

Helium, Argon, and Carbon in Some Natural Gases

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Abstract. Thirty-nine samples of natural gases representing varied chemical compositions and geological occurrences were analyzed for their helium, radiogenic argon, and atmospheric argon contents. The total range in the $(\text{He}/\text{A})_{\text{rad}}$ ratio was found to be 1.6 to 130 with most samples having values between 6 and 25. This range of values is essentially equal to the production ratio from the uranium, thorium, and potassium in average igneous rocks and a wide variety of sediments. This indicates that all of these natural gases have obtained their radiogenic gases from rather average rock types. This is true in spite of the fact that the gases range in helium content from 37 to 62,000 ppm.

A theoretical discussion of the origin of helium and argon in natural gases is given. It can be shown from the ratio of nitrogen to atmospheric argon that most of the nitrogen in these gases cannot come from the entrapment of air. From a consideration of the concentration of atmospheric argon in natural gases it is possible to estimate the proportion of gaseous and aqueous phases assuming diffusive equilibrium.

The isotopic composition of the carbon in the methane of these gases was found to be very light. It was shown that for coexisting CH_4 - CO_2 pairs the carbon dioxide was always isotopically heavier.

INTRODUCTION

The purpose of this study was to investigate the relationship between the abundances of helium and argon in natural gases of different compositions and environments and to examine the isotopic composition of the carbon in these gases. Since the discovery of terrestrial helium in natural gases by *Cady and McFarland* [1906], a vigorous search has been made for helium-rich gases, and a considerable number of total gas analyses that include helium determinations exist in the literature. These have been made using both volumetric and mass spectrometric techniques [*Rogers*, 1921; *Anderson and Hinson*, 1951; *Boone*, 1958].

The origin of high helium natural gases, some of which have helium contents as great as 10 per cent, has been the subject of considerable speculation. The He^4 contained in them is presumably the product of the radioactive decay of U^{235} , U^{238} , and Th^{232} , and their intermediate daughter products. A fundamental question arises whether these quantities of helium represent the accumulated decay products of a

reservoir greatly enriched in U and/or Th, or the accumulation from a rather normal rock reservoir. Lastly, there exists the possibility that the helium represents some more primordial gases trapped in the earth during its early history and subsequently partly released into stratigraphic and structural traps. These various possibilities have been recognized by some of the earliest investigators in the field [*Rogers*, 1921]. It has been found [*Faul, Gott, Manger, Mytton, and Sakakura*, 1954; *Sakakura, Lindberg, and Faul*, 1959] that several helium wells, i.e., wells containing over 0.5 per cent helium, are radioactive owing to a high radon content and appear to be associated with some uraniumiferous petroleum residues. Other high helium wells, however, are devoid of such radioactivity. In addition, many well gases have a high radon content and only small concentrations of helium [*Satterly and McLennan*, 1918]. The composition of helium-rich gases has been found to be quite variable, although in some gas fields a correlation has been suggested between helium and nitrogen content.

The isotopic composition of helium from gas wells has been investigated by *Aldrich and Nier* [1948] who report values of $\text{He}^3/\text{He}^4 \approx 10^{-7}$. The results of these authors represent the only published data on He^3 content in terrestrial gases. The origin of the He^3 in these gases has been considered by several workers. *Hill* [1941] suggested that this isotope of helium could be produced in rocks by the reaction $\text{Li}^6(n, \alpha)\text{H}^3 \rightarrow \text{He}^3 + \beta^-$. More recently, *Morrison and Pine* [1955] have discussed the relative production of He^3 and He^4 in rocks. As shown by *Wetherill* [1953, 1954], the principal sources of neutrons are the reaction $\text{O}^{18}(\alpha, n)\text{Ne}^{21}$ and spontaneous fission of U^{238} . By considering the various nuclear reactions which compete for neutrons, Morrison and Pine conclude that the He^3/He^4 ratio observed by Aldrich and Nier in natural gases is most reasonably the product of these processes in materials which contain neither uranium nor thorium, or both, in very great concentration. Their arguments would not, however, preclude the origin of this helium to be from finely divided uranium minerals disseminated in a rather normal rock. This would permit uranium concentrations of up to a few tenths of 1 per cent.

The radioactive decay of K^{40} gives rise to the possibility of high argon-containing natural gases. Since potassium is a principal element in most crustal rocks as compared with uranium and thorium, a study of the ratio of radiogenic helium to radiogenic argon, $(\text{He}^4/\text{A}^{40})_{\text{rad}}$, gives more direct information on the possible source of helium gas wells.

Some results using this approach were reported by *Wasserburg, Czamanske, Faul, and Hayden* [1957] for some helium wells in the Texas Panhandle. These workers showed that the argon in four helium wells was about 70 per cent radiogenic and that the ratio $(\text{He}^4/\text{A}^{40})_{\text{rad}}$ was about 10. This ratio was well within the values to be expected from the present-day production rates of He^4 and A^{40} in normal igneous rocks. They therefore concluded that these helium wells were probably formed from the accumulated radiogenic gases found in rocks with a ratio of U/K typical of normal igneous rocks, and that in no way could these gases be the result of accumulation from an enriched uranium reservoir. For these samples it was shown that the $\text{A}^{38}/\text{A}^{36}$ ratio was the same as that found in atmospheric argon and it was therefore possible to make

estimates of the contribution of atmospheric gases.

EXPERIMENTAL TECHNIQUES

We have studied a variety of natural gases covering a wide compositional and environmental range in order to attempt some understanding of their origin. In this study we have restricted our efforts to well gases and have not investigated volcanic or hot spring emanations. Thirty-nine samples were analyzed for their helium and argon contents and for isotopic composition. Partial gas analyses for other major constituents were also made. The isotopic composition of the total gas carbon, methane carbon, and carbon dioxide carbon were determined. The results of this investigation are presented in Tables 1 and 2, together with pertinent well data for each sample. The accompanying total gas analyses represent data supplied us by the participating petroleum and natural gas companies, partial gas analyses performed in our laboratory, and a combination of these two sources. With the exception of three samples, the H_2S contents were less than 0.01 per cent. For samples 14, 34, and 35, the H_2S contents were 0.04, 0.09, and 0.12 per cent, respectively.

With the exception of samples 29, 30, 31, and 32, the well gases were collected using standard high-pressure, stainless steel gas cylinders with valves on both ends. The cylinders were connected to the gas source and purged of air by passing well gas through them under positive pressure for several minutes. The outlet valve was then closed, and the pressure in the cylinder was allowed to reach a satisfactory value (20–3000 psig), and then the valve to the source was closed. All of these sample vessels were at a pressure of considerably over 1 atmosphere when they were used for analysis. Samples 29–32 from the Texas Panhandle gas field were obtained by Henry Faul in 1954. They were collected in glass cylinders that had openings at both ends. After allowing the gas to pass through the cylinders at slight positive pressure for a few minutes, both ends of the vessel were sealed off. In every instance the helium, argon, and carbon analyses were done on the same sample.

The gas cylinders were joined onto a vacuum line (Fig. 1) with metal-to-glass couplings and the system was evacuated with all the furnaces heated and outgassed before each run. After the

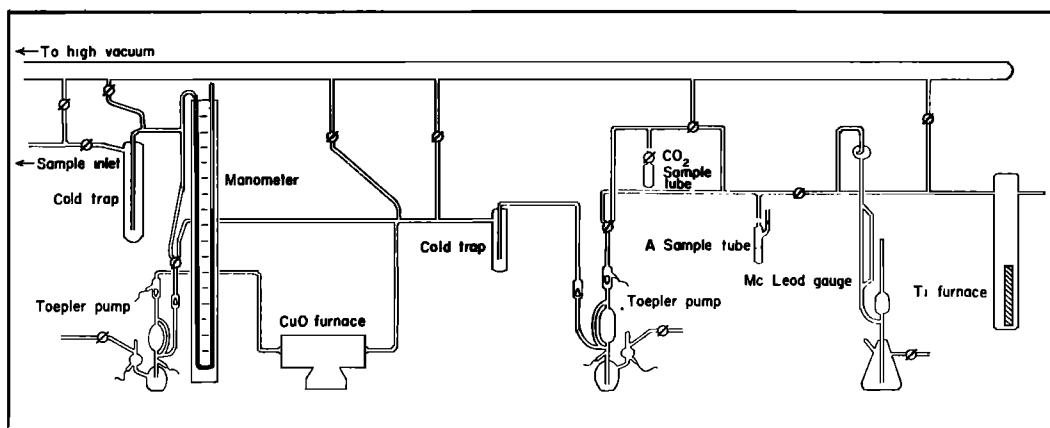


Fig. 1. Vacuum apparatus used for helium, argon, and carbon determination and extraction.

system was found to be vacuum tight, some gas was released into a part of the system of known volume and the pressure measured on a manometer. For most samples a tracer of A^{38} was introduced and the gases mixed. The sample size ranged from 2 to 100 cc STP. For total gas carbon analyses, all gas was then pumped directly into the combustion system. For methane carbon analyses, liquid N_2 was placed on a cold trap and the noncondensable fraction was continuously pumped into the combustion system until no gas phase remained. The combustion procedure used was similar to that described by *Craig* [1953]. A CuO furnace, made of fused quartz, was heated to $900\text{--}950^\circ\text{C}$, and the gases were cycled through it until complete combustion to CO_2 was obtained. During this combustion period, dry ice baths were placed on a cold trap to collect the water produced. After combustion, the dry ice baths were replaced with liquid nitrogen and the noncondensibles—including N_2 , He, and A—were transferred by a Toepler pump into another section of the line (of known volume) containing a Ti furnace, McLeod gages, and a sample tube filled with activated charcoal. The Ti furnace was heated to approximately 950°C and the gas sample purified. The amount of this noble gas residue was then measured, using a McLeod gage. Liquid N_2 was next applied to the charcoal trap and the condensible fraction quantitatively absorbed. The pressure was again measured and attributed to helium. The argon sample tube was sealed off from the line and mass spectrometrically analyzed. The helium yield

was checked by running samples of known helium concentration and by comparing the results of duplicate analyses in which the combustion time and the amounts of gas were varied by a factor of 4. The purity was checked by observing the Tesla discharge color. No detectable loss of helium by diffusion through the fused quartz combustion tubes was observed. According to the work of *Norton* [1953] on the diffusion of helium through fused quartz at various temperatures, it was expected that less than 1 per cent of the helium would be lost by diffusion during the combustion procedure. Blank runs carried out under conditions similar to those in which a sample was being analyzed showed no appreciable introduction of inert gases into the line.

