampling, it is interesting to observe that the Th/U ratios found in the lunar ma-

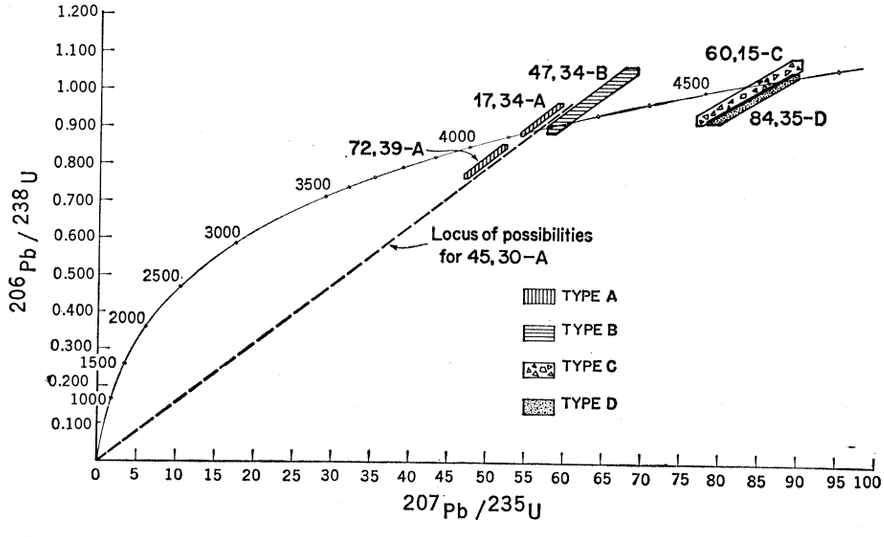

Fig. 1. Concordia diagram showing U-Pb isotope relationships in the analyzed lunar materials.

terials closely approximate those which are calculated for a general evolutionary model for the earth and meteorites (*4*). This is in marked contrast to the K/U ratios and Pb/U ratios observed. The Apollo 11 Preliminary Science Report (*1*) indicates K values ranging from 0.05 to 0.25 weight percent for the various samples of rocks and dust. This indicates K/U ratios of 2000 to 4000, values significantly lower than those found in meteorites or in the terrestrial crust.

An even more striking contrast with other solar system materials we know is found in the U/(initial lead) ratios. Expressed as observed μ-values ($^{238}U/^{204}Pb$) they are, for all samples studied, greater than 70 and probably greater than 200 to 700. Terrestrial basalts commonly are in the range of $\mu = 5$ to 10, and μ rarely exceeds 30 for terrestrial rocks of any kind.

One must conclude that K and Pb fractionation relative to U and Th has been extreme. Unidentified processes which discriminate the volatile K and Pb from the refractory U and Th to an extent unrecognized terrestrially appear to have been operative. These processes must be fundamental to lunar evolution.

The systematics of the U-Th-Pb isotope systems in the lunar materials are reported in Table 2. They are derived from the data in Table 1, utilizing a uranium isotopic composition of $^{238}U/^{235}U = 137.8$. Direct observations on the uranium isotopic composition have not been completed, but preliminary measurements support this or perhaps a very slightly lower value. Real differences would require some absolute but not relative changes in the values reported.

In order to calculate the isotope ratios in Table 2, it is necessary to select appropriate values for the nonradiogenic lead correction. These values can be either the initial (original) leads of the samples or a nonradiogenic contamination lead; it is probably some combination of both. Table 2 shows pairs of values based on both limits; the best values lie between the pairs. The following initial values have been inferred from earth and meteorite lead evolution models and from the apparent $^{207}Pb/^{206}Pb$ ages which are insensitive to these corrections:

	206/204	207/204	208/204
10084, 10060	9.6	10.4	29.7
10017, 10045			
10047, 10072	10.5	12.2	31.0
Contamination lead	18.2	15.6	38.0

Apparent ages from the relevant isotope ratios are also shown in Table 2. The choice of nonradiogenic lead has a negligible effect on the $^{207}Pb/^{206}Pb$ apparent age and affects the other apparent ages less as the sample leads are more radiogenic.

Assignment of compounded errors to all of the values in Table 2 is complex. They are best shown in dimensions of uncertainty in Fig. 1, where the U-Pb isotope ratios are plotted on a "Concordia" diagram (*5*). The error figures incorporate analytical error assignments and the uncertainties due to the selection of nonradiogenic lead corrections. Although a complete set of values is not available for sample 10045,30, the dashed line represents the locus of possibilities for its position, based upon a good set of lead isotopic composition data.

Inspection of the U-Pb systematics in Table 2 and Fig. 1 reveals some important relations, which are supported by the $^{208}Pb/^{232}Th$ data.

1) The dust and breccia samples have 4630 and 4600 million year $^{207}Pb/^{206}Pb$ ages, have U-Pb ages in near agreement, and are apparently as old as any earth or meteorite materials measured.