The argon content was determined by (1) the difference between the volumetrically determined total noble gas residue and the helium content, (2) a volumetric determination of the condensible fraction after a second purification (before which the helium was pumped off and the Ti furnace outgassed), and (3) isotope dilution using A^{38} tracers of known content as described by *Wasserburg and Hayden* [1955]. The volumetrically determined argon values are generally higher than the isotope dilution value. The first method yields argon contents up to 40 per cent higher than the isotope dilution value, whereas the second method shows discrepancies of up to 15 per cent. The results obtained by the first method were highly reproducible over a long period of time. They were, nevertheless, frequently in error, presumably owing to the

TABLE 1. Sample Data
 A. Location and description. Samples 40 and 41, supplied by Continental Oil Company, were run after final text was written.
 Sample 41 contains 12.2 per cent H₂S.

No.	State	County	Field	Owner	Name
1	California	Glenn	Willows-Bee Hive Bend	Gen. Pet. Corp. of Calif.	Unit 1
2	California	Sacramento	Rio Vista	Standard of Calif.	Jordan Unit 1
3	California	Sacramento	Rio Vista	Rio Vista State	H-8
4	California	San Joaquin	Gait	Amerasia Pet. Corp.	Bankline Comm. 1
5	California	San Joaquin	West Thornton	Standard of Calif.	McCormack-Williamson 1
6	California	Sutter	Marysville Buttes	Buttes Oil and Gas Co.	A-5
7	California	Yolo	Dunigan Hill	Standard of Calif.	Hermle 1
8	Colorado	Moffat	Ace	Mountain Fuel Supply Co.	Unit 1
9	Colorado	Moffat	East Hiawatha	Mountain Fuel Supply Co.	Unit 1
10	Colorado	Moffat	Powder Wash	Mountain Fuel Supply Co.	J. C. Donnel No. 3
11	Colorado	Wallace	Sexson	Mountain Fuel Supply Co.	N. D. Sexson No. 1
12	Colorado	Webster Parish	Cotton Valley	Skelly Oil Co.	Grant No. 2
13	Louisiana	Webster Parish	Cotton Valley	Cotton Valley Oper. Comm.	Hodges No. 3
14	Louisiana	Hillisdale	Cotton Valley	The Ohio Oil Co.	Stephens No. 1
15	Mississippi	Forest	Maxie	The Ohio Oil Co.	Unit SE 12 No. 1-E
16	New Mexico	Harding	Bueyeros	Carbonic Chemicals Corp.	Mitchell No. 4
17	New Mexico	Harding	Bueyeros	Carbonic Chemicals Corp.	Mitchell No. 12
18	New Mexico	Lea	Blinebry	The Ohio Oil Co.	L. Warthan No. 9
19	New Mexico	Lea	Drinkard	The Ohio Oil Co.	L. Warthan No. 10
20	New Mexico	Lea	Hobbs	The Ohio Oil Co.	St. Sec. 30-18-38 No. 3
21	New Mexico	Rio Arriba	Blanco	El Paso Natural Gas	Klein No. 6
22	New Mexico	San Juan	Wildcat	Pan American Pet. Co.	Navajo C-1
23	New York	Erie	Keyes	Iroquois Gas Corp.	Well 1686
24	Oklahoma	Cimarron	Keyes	Shell Oil Co.	Sleeper No. 1
25	Pennsylvania	Cameron	Keyes	The Sylvania Corp.	Well 342
26	Pennsylvania	Mercer	Keyes	United Natural Gas Co.	Well 2651
27	Pennsylvania	Venango	Keyes	United Natural Gas Co.	Well 4329
28	Texas	Coke	Bronte	Humble Oil and Refining Co.	Bronte Gardner
29	Texas	Hartley	W. Panhandle	Colorado Interstate Gas Co.	Bivins A-71
30	Texas	Moore	W. Panhandle	Colorado Interstate Gas Co.	Thompson C-1
31	Texas	Moore	W. Panhandle	Phillips Petroleum Co.	Ola
32	Texas	Moore	W. Panhandle	Phillips Petroleum Co.	Rubin No. 4
33	Texas	Moore	W. Panhandle	Phillips Petroleum Co.	Pipeline
34	Utah	Carbon	Farnham Dome	Carbon Dioxide and Chem. Co.	No. 2
35	Utah	Carbon	Farnham Dome	Phillips Petroleum Co.	Equity
36	Wyoming	Sweetwater	Canyon Creek	Mountain Fuel Supply Co.	Unit 3
37	Wyoming	Sweetwater	East Hiawatha	Mountain Fuel Supply Co.	M. W. Newberger No. 1
38	Wyoming	Sweetwater	South Baxter Basin	Mountain Fuel Supply Co.	Unit 2
39	Wyoming	Uinta	Church Buttes	Mountain Fuel Supply Co.	Unit 4
40	Texas	Crockett	Church Buttes	Continental Oil Co.	...
41	Alberta	...	Church Buttes	Hudson's Bay Oil Co.	...

TABLE 1. Continued

No.	Location		R	Date Sampled	Depth to Producing Zone (ft)	Initial Pressure psia	System	Formation
	S	T						
1	29	20N	2W	4/25/57	3400	1400	Cret.	Unit VI F-1 sand
2	29	3N	3E	3/20/57	4100	1510	Eocene	Nortonville
3	29	4N	3E	3/20/57	5400	2060	Eocene	Marg. Hamilton
4	1	4N	6E	3/20/57	2340	960	Eocene	Domingue
5	30	5N	5E	3/20/57	2500	1410	Eocene	Meganos sh.
6	8	15N	2E	3/20/57	5400	...	Cret.	Glenn sh.
7	22	11N	1W	3/20/57	2500	1000	Eocene	Capay
8	34	12N	97W	3/26/59	8075	...	Paleocene	Fort Union
9	14	12N	100W	3/26/59	4885	1760	Paleocene	Fort Union
10	29	12N	97W	3/26/59	2851	...	Eocene	Wasatch
11	19	13S	42W	10/27/59	5006	...	Penn.	Morrow sand
12	7	21N	9W	10/23/59	8554	...	U. Jur.	Schuler (Bodeaw)
13	19	22N	9W	10/23/59	9174	...	U. Jur.	Schuler (Justliss)
14	10	5S	3W	11/11/59	3755	...	M. Ord.	Trenton-Black River
15	6	1S	12W	9/30/59	7303	...	U. Cret	Eutaw E-3
16	13	19N	29E	8/11/59	2075	580	Penn.	Abo
17	20	19N	30E	8/11/59	2074	580	Penn.	Abo
18	11	22S	37E	9/25/59	5330	...	Penn.	Clear Fork-Yeso
19	11	22S	37E	9/25/59	6420	...	Penn.	Clear Fork-Yeso
20	30	18S	38E	9/30/59	3900	1500	Penn.	San Andres
21	35	26N	6W	5/ /58	2630	...	Cret.	Pictured Cliffs
22	1	29N	17W	8/3/59	6366	3000	Penn.	Hermosa fm
23		Collins Twp		1/29/60	3011	1290	Silurian	Medina sand
24	35	6N	9E	8/3/59	4628	850	Penn.	Keyes sand
25		Gibson Twp		1/29/60	6627	2565	Devonian	Oriskany sand
26		Worth Twp		1/29/60	590	168	Mississippian	Berea sand
27		Rockland Twp		1/15/59	5200	...	Devonian	Speckley sand
28	...	Blk. 21	...	3/10/54	3200	440	Penn.	Strawn
29	Sec. 9	Blk. 10	CCS Surv.	3/10/54	2560	440	Penn.	Wolfcamp dolo
30	Sec. 2	Blk. 44	El RR Surv.	3/10/54	3525	440	Penn.	Wolfcamp dolo
31	Sec. 162	Blk. 1	H TC Surv.	3/10/54	3000	440	Penn.	Wolfcamp dolo
32	Sec. 16		P. D. Parks Surv.	8/3/59	Penn.	Wolfcamp dolo
33	...	15S	11E	9/10/59	3100	970	Penn.	Coconino ss
34	12	15S	11E	9/10/59	3100	970	Penn.	Coconino ss
35	12	15S	11E	3/27/59	5400	...	U. Cret.	Mesaverde
36	3	12N	101W	3/26/59	2375	935	Eocene	Wasatch
37	13	12N	100W	3/30/59	2605	900	U. Cret.	Frontier
38	29	16N	104W	3/27/59	12768	5400	U. Cret.	Dakota
39	29	16N	112W	4/13/60	8200	3450	Penn.	Strawn
40				4/13/60	8400	3800	Dev.	Woodbend

TABLE 1. Continued
B. Analytical data

No.	Lithology of producing zone	CH ₄ %	C ₂ H ₆ %	N ₂ %	CO ₂ %	He ppm	A ppm
1	ss	98.16	0.13	1.60	0.11	47.5	57.4
2	ss	95.43	2.37	1.57	0.09	41.2	52.2
3	ss	95.12	3.96	0.86	0.06	37	67
4	ss	68.91	0.01	30.97	0.09	96.6	140
5	ss	96.20	0.04	3.76	0.00	101	88.2
6	ss	90.70	0.11	9.15	0.03	37.6	53.1
7	ss	97.32	0.01	2.65	0.02	85	125
8	ss	84.5	10:5	4.03	1.03	101	32
9	ss	90.5	5.3	2.40	1.82	63	39
10	ss	86.7	11.0 ¹	2.30	...	140	118
11	ss	53.5	6.6	36.6	0.57	26000	1400
12	ss	82.7	14.8	1.0	1.52	152	26.5
13	ss	75.1	23.2	0.87	0.77	151	42.0
14	lms	56.1	21.4	22.2	0.1	1350	360
15	ss	96.52	1.06	1.48	0.90	359	81.9
16	sh and ss	0.0	0.0	0.12	99.9	44.5	28.0
17	sh and ss	0.0	0.0	0.15	99.8	46.6	29.2
18	ss	82.58	15.36	1.98	0.05	348	57.3
19	ss	82.4	14.8	2.6	0.17	480	66.8
20	lms	86.3	10.0	3.4	0.25	69.4	117
21	ss	91.10	7.87	0.94	0.07	172	46.1
22	lms	38.0	10.6	42.5	2.1	62200	5630
23	ss	86.2	8.0 (1)	5.6	...	1640	77.1
24	ss	65.3	6.7	24.9	0.7	22600	1080
25	ss	97.5	2.0 (1)	0.50	...	203	6.8
26	ss	95.1	2.8 (1)	1.9	...	1575	35.8
27	ss	75.7	23.6 (1)	0.64	...	805	14.9
28	ss and lms	76.5	15.9	6.5	0.9	1720	376
29	dolo	73.8	9.6 (1)	16.6	...	9370	877
30	dolo	84.0	6.4	8.95	0.1	4180	470
31	dolo	90.3 ²	...	9.7	...	4480	482
32	dolo	90.4 ²	...	9.6	...	4170	461
33	dolo	72.2	11.8	15.2	0.0	7000	710
34	ss	0.0	0.0	0.60	99.3	232	79.5
35	ss	0.0	0.0	0.55	99.3	187	65.4
36	ss	86.2	9.4	2.08	2.29	75	27
37	ss	88.4	10.3	1.22	0.10	158	73.4
38	ss	94.9	5.4	1.8	0.85	757	66.8
39	ss	89.8	7.0	3.09	0.85	152	17.5
40	lms reef	72.6	24.2	2.5	0.6	593	117
41	lms reef	71.1	7.9	3.6	5.0	1670	418

¹ Includes CO₂; ² Includes C₂H₆ and higher carbons, and CO₂.

presence of contaminating gases. A second purification as described in (2) gave volumetric values in relatively good agreement with (3). All samples except 3, 7, 8, 9, 10, and 36 have been run by isotopic dilution, and, except for these samples, the values for argon content listed in Table 1 have been determined by isotope dilution.