2) The four individual rocks have $^{207}Pb/^{206}Pb$ ages in the range of 4130 to 4220 million years and appear to be at least 400 million years younger than the composite dust and breccia samples. They are older than any known terrestrial rocks. The three rocks for which complete data are available are nearly concordant, but it appears that the slight discordance of 10017,34 is real.

If the four rocks represent sources which have contributed to the dust also, and many data suggest this, then it may be inferred that the dust contains some materials with higher $^{207}Pb/^{206}Pb$ ratios than that measured from the composite sample. This would imply an even greater age than 4.63 billion years for some part of the lunar surface. It is difficult to reconcile the significant differences between the rocks and the regolith if material of the regolith is comprised principally of constituents isotopically similar to the rocks. Unfortunately, the patterns of discordance are too loosely defined by the present data to permit evaluation of several possibilities which might exist. It will be necessary to refine these data and add others before a complete understanding is possible.

The relative ages of the four rock samples appear to be partially resolvable. Rock 10047,34, a type B cristobalite-gabbro, appears distinctly older than the other three rocks, which appear to be close to the same age. It is possible, of course, that rock fragments 10017, 10045, and 10072 were torn from the same outcrop and are different parts of the same genetic mass. More petrologic and mineralogical information about these samples is necessary for evaluation of this possibility.

It is noteworthy that the apparent age of the regolith is similar to ages determined from many meteorite samples. The lunar surface has been a postulated source for some meteorites. The only stony meteorite which has yielded a significantly radiogenic lead is Nuevo Laredo, a basaltic achondrite, which also yields a 4.6×10^9 $^{207}Pb/^{206}Pb$ age (*6*, *7*).

The U-Th-Pb isotope relations among

Table 2. U-Th-Pb isotope data for some Apollo 11 materials.

Sample	Type	Isotope ratio*				Apparent age (10^6 years)			
		$^{207}Pb/^{206}Pb$	$^{206}Pb/^{238}U$	$^{207}Pb/^{235}U$	$^{208}Pb/^{232}Th$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{238}U$	$^{207}Pb/^{235}U$	$^{208}Pb/^{232}Th$
10084,35	D Fines	0.623$_2$	1.05$_2$	90.$_4$	0.24$_8$	4630	4675	4645	4535
		0.627$_6$	.99$_6$	85.$_8$	0.23$_4$	4635	4500	4600	4310
10060,15	C Breccia	0.609$_5$	1.05$_1$	88.$_3$	0.32$_5$	4595	4675	4620	5760
		0.610$_8$	.92$_8$	78.$_1$	0.17$_8$	4600	4270	4495	3365
10017,34	A Rock	0.445$_9$	0.95$_9$	59.$_1$	0.26$_2$	4130	4375	4210	4790
		0.446	0.93	57.$_3$	0.25$_6$	4130	4275	4180	4670
10072,39	A Rock	0.446$_4$	0.81$_2$	49.$_9$	0.21$_1$	4130	3865	4045	3925
		0.446$_4$	0.80	49.$_3$	0.20$_8$	4130	3825	4030	3880
10045,30	A Rock	0.457				4170			
		0.458$_2$				4170			
10047,34	B Rock	0.470	1.05$_4$	68.$_3$	0.27$_1$	4210	4680	4360	4950
		0.473$_6$	0.93$_6$	61.$_1$	0.24	4220	4300	4245	4410

*No initial leads have been determined; upper values corrected with model initial lead; lower values with contamination lead composition.

the rocks and the regolithic material indicate an extended history of rock-forming events for the moon which may be studied with profit by these techniques, particularly when coupled with systematic geologic documentation of sample sources. The question posed by the discrepancy between the apparent ages of the rock fragments and the associated lunar dust and breccia raises the possibility that fundamental and unexpected rock-forming processes exist.

LEON T. SILVER
California Institute of Technology, Pasadena 91109

References and Notes

1. "Apollo 11 Preliminary Science Report," *NASA SP 214* (Washington, D.C., 1969).
2. M. Tatsumoto, *Science* **153**, 1094 (1966).
3. M. Tatsumoto, C. E. Hedge, A. E. Engel, *Science* **150**, 886 (1965).
4. V. R. Murthy and C. C. Patterson, *J. Geophys. Res.* **67**, 116b (1962).
5. G. W. Wetherill, *Am. Geophys. Union Trans.* **37**, 320 (1956).
6. M. D. Duke, L. T. Silver, *Geochim. Cosmochim. Acta* **31**, 1661 (1967).
7. C. C. Patterson, *ibid.* **7**, 151 (1955).
8. Essential to this work was the dedicated laboratory participation and cheer of Geraldine Baenteli and Dolly Pearson. E. V. Nenow and C. Bauman provided important technical support. E. Brown wrestled untiringly with NASA, which supported the major part of this research under contract NAS 9-7963. California Institute of Technology Contribution No. 1707.

4 January 1970

Rubidium-Strontium, Uranium, and Thorium-Lead Dating of Lunar Material

Abstract. *Rubidium and strontium concentrations and strontium isotopic compositions have been measured on whole rock samples and density fractions of microgabbro. Density fractions on two rocks define isochrons of 3400 and 4500 million years with large uncertainties owing to low enrichment of radiogenic strontium. Lead from fine surface material is highly radiogenic. An age of 4750 million years has been calculated from the ratio of $^{207}Pb/^{206}Pb$. The concentrations of uranium, thorium, and lead isotopes are consistent with the evolution of lead in a 4700-million-year-old closed system characterized by the ratios of uranium to lead and of thorium to lead in this surface material.*

A time scale established by dating significant events in lunar history will permit one to relate lunar history to that of the earth and solar system and will place absolute values on relative chronologies established by photogeology. The first step in this program is to assess the usefulness of available lunar materials for dating purposes and to establish the approximate range of ages with which we will be dealing in the dating of lunar rocks.

Initial Rb-Sr dating has been carried out on samples of crystalline rock, in the belief that the interpretation of results on such rocks should be more straightforward than that on the microbreccia samples. The concentrations of K, Rb, and Sr found by mass spectrometric isotope dilution analysis of five such rocks, as well as in a sample of fine lunar surface material, are given at the top of Table 1. The data are plotted in Fig. 1. These rocks are characterized by low Rb/Sr ratios, resulting in small (~1 percent) enrichments in radiogenic strontium-87.

These values of $^{87}Sr/^{86}Sr$, not greatly enriched over the primordial values found from meteorite studies, indicate that, like the earth, the source of these lunar rocks acquired a Rb/Sr ratio much lower than the chondritic or solar value very early in the history of the solar system.

These small enrichments place constraints on the interpretation of the Rb-Sr data in terms of ages. Consequently, any such interpretations given herein must be regarded as preliminary. Improvements in our techniques for measuring Sr isotope ratios, such as conversion to digital recording, are currently being made, and more definitive results will soon be obtained by remeasurement of these same Sr samples.

Rb-Sr measurements define the time at which a Rb-Sr fractionation took place in the chemical system being studied. In the case of rock systems, this requires measurement of at least two samples with differing Rb-Sr ratios, which had the same Sr isotopic composition at the time of the event being dated. This is the case for cogenetic materials in which the Sr isotopic composition was initially homogeneous. For whole-rock dating, it is therefore preferable that independent evidence exists for the cogenesis of the rocks, in order that the entire burden of the argument for cogenesis does not rest upon the colinearity of the data when plotted on a Sr evolution diagram. This independent evidence is lacking in the case of these lunar rocks. Therefore, our initial effort has been directed to the study of the "internal ages" of single rock samples, obtaining varying Rb-Sr ratios by separation of density fractions of finely ground ($< 88\ \mu m$) rock. These are not pure mineral separates, but have the advantage that an insignificant quantity of material is rejected in the process of separation.

The separation procedures were described in work on density fractions from enstatite and shocked hypersthene chondrites (*1*). The chemical procedures are identical to those employed in our published work on meteorites (*2*). As in this work, K, Rb, and Sr blanks are ~50, 0.1, and 1 ng, respectively, and they represent a negligible contribution to our results.

The most radiogenic fraction from two samples of microgabbro (Table 1) has a density of ~3.3 g/cm^3 and probably represents a pyroxene concentrate. The least radiogenic fraction has a density of less than 2.96 g/cm^3 and was found to consist almost entirely of plagioclase. The $^{87}Rb/^{86}Sr$ ratios range over a factor of about three, and with

Table 1. The Rb and Sr analytical results.

Sample	K (μg/g)	Rb (μg/g)	Sr (μg/g)	$^{87}Sr/^{86}Sr$ (atomic)
84,25 (fines)	1100	2.83	164.7	0.7017
72,38	2539	5.72	168.8	0.7043
24,24	2814	6.20	183.9	0.7044
17,41	2500	5.80	174.2	0.7044
50,30	665	0.788	188.9	0.7002
22,45		5.66	165.5	0.7047
17,41 fractions:				
$\rho<2.96$		9.52	548.3	0.7022
$2.96<\rho<3.32$ (coarse)	4090	9.19	257.3	0.7047
$3.32<\rho$ (coarse)	1545	4.01	77.9	0.7070
$3.15<\rho<3.25$ (fine)		7.79	134.0	0.7080
$3.25<\rho$ (fine)	843	2.30	45.8	0.7065
24,24 fractions:				
$\rho<2.96$		14.27	598.2	0.7026
$2.96<\rho<3.15$		19.42	520.0	0.7050
$3.15<\rho<3.32$		15.43	286.2	0.7081
$3.32<\rho$		2.82	47.7	0.7083