After the noncondensibles were pumped out of the part of the line containing the CuO furnace, the liquid nitrogen baths that hold H₂O and CO₂ were again replaced by dry ice baths and the CO₂ was allowed to sublime into this part of the line. The CO₂ was then transferred into a sample tube for isotopic analysis.

The carbon dioxide in the natural gases was removed by placing liquid nitrogen on a cold trap and pumping off the noncondensibles through another cold trap in order to retain any CO₂ that might be lost from the first trap. The remaining gases, which include CO₂ and hydrocarbons less volatile than CH₄, were then transferred into a reaction vessel containing a saturated Ba(OH)₂ solution with 80 per cent phosphoric acid in a side arm. The CO₂ was then converted to the carbonate, and the hydrocarbons were pumped off. The carbonate was reconverted to CO₂ by reaction with phosphoric acid and the CO₂ transferred to a vessel with liquid nitrogen.

TABLE 1. Continued
B. Analytical data

No.	A _{rad} ppm	A _{air} ppm	ε %	He/A _{rad}	A ⁴⁰ /A ³⁶	A ³⁸ /A ³⁶	(N ₂ /A _{air})	f _A ^ε	V ^ε /V ^ε
1	3.69	53.7	6.4	12.9	316 ± 3	0.219 ± 0.018	298	0.68	25
2	3.9	48.3	7.5	10.6	320 ± 3	...	325	0.69	24
3	4.4	63	6.6	8.4	317 ± 3	0.202 ± 0.015	137	0.46	62
4	15.7	124	11.2	6.15	334 ± 2	...	2500	0.49	55
5	4.64	83.6	5.3	21.8	312 ± 6	0.196 ± 0.007	450	0.50	53
6	9.47	43.6	17.8	3.97	361 ± 2	0.195 ± 0.015	2100	0.56	42
7	9.3	116	7.4	9.2	320 ± 6	0.194 ± 0.007	228	0.51	51
8	11.2	21	35.0	9.0	456 ± 14	0.201 ± 0.009	1920	0.68	25
9	4.8	35	12.3	13.1	337 ± 2	0.195 ± 0.007	706	0.74	19
10	13.6	104	11.5	10.3	336 ± 2	0.195 ± 0.010	221	0.44	67
11	1260	140	90.0	20.6	2818 ± 140	...	2610	-0.31	...
12	15.9	10.6	60.0	9.56	736 ± 8	...	943	0.83	11
13	27.2	14.8	64.8	5.55	841 ± 12	...	588	0.74	19
14	270	90	75.0	5.00	1185 ± 12	...	2470	0.37	90
15	48.2	33.7	58.8	7.46	720 ± 6	...	439	0.54	45
16	27.6	0.4	98.4	1.61	22500 ± 1100	...	3000	1.00	0
17	29.0	0.2	99.3	1.61	34000 ± 4000	...	7500	1.00	0
18	28.2	29.1	49.2	12.3	587 ± 3	...	680	0.71	22
19	37.9	28.9	56.7	12.7	684 ± 3	...	900	0.65	29
20	28.1	89	24.0	2.47	389 ± 2	...	382	0.43	70
21	13.4	32.7	29.1	12.8	417 ± 2	...	287	0.84	10
22	5580	50	99.0	11.1	29100 ± 4000	...	8500	0.36	94
23	62.6	14.5	81.3	26.2	1570 ± 20	...	3860	0.92	5
24	969	111	89.6	23.3	2720 ± 140	...	2240	0.60	35
25	4.2	2.6	61.8	48	775 ± 30	...	1920	0.97	1.6
26	17.7	18.1	49.5	89	587 ± 5	...	1050	0.99	0.6
27	6.0	8.9	40.2	134	494 ± 5	...	720	0.97	1.6
28	250	126	66.5	6.88	883 ± 10	...	515	-0.22	...
29	697	180	79.3	13.4	1435 ± 14	0.197 ± 0.003	922	0.66	27
30	375	95	79.7	11.2	1465 ± 15	0.201 ± 0.014	942	0.82	12
31	359	123	74.5	12.5	1160 ± 12	0.186 ± 0.023	789	0.77	16
32	336	125	72.9	12.4	1100 ± 11	0.198 ± 0.004	768	0.77	16
33	518	192	72.9	13.5	1195 ± 11	...	792
34	75.2	4.3	94.5	3.09	5300 ± 120	...	1395	0.98	1.1
35	60.7	4.7	92.7	3.08	4150 ± 95	...	1170	0.98	1.1
36	10.0	17	37.0	7.5	472 ± 15	0.203 ± 0.010	1224	0.82	12
37	12.5	60.9	17.0	12.6	355 ± 3	0.188 ± 0.008	200	0.76	17
38	59.1	7.7	88.4	12.8	2560 ± 130	0.204 ± 0.024	2340	0.97	1.6
39	12.2	5.3	69.7	12.5	960 ± 24	0.178 ± 0.018	5830	0.88	7
40	73.4	43.6	62.8	8.09	796 ± 10	...	573	0.35	96
41	381	37	91.1	4.38	3316 ± 150	...	973	0.29	130

The accompanying water was then held with a dry ice bath, and the purified CO₂ transferred into a sample vessel and mass analyzed.

In some of the carbon dioxide well samples, hydrocarbons were not detected, and therefore the CO₂ was purified by simply pumping off the noncondensibles at liquid nitrogen temperature. The Farnham Dome samples contained considerable amounts of H₂S, and this was removed by passing the gas repeatedly over heated silver filings.

All of the helium analyses and those argon analyses that were determined by isotopic dilution are most probably accurate to within 10 per cent. The helium was not isotopically

analyzed; the argon isotopic composition is given in Table 1 along with the mean deviation of the analysis. A³⁸/A³⁶ ratios are given for samples on which a run was made without using a tracer. The total carbon and methane carbon isotopic analyses are reproducible to within 0.2 per mil, and the CO₂ carbon analyses are reproducible to within 1 per mil. The isotopic composition of the argon was determined on mass spectrometers at the California Institute of Technology and the University of California at Berkeley. Agreement was good on several samples run by both laboratories. The background was always much lower than the sample peak heights.

The carbon was analyzed at the California Institute of Technology on a 6-inch mass spectrometer in Dr. Epstein's laboratory. All samples on which carbon isotopic analyses were made were run as carbon dioxide according to the procedure described by *McKinney, McCrea, Epstein, Allen, and Urey* [1950]. The samples were analyzed relative to Caltech Working Standard II, and then converted to corresponding values relative to the Chicago Standard PDB.

NITROGEN AND ATMOSPHERIC ARGON

Mass spectrometric analyses of the extracted argon samples showed that while the A^{40}/A^{38} ratios ranged from 312 to 34,000, the A^{38}/A^{36} ratio was practically constant and was, to within experimental error, equal to the value of 0.187 found in atmospheric argon.

Each sample was found to have an A^{40}/A^{36} ratio greater than 295.6, the value for air argon [*Nier*, 1950]. These gases appear to be mixtures of radiogenic argon (A_{rad}) and atmospheric argon (A_{at}). The fraction, ϵ , of the total argon that is radiogenic is given by the expression

$$\epsilon = \frac{A_{rad}}{A_{total}} = 1 - \frac{296.8}{(A^{40}/A^{36})_s + 1.2} \quad (1)$$

where $(A^{40}/A^{36})_s$ is the ratio in the sample.¹ These parameters are presented in Table 1.

It is not possible to say under what conditions the atmospheric argon was introduced into the samples. Air bubbles trapped in the original

¹ The formulas used to calculate the amounts of radiogenic (A^{40}), and total sample (A^{40}), when a tracer, t , was used are:

$$\begin{aligned} (A^{40})_r = (A^{38})_t & \left\{ \left(\frac{A^{40}}{A^{38}} \right)_\mu - \left(\frac{A^{36}}{A^{38}} \right)_\mu \left(\frac{A^{40}}{A^{36}} \right)_n \right. \\ & + \left(\frac{A^{36}}{A^{38}} \right)_\mu \left(\frac{A^{38}}{A^{36}} \right)_n \left(\frac{A^{40}}{A^{38}} \right)_t \\ & - \left(\frac{A^{40}}{A^{38}} \right)_\mu \left(\frac{A^{38}}{A^{36}} \right)_n \left(\frac{A^{36}}{A^{38}} \right)_t \\ & \left. + \left(\frac{A^{40}}{A^{36}} \right)_n \left(\frac{A^{36}}{A^{38}} \right)_t - \left(\frac{A^{40}}{A^{38}} \right)_t \right\} \\ & \frac{1}{1 - \left(\frac{A^{36}}{A^{38}} \right)_\mu \left(\frac{A^{38}}{A^{36}} \right)_n} \end{aligned}$$

and

sediments, air dissolved in water associated with the sediments, gases brought in at some later time by circulating ground water, and contamination during sampling and analysis are all possible sources. By means of blank runs and repeat analyses, it was possible to show that essentially none of the atmospheric argon was due to contamination from laboratory procedures. Samples were run with atmospheric argon contents as low as 0.2 ppm without any difficulty. Repeat analyses of samples at different times yielded identical A^{40}/A^{36} ratios. Inspection of the A^{40}/A^{36} ratios shows that these values tend to be rather constant within certain gas fields. Although some of the samples may possibly have been contaminated during sample collection, it is our conclusion that, for most cases, the atmospheric fractions represent the accumulated air argon associated with these gases during their natural evolution. While the composition and abundance of atmospheric argon may have changed through geologic time, we have assumed the present-day values. It is conceivable that measurements of the A^{40}/A^{36} ratio may prove useful as a tracer in identifying and studying gas reservoir characteristics.

The natural gases analyzed contained amounts of nitrogen varying from 0.1 to 42.5 per cent. Gases composed of essentially 100 per cent nitrogen have been reported in the literature, but we have not been able to obtain such samples. The origin of nitrogen in natural gases has been often discussed [*Hoering*, 1957; *Scalan*, thesis, University of Arkansas; *Rayleigh*, 1939; *Rogers*, 1921; and *Zobell*, 1952] in terms of (1) the introduction of atmospheric nitrogen, (2) the release of nitrogen by the bacterial decomposition

$$\begin{aligned} (A^{40})_s = (A^{38})_t & \left\{ \left(\frac{A^{40}}{A^{38}} \right)_\mu - \left(\frac{A^{40}}{A^{38}} \right)_t \right. \\ & \left. + \left(\frac{A^{40}}{A^{38}} \right)_\mu \left[\frac{1 - \left(\frac{A^{36}}{A^{38}} \right)_t \left(\frac{A^{38}}{A^{36}} \right)_\mu}{\left(\frac{A^{38}}{A^{36}} \right)_\mu \left(\frac{A^{36}}{A^{38}} \right)_n - 1} \right] \right\} \end{aligned}$$

where the subscripts t , n , and μ refer to the appropriate ratio in the tracer, in normal atmospheric argon, and in the sample-tracer mixture, respectively.

of nitrogen-bearing compounds, (3) the release of nitrogen by the inorganic chemical breakdown of organic compounds, and (4) the liberation of inorganic nitrogen from igneous (and metamorphic) rocks.

One of the processes called upon most frequently to explain the presence of nitrogen in well gases is the incorporation of air in the pore space of various reservoir rocks. If air is included in the sediments, they will contain not only N_2 but other atmospheric gases as well. Some workers have assumed that when gases have a (N_2/A) ratio approximately equal to that in air, the nitrogen is due to atmospheric contamination. It was pointed out by *Wasserburg, Czamanske, Faul, and Hayden* [1957] for certain high helium gases from the Texas Panhandle that while the total (N_2/A) ratios of these gases were approximately equal to the atmospheric value, most of the argon was of radiogenic origin, and the actual (N_2/A_{s1r}) ratio was about 850. They concluded, therefore, that most of the nitrogen could not be due to trapped air. Following this approach, we have made a similar calculation of the (N_2/A_{s1r}) ratio for our samples. The results are given in Table 1. The ratio is observed to range between 137 and 8500. The atmospheric ratio of nitrogen to argon is 84, and the ratio for the dissolved gases in water in equilibrium with the atmosphere at 20°C is 38. Although it may be reasonable to postulate simple mechanisms of gas solution and effervescence, which could account for a factor of 2 or 3 change in the atmospheric (N_2/A_{s1r}) ratio, most of the gas samples show much higher nitrogen enrichments. Therefore, in most instances only a small fraction of the nitrogen content of these gases reasonably can be attributed to incorporated air.

As will be shown later, the ratio of $(He/A)_{rad}$ in all samples investigated in this report had values of 1.6-130. Such a range in this ratio is believed to be characteristic of all natural gases, and therefore, if a gas shows a (He/A) ratio of much less than this, it may be assumed, in lieu of an argon isotopic analysis, that the argon is mainly nonradiogenic and has a corresponding amount of atmospheric nitrogen associated with it.

HELIUM-ARGON RATIO

If essentially all of the helium contained in natural gases is produced by the radioactive

disintegration of uranium and thorium, and the radiogenic fraction of the argon by the electron-capture decay of K^{40} , we can make certain theoretical calculations to determine the values to be expected for the radiogenic helium and argon abundances and their ratio ($R = (He/A)_{rad}$). In order to discuss the abundances of helium and argon observed in natural gases, it is necessary to consider (1) the variation of He^{4-} and A^{40-} production with time, (2) the natural distribution of uranium, thorium, and potassium in rocks and their distribution among the mineral phases present, (3) the efficiency with which the helium and argon can escape from crystal lattices and become available for accumulation, and (4) the process of gas migration and accumulation into gas reservoirs. The first part of the discussion will be devoted principally to estimates of the $(He/A)_{rad}$ ratio. The problem of absolute concentrations and amounts of these noble gases will be treated later.

Because the half-lives of the uranium, thorium, and potassium isotopes are of the order of 10^9 years or more, the rates of production of helium and argon are rather constant for the past several hundred million years. For such a time period we obtain the relationships

$$N_{He} \simeq (1.20 U + 0.29 Th) \tau \times 10^{-7} \quad (2a)$$

$$N_A \simeq 3.99 K \tau \times 10^{-12} \quad (2b)$$

where N_{He} and N_A are the cc STP of helium and argon, respectively, produced by radioactive decay during a time interval of τ years, and U , Th , and K are the weights of uranium, thorium, and potassium in grams. Dividing these equations we see that the ratio R of the accumulated radiogenic gases is given approximately by

$$R \simeq [(U/K) \times 10^4(3.0 + 0.72(Th/U))] \quad (3)$$

which is independent of the time. It can be seen that R is not very sensitive to changes in the Th/U ratio as a shift of from 0 to 4 in this quantity only changes R by a factor of 2. With the exception of several thorium-rich minerals, the Th/U ratio is rarely greater than 10. Using values of 3.5 ppm, 10 ppm, and 2.6 per cent for the average rock concentration of uranium, thorium, and potassium, respectively, we obtain $R \simeq 7$. This is in rough agreement with the average of the observed results (see Table 1).

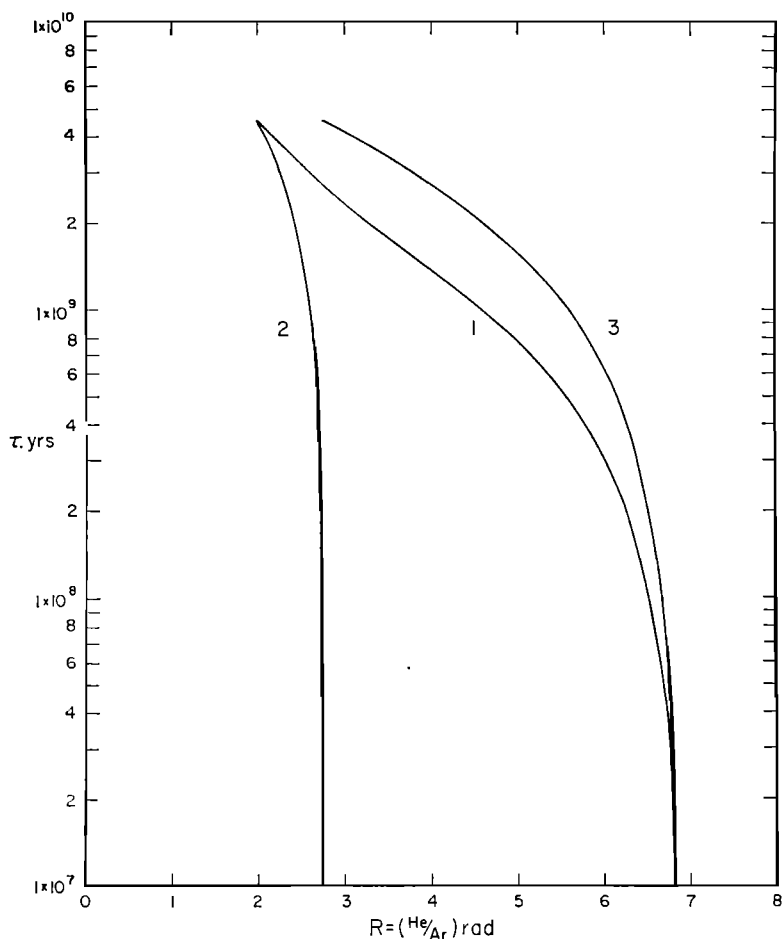


Fig. 2. Variation of $R = (\text{He}/\text{A})_{\text{rad}}$ with time. (1) The ratio R of the production rates at a time τ years ago. (2) The ratio R of the total gases produced in the interval from a time 4.5×10^9 years ago until τ years ago. (3) The ratio R of the total gases produced in the interval from τ years ago to the present.

In order to consider the effects of time on R over time intervals longer than a few hundred million years, we have calculated this quantity for the following instances:

1. The ratio R of the production rates at a time τ years ago.
2. The ratio R of the total gases produced in the interval from a time 4.5×10^9 years ago until τ years ago.
3. The ratio R of the total gases produced in the interval from τ years ago to the present.

These curves are shown in Figure 2. The previously stated values of uranium, thorium, and potassium were used to represent the present

concentrations in an average igneous rock as estimated from selected values in the literature.

Inspection of Figure 2 shows that the time dependency of R is rather slight. This ratio changes from 2.0 to 6.8 in the extreme cases considered. Except for the dependency on the Th/U ratio, similar curves of this shape are generated by any U/K ratio. They are simply shifted along the abscissa in proportion to the U/K ratio. As indicated above, the range in R is a factor of 3.4. If the helium and argon contained in traps in the upper sedimentary crust are composed of locally derived radiogenic material, we would expect the $(\text{He}^4/\text{A}^{40})_{\text{rad}}$ ratio to be close to the instantaneous value. If these

gases are composed chiefly of material in the process of upward transport from the deeper crust and mantle, we might well be dealing with a $(\text{He}^4/\text{A}^{40})_{\text{rad}}$ ratio somewhere between the instantaneous value and the cumulative ones.

The validity of employing such an 'average' rock as used above is indeed questionable, and

TABLE 2. Carbon isotopic composition of the total gas, CH_4 , and CO_2 contained in some natural gases. Apparent temperatures calculated from *Craig* [1953] for the pair $\text{CH}_4\text{-CO}_2$ are also given. All carbon isotopic data are given as per mil difference in the $\text{C}^{13}/\text{C}^{12}$ ratio between the sample and the Chicago standard, PDB.

No.	δ_{Total}	δ_{CH_4}	δ_{CO_2}	Calculated $T, ^\circ\text{C}$
1	-36.0
2	-38.3
3	-35.1
4	...	-49.2
5	-57.6
6	-29.7	-29.2
7	-40.2
8	-36.7	-39.2	-19.5	307
9	-37.2	-39.7	+8.1	71
10	-40.1	-43.5
11	...	-40.3	-20.9	314
12	...	-44.1	-7.9	139
13	...	-46.4	-21.9	242
14	...	-41.6
15	...	-31.9	-18.7	486
16	-3.9	...
17	-4.1	...
18	...	-43.6
19	...	-44.1
20	...	-50.3	-12.4	128
21	...	-41.0
22	-32.0	-35.8	-7.3	198
23	...	-39.8
24	-37.5
25	...	-34.5
26	...	-49.8
27	-43.2	-47.0
28	...	-41.7	-19.4	...
29	-39.9	-42.0
30	-38.8	-40.0
31	-38.5
32	-39.6
33	-39.2
34	-5.0	...
35	-5.9	...
36	-35.2	-39.5	-15.0	244
37	-38.6	-40.5
38	-39.4	-41.5	+12.8	48
39	-37.5	-38.5	-8.8	185
40	...	-45.4
41	...	-38.3	-0.5	120

it is necessary to consider in more detail the abundances of the radioactive elements in different rocks. A compilation of the abundances in various lithologies is presented in Table 3. Wide variations in concentrations and U/K and Th/U ratios are apparent. For unusual rock types (Kolm from Sweden), or where the rock is the host for a mineral deposit (Colorado Plateau uranium deposits), the ratios may vary over many powers of 10. Of the normal rock types tabulated, it is seen that the purer carbonates, although not rich in uranium, have very low potassium contents yielding ratios as much as one hundred times greater than granites. On the other hand, an evaporite produced from uncontaminated sea water would yield a U/K ratio one hundred times less, and, in addition, may have a Th/U ratio close to zero. Exclusive of carbonates, however, the normal rock types exhibit a rather constant U/K ratio.

The possible range in the U/K ratio is about 5 powers of 10 in extreme rock types. If some natural processes operate over a sufficiently large scale, they will tend to average over such variations. For example, carbonate rocks are frequently intercalated with shales tending within a given stratigraphic unit to cancel the differences obtaining in the pure lithologies: a 50-50 mixture of a pure limestone and a shale will yield a rather normal U/K ratio. In general, it will be exceedingly difficult to relate the radiogenic helium and argon in any reservoir to a particular rock source, since these gases undoubtedly will have migrated over some distances and through different rock types. In certain instances it may be possible to show that these gases could have been produced within their present reservoir, but this will not be a unique attribute. Considering the wide variations possible in R , owing to variations of the U/K ratio, it is remarkable that the measured values lie within such a restricted range. It is our interpretation that this is because of the large- and small-scale averaging inherent in the processes of accumulation with the total source having a 'normal' U/K ratio.

One of the important factors concerning the He and A to be investigated is the escape of these gases from the minerals in which they originated. That $\text{A}^{40}\text{-K}^{40}$ and helium age-dating methods work at all attests to the retention of at least some of these gases in the source minerals.

TABLE 3. The Abundance of K, Th and U in Some Common Rocks and Minerals

Lithology	K, %		Th, ppm		U, ppm		K $\times 10^{-4}$		Th		References*
	average	range	average	range	average	range	U	U	U		
Chondrites	0.09	...	0.04	...	0.01	...	9	4.0	4.0	1, 2, 3	
Orthoquartzitic ss	0.6	...	1.7	0.7-2.0	0.5	0.2-0.6	1.2	3.4	3.4	4	
Arenaceous rocks	1.7	0.7-3.8	5	5, 6	
Argillaceous rocks	2.9	1.6-4.2	11	8-14	4	3-6	0.7	...	2.8	5	
Shales (except for certain black sh)	3.3	1.6-8.5	12	2-47	4	1-13	0.8	3.0	3.0	7	
Chatanooga sh	2.8	...	5.8	...	74	...	0.04	0.08	0.08	7	
Kolm (Sweden)	8	
Asphaltite (Utah)	9	
Evaporated sea water	1.1	10 ⁻⁴	...	up to 1%	10	
Carbonate rocks	0.6	0.04-1.7	2.4	1-7	2.1	0.03-0.1	0.3	0.0	1.1	5, 7	
Pure limestones	0.09	0.001-0.5	2.2	...	0.04	This paper	
Shells (modern and fossil)	0.006	0.003-0.02	3	0.01-8.1	0.002	This paper	
Granitic rocks	3.1	...	14	...	4	...	0.8	3.5	11, 12	11, 12	
Intermediate rocks	3.0	...	10	...	3	...	1.0	3.3	3.3	11, 12	
Gabbroic rocks	0.8	...	4	...	1	...	0.8	4.0	4.0	11, 13	
Carnotite	8.6	0.0%	...	51%	14	
Uraninite	0.0	0.0-12%	...	55-75%	14	
Halite-sylvite	...	0-52	...	0.4-0.5	...	0.1-0.2	15, 16	

* References: (1) Bate, Huizenga, and Potratz, 1959; (2) Geiss and Hess, 1958; (3) Hamaguchi, Reed, and Turkevich, 1957; (4) Murray and Adams, 1958; (5) Baranov, Ronov, and Kunashova, 1956; (6) Joly, 1910; (7) Adams, Richardson, and Templeton, 1958; (8) Eklund, 1946; (9) Tomkeief, 1946; (10) Rankama and Sahama, 1950; (11) Nockolds, 1954; (12) Senfite and Keevil, 1947; (13) Evans and Goodman, 1941; (14) Palache, Berman, and Frondel, 1944; (15) Bell, 1956; (16) Palache, Berman, and Frondel, 1951.

Much work has been done by *Keevil* [1941] and *Hurley and Goodman* [1941] on the loss of He from individual minerals and total rock, and corresponding work by *Wasserburg, Hayden, and Jensen* [1956] and *Goldich, Baadsgaard, Nier, and Hoffman* [1957] yields some information on the argon retention ability of several common potassium minerals. Some data on He and A losses from minerals and rocks are presented in Table 4. Since, in general, the observed helium and argon losses are roughly proportional to the helium and argon contents, respectively, of the mineral, the $(\text{He}^4/\text{A}^{40})_{\text{rad}}$ ratio of the 'available' gas will be equal to the $(\text{He}^4/\text{A}^{40})$ production ratio in the total rock multiplied by some constant, which will be taken to be time independent. The value of this constant will be the fractional helium loss, ξ_{He} , divided by the fractional argon loss ξ_{A} . As an approximation we might expect a fresh igneous rock to lose 3/5 its He^4 and 1/5 its A^{40} into interstitial pore spaces. Weathering and diagenetic processes can do little to increase the already high yield for He^4 from the rock, but they offer ample opportunity for breaking down potassium-bearing minerals and releasing much retained argon. Thus, we might expect sediments to favor the outgassing of argon more highly than an equivalent fresh igneous rock. The relative rates of escape of helium and argon from rocks at elevated temperatures and pressures are poorly known. However, a more complete loss of both gases might be expected under conditions of metamorphism. If a rock which

TABLE 5. Henry's Law Constants for Several Selected Gases

Gas	$K_i = C_i^g/C_i^l$ Solvent			
	Fresh Water		Marine Water	
	15°C	50°C	15°C	50°C
N_2	56	87	73	114
A	25	40	33	53
He	113	111
CH_4	27	46

has retained 80 per cent of its argon and 40 per cent of its helium is later completely outgassed by metamorphism or fusion, the gas thereby evolved might be preferentially enriched in argon by a factor of 2. Thus, from an average igneous rock we might expect extreme 'available' $(\text{He}^4/\text{A}^{40})_{\text{rad}}$ ratios of about 3 and 20, depending on whether the gases represented the value attained by complete outgassing of a rock which had formerly preferentially lost helium or by the low temperature diffusion of helium and argon out of a young rock. If the source rock differs considerably in its K, U, and Th abundances from an average igneous rock, the resultant available $(\text{He}^4/\text{A}^{40})_{\text{rad}}$ ratio will, of course, reflect this. Gases originating in pure carbonate rocks may have high values of R .

A number of gas transport mechanisms could produce a fractionation of argon and helium. If, during the time of gas accumulation, the helium and argon are transported by solution in connate water, fresh water, or petroleum, the $(\text{He}^4/\text{A}^{40})_{\text{rad}}$ ratio that we actually observe in a natural gas sample will be influenced by the relative solubilities of these gases in the transporting medium. If diffusive equilibrium is attained, we would expect the following relationship to hold:

$$R^g = \frac{K_{\text{He}}}{K_{\text{A}}} R^l = K' R^l \quad (4)$$

where R^g and R^l are the atomic ratios of the helium to argon in solution and in the gas reservoir respectively, and K_{He} and K_{A} are the Henry's law constants for helium and argon, respectively. The Henry's law constants for several gases at various temperatures are given in Table 5. *Rakestraw and Emmel* [1938] showed

TABLE 4. Helium and Argon Retentivity in Some Common Rocks and Minerals*

Mineral or Rock	Fractional Retentivity	
	Helium	Argon
Quartz	0.33	
Feldspar	0.25	0.75
Mica	0.50	1.00
Pyroxene	0.75	
Magnetite	1.00	
Hornblende	1.00	
"Granite"	0.40	
Diabase	0.60	

* References included *Keevil*, 1941; *Hurley and Goodman*, 1941; *Wasserburg, Hayden, and Jensen*, 1956; and *Goldich, Baadsgaard, Nier, and Hoffman*, 1957.

that argon is only about 80 per cent as soluble in marine water of normal salinity as it is in fresh water. Similar work by *Åkerlof* [1935] on the effect of salinity on helium solubility suggests about the same behavior for this gas. The solubility of argon and helium in crude petroleum is unknown, as is the importance of noble gas transport by this means. In water solutions for temperatures of 50–80°C, $K' \simeq 2.8$, and, therefore, the gas phase would be enriched in helium relative to argon as compared with the solution. Thus, if much more gas is contained in solution than occurs in the gas phase, the equilibrium ratio of He/A in the gas reservoir would be 2.8 times greater than the 'available' ratio. A more rigorous treatment of this problem is given later in the paper.

The differences in solubility of various natural gas components could in principle, through a multistage process of solution and effervescence, cause considerable variations in R . It would be possible under ideal conditions to produce a range in R of over 20 by employing only three stages of distillation. It is not possible at present, however, to say how effective multistage distillation actually is in achieving variations in R . That many stages of distillation do not operate is indicated by the limited range observed in R .

If compositional variations are ignored, it is seen that the effects of the other parameters will permit over an order of magnitude variation in R . Thus, the value of R actually observed in natural gas may range between extremes of at least 3–50 without any need for assuming compositional differences. All of the samples analyzed have values of R that fall within the range of 1.6 to 130. Most of these results agree quite well with this model, assuming only minor variations in the U/K ratio. It is, of course, possible to attribute the observed variations in R to compositional differences instead of diffusion and solubility effects. It is not possible at present to say precisely which factors account for the variation.

Damon and Kulp [1958] have measured the ratio of excess radiogenic helium to argon in beryls and cordierites. They obtained ratios ranging from 0.5 to 130 with an average value of 20. Our results on well gases are thus rather similar to the values found for these trapped magmatic gases.

It must be pointed out that, with the exception

of certain potassium evaporite salts such as sylvite ($K \simeq 50$ per cent) and some very pure carbonate rocks ($K < 0.01$ per cent), the potassium content of most rocks generally shows less than an order of magnitude variation. This major rock-forming element makes up from 1 to 4 per cent of many sedimentary and igneous rocks. However, uranium and thorium, which generally occur as trace elements, are subject to wide variations in abundance, and the possibility of local enrichments must be considered. Indeed, one of the early theories proposed for the occurrence of high helium wells attributed the high helium content to an underlying uranium deposit [*Rogers*, 1921]. If an order of magnitude or larger enrichment in the helium content of a natural gas is affected by this process, the gas should show an abnormally high $(\text{He}/\text{A})_{\text{rad}}$ ratio. The large increase in the abundance of a major rock-forming element such as potassium as would be needed to maintain the observed $(\text{He}/\text{A})_{\text{rad}}$ ratios could not occur in common rocks. That such an enrichment in radiogenic helium over radiogenic argon does not exist in the case of the Texas Panhandle gas field was shown by *Wasserburg, Czamanske, Faul, and Hayden* [1957]. The results of the present investigation also tend to disprove the idea of high enrichments in helium due to abnormal uranium or thorium concentrations for a number of high helium gas fields.

The problem of recognizing the contribution of gases from the mantle or lower crust is extremely difficult. This is particularly true for helium and argon, since the earth is a highly differentiated body and the production of these elements is dependent on the U, Th, and K concentrations. The ratio R in modern material of chondritic composition is about 1; the ratio R in an average igneous rock 4.5 billion years ago would be 2.0 as compared with the present value of 6.8.

Some of the lowest values of $(\text{He}^4/\text{A}^{40})_{\text{rad}}$ were in CO_2 wells that are associated with igneous activity. These values are in the direction effected by great age or chondritic production rates. These results, of course, are only suggestive inasmuch as they could be produced by a variety of mechanisms.

It should be noted that the argon from the CO_2 wells is extremely radiogenic. If this represents juvenile argon, it indicates that very little A^{36} is associated with it. This is compatible with

the results derived from the solubility model for air argon. The latter data indicate that no significant amount of atmospheric type argon occurs in these gases above the amount that would be present from original equilibration with air. We infer from this that no deep-seated gases are contributing significant amounts of argon of this composition.

NOBLE GAS ABUNDANCES IN NATURAL GASES

The helium content of the gas samples investigated varies between 37 and 62,200 ppm and the radiogenic argon content varies between 3.7 and 5580 ppm. Since any attempt to explain the occurrence of the rare gases in natural gases must account for the absolute amounts and concentrations as well as for the ratio of radiogenic helium to radiogenic argon, factors influencing helium and argon abundances will now be discussed.

Whereas the $(\text{He}/\text{A})_{\text{rad}}$ ratio is only weakly time-dependent over times comparable to the age of the earth, the actual production of these gases is strongly time-dependent. The radiogenic helium and argon content of a natural gas reservoir is not necessarily proportional to the age of the source rock, but is, rather, a complicated function of the accumulation history of the gas. It is possible that much of the radiogenic gases are incorporated into the natural gas by a sweeping-up effect during the time of migration from the source to the reservoir rock. In such an event, the He and A content of the rocks at the time that they were traversed by the accumulating gases would be an important factor. If there was little noble gas escape before gas migration, the length of time between rock formation and petroleum accumulation would determine the concentration of He and A in the pore space. Studies of a number of oil and gas fields have shown that this time between source rock deposition and petroleum migration may vary from between tens of millions and hundreds of millions of years. The outgassing of very old basement rocks through metamorphism would be a possible source of high concentrations of these radiogenic gases. Such gases may leak into a sedimentary section through various fractures or faults. It may also be true for some cases that the noble gases have escaped continuously from the rocks during all times except the period of gas accumulation. In this

event, the important time factor would be the length of the time interval over which gas migration took place.

Once the gases have been removed from the crystal lattices they become available for migration either by solution or by gaseous transfer. Under equilibrium conditions, the distribution of any gas between a gaseous and liquid phase is related approximately by Henry's law. It is, of course, questionable that equilibrium conditions prevail over large distances between the accumulated gases and interstitial pore fluids. It will, however, be assumed in the following discussion that diffusive equilibrium obtains for the rare gases and the consequences of such a model will be investigated.

Equilibrium model. Goryunov and Kozlov [1940] have pointed out the importance of solubility phenomena in natural gas accumulation, and part of the following discussion parallels their work.

Let us consider an equilibrium reservoir model in which the rock has a porosity p , and suppose the pore space to be occupied by both an aqueous phase (s) and a gas phase (g), all under a hydrostatic pressure of P atmospheres. Let the volumes occupied by the gas and aqueous phase be V^g and V^s , respectively, and the concentrations of gas species i in each of these phases be C_i^g and C_i^s , in units of standard cc per cm^3 . The total amount of species i in the pore system is then $C_i^g V^g + C_i^s V^s$, and the fraction f_i^g of this species in the gas phase is

$$f_i^g = \frac{C_i^g V^g}{C_i^g V^g + C_i^s V^s} \quad (5)$$

Suppose that each species satisfies a Henry's law relationship of the form $C_i^g = K_i C_i^s$ where K_i is the Henry's law constant for species i . We then have

$$\begin{aligned} f_i^g &= V^g / \left(V^g + \frac{V^s}{K_i} \right) \\ &= 1 / \left(1 + \frac{V^s}{K_i V^g} \right) \quad (6) \end{aligned}$$

Since $K_{\text{He}} \simeq 110$ and $K_{\text{A}} \simeq 40$ for aqueous solutions at 50°C , f_{He}^g and f_{A}^g will be close to 1 when more than about 5 per cent of the pore space is occupied by a gaseous phase.

In the units used, C_i^g is (assuming ideality) numerically equal to the partial pressure in

atmospheres of species i . The condition that a pure gas phase i exists when the hydrostatic pressure is P is $P/K_i = C_i^g$. It follows that for any given concentration C_i^g there is a maximum depth at which a gas phase of pure i may exist. If we consider an infinitesimal helium bubble at 1000-foot depth under a hydrostatic pressure of 30 atmospheres pressure, this will require $C_{He}^g \simeq 0.3$ cc STP/cc pore vol. If we assume the porosity to be as low as 10^{-2} , this will correspond to 3×10^{-3} cc STP of He per cc of rock. As will be shown later, such a value is obtainable only under extreme conditions. It is, of course, obvious that if, in a certain environment, radiogenic helium had associated with it another component not subsequently removed, we would not find a pure helium gas.

If we let C_i equal the mean concentration of gas species i in the total pore space of the system, then, from (6) we have

$$C_i^g = C_i [K_i - (K_i - 1)f_i^g] \quad (7)$$

From (7) we see that if all of the gas species i occurs in the gas phase the mean concentration will simply equal the concentration in the gaseous phase. If, however, because of the rather insoluble nature of some gases, we have most of the gas dissolved in an aqueous phase with only a very small gas bubble in equilibrium with it ($f_i^g \simeq 0$), we gain a factor of K_i in C_i^g over the mean pore space concentration. Thus, an infinitesimal bubble of helium in equilibrium with a liquid at 50°C will have a He concentration of 110 times higher than the new concentration. As will be shown below, most reservoir gases appear to have significant amounts of gas in a dissolved phase.

The previous model has treated only a gas with an aqueous phase. For gases associated with a liquid petroleum phase, the equilibrium relationship involving this phase in addition to an aqueous and a gaseous phase must be considered. This will obviously increase the number of variables in the model calculations. The effect of water salinity must also be taken into account in a more precise calculation.

In addition to the radiogenic noble gas content of natural gases, argon having the composition of present-day atmospheric argon is found to be present in all of the gas samples. As discussed previously, the origin of this air argon is uncertain. For purposes of discussion, we assume it

to be due to the release from connate or ground waters which were originally saturated with argon under atmospheric conditions. If the system is closed subsequent to burial, we have

$$\begin{aligned} C_a^{s0} V^{s0} &= C_a^g V^g + C_a^g V^g \\ &= C_a^g \left(V^g + \frac{V^g}{K_A} \right) \end{aligned} \quad (8)$$

where the subscript a represents air argon. C_a^{s0} is the initial concentration of air argon in solution and V^{s0} is the initial volume of the solution. If we assume that the volumes of the initial and final water bodies are equal, we obtain

$$\frac{V^g}{V^g} = \frac{C_a^g K_A}{K_A C_a^{s0} - C_a^g} \quad (9)$$

In a diffusive equilibrium model, the system is assigned values of V^g and V^g . This is, of course, unrealistic, since the natural system will not have sharply defined boundaries. The ratio V^g/V^g as calculated will therefore apply for some effective volume over which equilibrium is attained. Under atmospheric conditions at 15°C and in equilibrium with ocean water of normal salinity, we have $C_a^{s0} \simeq 3.0 \times 10^{-4}$ cc STP/cc H_2O [Rankama and Sahama, 1950]. The value of C_a^g is determined by the measured concentration of air argon in the natural gas at the well pressure. Substituting this expression for V^g/V^g in (6), and using $K_A = 53$ (for 50°C and normal marine salinity) we have for radiogenic argon

$$\begin{aligned} f_A^g &= \frac{1}{1 + \frac{V^g}{K_A V^g}} \\ &= 1 - \frac{C_a^g}{K_A C_a^{s0}} \simeq 1 - 63 C_a^g \end{aligned} \quad (10)$$

and for other arbitrary species

$$f_i^g = \frac{1}{1 + \frac{C_a^g K_A}{K_i (K_A C_a^{s0} - C_a^g)}} \quad (11)$$

We see that for the assumed equilibrium model it is possible to calculate the fraction of species i which is in the gas phase. This may be applied to other gases as well as to radiogenic He and A. In Table 1 are given the calculated values of V^g/V^g and f_A^g for the fraction of radiogenic argon occurring in the gaseous phase. Because of the many obvious uncertainties

regarding the assumptions involved, it is doubtful that the calculations are strictly applicable to real natural gas reservoirs. Nonetheless, such considerations are useful as a means of comparing the behavior of natural systems to the simple idealized model. Usually the calculated values of f_A^o and V^o/V^o appear to be quite reasonable. Only two samples (11 and 24) give impossible values of f_A^o , and these discrepancies are not extreme.

If there were originally entrapped air bubbles in the pore space, or if $V^o < V^{*o}$ was due to hydration reactions in diagenesis, then the calculated value of V^o/V^o in (9) will be larger than the true value. The calculated values of f_i^o will be too small, owing to such effects.

Next, let us look at the effect of porosity, p , on concentration. If we assume the mean noble gas concentration in the pore space, C_i , to be essentially proportional to the N_i , noble gas concentration produced in the mineral phase per cc of rock, we have

$$C_i = \frac{\xi_i}{p} N_i \quad (12)$$

where C_i , as before, has the units of cc STP/cc of pore space, N_i has the units of cc STP/cc of system, and ξ_i is the rock degassing factor. The concentration of the noble gases in the pore space is inversely proportional to the porosity. N_i for radiogenic helium and argon is given by (2a) and (2b), respectively, calculated per cc of rock. The molecular abundance in ppm of species i in the gas phase is Γ_i ,

$$\Gamma_i = \frac{C_i^o}{P} \times 10^6 \quad (13)$$

where P is the pressure of the reservoir in atmospheres. This equation assumes the gases to be perfect. For hydrostatic pressure $P \simeq 0.030h$, where h is reservoir depth in feet below the surface.

Combining (2), (7), (12), and (13), we have

$$\Gamma_{He} = \frac{\xi_{He}(0.120 U + 0.029 Th) \tau}{P \cdot p} \cdot (K_{He} - [K_{He} - 1]f_{He}) \quad (14a)$$

$$\Gamma_A = \frac{\xi_A(3.99 \times 10^{-6} K) \tau}{P \cdot p} \cdot (K_A - [K_A - 1]f_A) \quad (14b)$$

All the parameters given in (14) are expressed as the effective values for the system under investigation. Substitution of reasonable estimates for these parameters yields radiogenic helium and argon concentrations in natural gases quite consistent with actually observed values. For example, let us calculate the radiogenic helium and argon content of two extreme reservoir cases. Let us assume a rock density of 2.5 and an effective U, Th, and K concentration in the rocks of 3.5 ppm, 10 ppm, and 2.6 per cent, respectively. In the one instance, let us set $\tau = 5 \times 10^8$ yr., $\xi_{He} = \xi_A = 1$, $f_{He}^o \simeq f_A^o \simeq 0$, $P = 10$ atmospheres (147 psia), and $p = 1$ per cent. This corresponds to an environment in which the total radiogenic noble gas content produced by one-half billion years of decay is completely released into rock of 1 per cent mean porosity having a hydrostatic pressure of 10 atmospheres. Geologically, this could be brought about by the continuous release of radiogenic gases into overlying sediments of one-half billion-year age, or by the complete retention of such gases in basement rocks over this time interval, followed by some metamorphic event which then released the gas. This former possibility would appear unlikely where no sedimentary cover of sufficient age was present to trap the continuously released gas. The gas is virtually all dissolved in an aqueous phase, and thus the concentration in the gas phase is increased over the mean pore space concentration by the numerical value of the Henry's law constant. These conditions yield $\Gamma_{He} \simeq 10^6$ ppm and $\Gamma_A \simeq 5 \times 10^4$ ppm.

For contrast, let us consider a case in which $\tau = 5 \times 10^7$ years, $\xi_{He} \simeq \xi_A \simeq 0.5$, $f_{He}^o \simeq f_A^o \simeq 1$, $P = 100$ atmospheres (1470 psia), and $p = 5$ per cent. This corresponds to a situation in which one-half of the radiogenic noble gas production over a 50-million-year period is released into rock of 5 per cent mean porosity having a hydrostatic pressure of 100 atmospheres. These conditions yield $\Gamma_{He} = 10$ ppm and $\Gamma_A = 1$ ppm. If, instead, the gas were mainly dissolved ($f \sim 0$), the value of Γ_{He} would become a factor of 100 larger.

An average reservoir might have effective values of $\tau = 10^8$ years, $\xi_{He} = 4/5$, $\xi_A = 1/2$, $f_{He}^o \simeq 0.9$, $f_A^o \simeq 0.75$, $P = 50$ atmospheres (735 psia), and $p = 3$ per cent. Assuming the same U, Th, and K abundances and rock density

as above, we have $\Gamma_{\text{He}} = 1040$ ppm and $\Gamma_{\text{A}} = 86$ ppm with $R \approx 12$. In this case we have 80 per cent and 50 per cent of the accumulated radiogenic helium and argon, respectively, resulting from one hundred million years of decay being released into rock of 3 per cent mean porosity. The values of f_i^o correspond to having $V^o/V^e \approx 10$.

In order to make an estimate of the volume of rock swept out during the formation of a gas reservoir, let us consider the helium-producing zone of the Rattlesnake Gas Field, San Juan County, New Mexico. W. M. Deaton, chief helium consultant for the Bureau of Mines Helium Activity (personal communication) estimates the total original volume of the reservoir gas to be about 2.4×10^9 cubic feet at 15.0 psia and 60°F. About half of the total gas has been removed, and the field is not being produced at the present time. The gas, which has a helium content of 7.6 per cent, was produced from the Leadville-Ouray (Mississippian-Devonian) formations and had an initial pressure of about 3000 psia. Thus the reservoir is approximately 1.2×10^7 cubic feet, and assuming $p = 2$ per cent and $V^o/V^e \approx 94$ (approximate values of near-by Navajo C-1), we see that this corresponds to a volume of V^o/p of 5.6×10^9 cubic feet, or 0.4 cubic mile. Assuming an average uranium and thorium abundance in the rock $\xi_{\text{He}} = 1$, and an effective τ of 3×10^8 years, we calculate from (14) that $\Gamma_{\text{He}} \approx 7000$ ppm. This is lower than the observed value by a factor of 10. Let us now look at some possible explanations for this discrepancy. Since the gas has a $(\text{He}/\text{A})_{\text{rad}}$ ratio which is characteristic of common rocks, we cannot reasonably assume that either the uranium or thorium concentrations, or both, in this source are abnormally high, although a factor of 2 increase may well occur. Although the gas reservoir is in Pennsylvanian strata, it is possible that the radiogenic fraction of the gas was chiefly derived by the outgassing of much older basement rock containing a correspondingly higher helium concentration. Also, the possibility that our equilibrium solubility model is incorrect would allow for a twofold increase in the helium concentration in the gas phase above that calculated. A favorable combination of these three effects could just allow for the observed helium concentration in the gas. In addition, it is possible that whereas the porosity

of the reservoir rock is 2 per cent, the effective porosity of the entire source rock system is much lower. This might be expected if most of the helium were derived from a very tight basement complex. It is difficult to tell which are governing factors in this case. At present, we surmise that this gas has probably been produced by the favorable conjunction of several of these effects. It should be emphasized that it is rather difficult to account for this factor of 10; if an additional factor of 10 were required, it would be impossible to obtain this reasonably in terms of the present model.

If we compare the San Juan high helium gas with that from the Texas Panhandle, we see that the former gas not only contains more than a fivefold higher abundance in helium, but also a 35 times greater helium concentration, due to the higher pressure of the San Juan gas.

It should be pointed out that a gas that existed at rather shallow depths with a particular abundance of helium and subsequently transported as a closed system to a great depth will retain the same helium abundance, but it will have a much higher helium concentration. Such a gas will, of course, not be in equilibrium with the surrounding aqueous reservoir and will ultimately return to a lower helium concentration. There is no evidence supporting such a transportation history for the San Juan gas.

We have seen that under equilibrium conditions the concentration of a slightly soluble gas such as He or A in the gaseous phase is of the order of 10^3 times its concentration in solution. The uniform release of these gases from a homogeneous source rock into a system which contains both pore liquid and gas would, in the absence of complete diffusive equilibrium, tend to make $C_i^o < K_i C_i^e$. Under such conditions, the concentration of species i in the gas phase would be lower than expected by diffusive equilibrium. Except for minor effects brought about by the temperature dependency of the Henry's law constant, it is difficult to envision a natural situation which would tend to make $C_i^o > K_i C_i^e$. With reference to radiogenic helium, only if a source material is selectively contributing the helium to a gas phase at a rate of K_{He} times faster than it is feeding a liquid phase can C_{He}^o be greater than $K_{\text{He}} C_{\text{He}}^e$.

Radon. The existence of radon in many natural gases has sometimes been used to infer

the presence of a concentration of uranium in the neighborhood of such occurrences. *Faul, Gott, Manger, Mytton, and Sakakura* [1954] have reported on the Rn content of some helium-rich natural gases. These workers conclude that it is uncertain whether the high helium content of certain gases is related to the presence of Rn. This problem is of interest in considering the possibility that a significant portion of the He in some natural gases can be the product of U, Th decay in their present reservoir.

Sakakura, Lindberg, and Faul [1959] have reported the radon content in the gases from four wells as a function of the cumulative production, starting from a situation where the wells had been shut down for 2 or 3 weeks. The net gas flow required before the Rn concentration reached a constant value was small and of such a value as to indicate that the principal source of the activity was not in the well hole itself but immediately adjacent. These workers have presented a theoretical treatment of the problem of the gas transport of Rn. They conclude that for the Texas Panhandle gases the Rn is due to a uranium concentration of between 0.4 and 9.0 ppm, assuming an emanating power of 10 per cent.

In the following, we will present a simplified treatment of the steady state transport problem that will suffice for the purpose at hand.

The equation governing the steady state concentration of Rn in a fluid phase for the case of cylindrical symmetry is given by

$$\frac{1}{r} \frac{d[r \cdot C(r) \cdot J(r)]}{dr} = -\lambda p C(r) + p q(r) \quad (15)$$

Here $C(r)$ is the concentration of Rn in the fluid phase at distance r , $J(r)$ is the outward radial volume flux of fluid with the dimensions of velocity, p is the porosity, $q(r)$ is the rate of generation of Rn per cc of pore space, and λ is the decay constant for Rn. If the fluid is incompressible, $J(r) = Q/2\pi Hr$, with $-Q/H$ being the volume of fluid yielded by the well per unit height of the producing horizon.

If the production rate of Rn is everywhere constant, we see that $C = q/\lambda$. The Rn activity is then constant and equal to the production rate. If the fluid is compressible, the concentration is a more complicated function of position due to the fact that at lower pressures the fluid occupies a greater volume. For simplicity, we

will consider gases as incompressible, and take the rate of production Q in units of cc volume at well pressure per unit time.

For the case of the uniform production of Rn within a cylinder of radius R center about the origin and no production outside of this region, the value of C at the well is

$$C(0) = q/\lambda \left[1 - \exp \frac{\lambda \pi H p R^2}{Q} \right] \quad (16)$$

It is clear that $C(0)$ is insensitive to changes in the parameters at distances much greater than $r = (-Q/\lambda \pi H p)^{1/2}$, i.e., distances for which the time of travel to the well is equal to the mean life. This distance is probably not in excess of a few hundred feet for most wells.

The highest Rn concentration in the Panhandle helium wells reported by *Faul, Gott, Manger, Mytton, and Sakakura* [1954] is 500 micromicrocuries per liter at STP. Using a well head pressure of 16 atmospheres we obtain for a uniform source $q = \lambda C \approx 0.24$ Rn decay/sec. cc of pore space. Assuming a porosity of 10 per cent, this corresponds to an emanating uranium concentration of 10^{-8} g U/g rock. If but 1 per cent of the emanation escapes to the pores, this corresponds to a uranium concentration of only 100 ppm. For a well in the San Juan basin containing 6 per cent He, *Faul, Gott, Manger, Mytton, and Sakakura* [1954] report a Rn activity of only 5 micromicrocuries/liters STP.

In some of the cases reported, the Rn level was sufficient to account for the helium present, assuming steady production for 10^8 years. In others, it could contribute only 0.1 per cent of the He. Since more He may escape from the reservoir rocks than is indicated by the Rn concentration, it is quite possible that some gases obtain their helium after their final entrapment. In any case, the Rn data do not support the case for the generation of these helium containing gases from high uranium concentrations.

Helium distribution function. There are about 3400 helium analyses for natural gases as reported by the U.S. Bureau of Mines [*Anderson and Hinson*, 1951; *Boone*, 1958]. The gases analyzed come from a wide variety of geological situations and, excluding the very high helium wells, should be a representative sample of natural gas accumulations. Because of the large number of analyses, it should be possible to get a rather

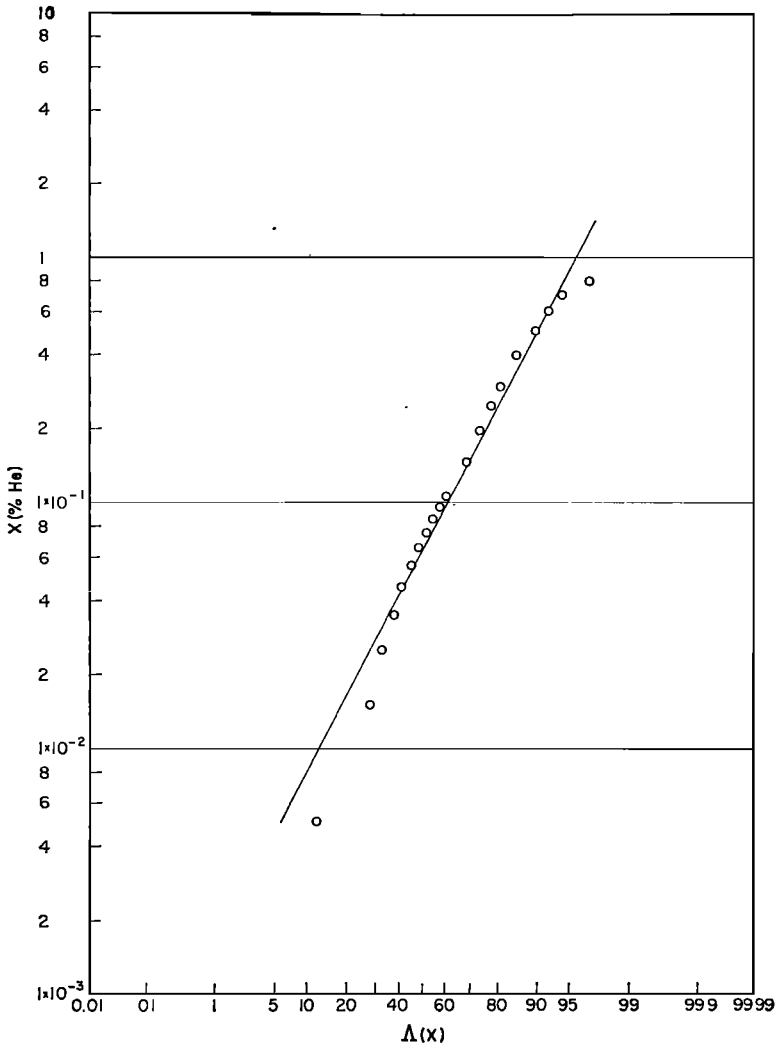


Fig. 3. Log probability plot of the helium abundance in natural gases. Statistics for abundances less than 0.8 per cent and estimates for high helium production are taken from U. S. Bureau of Mines data.

good description of their frequency curve. The data used were 3000 analyses of samples containing less than 0.8 per cent He. Because an excessive number of samples were analyzed from known He-producing areas, we have discarded all analyses reporting over 0.8 per cent He. Using estimates of the total annual gas production and their helium content, we obtained the result that 3 per cent of the total gases contained helium in a concentration of over 0.8 per cent. This fraction of the annual gas

production has an average He concentration of 1.5 per cent [*U. S. Bureau of Mines, 1959*].

Using these data, a frequency histogram was constructed. The cumulative data, plotted on log probability paper, are shown in Figure 3. It is evident that a lognormal distribution represents the data fairly well. The percentiles were determined [*Aitchison and Brown, 1957*], using the straight line drawn through the points. The following values were determined for this curve:

mean = 0.2170%
 median = 0.0610% $\sigma = 1.59$
 mode = 0.0049% $\mu = 2.80$

Figure 4 illustrates the frequency curve and uses these parameters for the frequency function

$$\frac{d\Delta(x)}{dx} = \frac{1}{2\pi\sigma x} \exp - \left\{ \frac{(\ln x - \mu)}{\sqrt{2\sigma}} \right\}^2 \quad (17)$$

This curve may be compared with the histogram.

The histogram does not appear to have bimodal characteristics. This observation further suggests that the high He gases do not (in a statistical sense) represent any special mechanism, but rather represent low-probability events on the tail of a continuous-probability curve.

SAMPLES

Samples 1-7 are gases from Eocene and Cretaceous sands of the Sacramento Valley, California. They have a wide range in $(\text{He}/\text{A})_{\text{rad}}$ and $(\text{N}_2/\text{A}_{\text{air}})$ ratios, and their ϵ is rather low. The radiogenic helium and argon content of these

gases is among the lowest observed in any analyzed samples. The atmospheric argon content of these gases ranges between 44 and 124 ppm; the nitrogen varies from less than 1 per cent to over 30 per cent. Geologic evidence indicates that the reservoir rocks may be in communication with ground water circulation. These Tertiary and Cretaceous sediments crop out a short distance to the east along the western foothills of the Sierra Nevada. The young age of the sediments may account for the low radiogenic noble gas content of these natural gases, and the possibility of open system conditions or heterogeneity in the source material is suggested by the large variations in the $(\text{He}/\text{A})_{\text{rad}}$ and $(\text{N}_2/\text{A}_{\text{air}})$ ratios. Chemically, the Sacramento Valley gases are extremely dry, with methane making up essentially all the hydrocarbon fraction and nitrogen varying between 1 and 30 per cent. That all this nitrogen cannot be of direct atmospheric origin has been discussed previously. Sample 6 from the Marysville-Butte field was taken from gas closely associated with Pleistocene volcanic extrusives.

Samples 8-10 and 36-39 are gases occurring

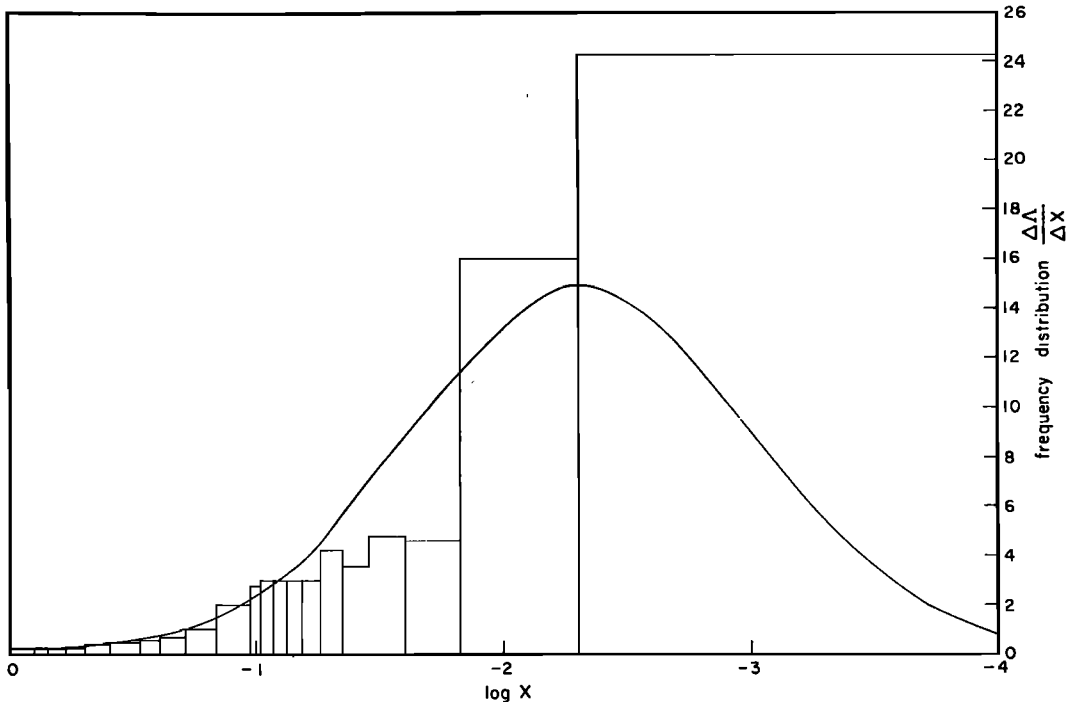


Fig. 4. Frequency curve and histogram showing the distribution of helium in natural gases.

in rocks of Cretaceous to Eocene age from northwestern Colorado and southwestern Wyoming. Although these gases also show wide variations in (N_2/A_{air}) and ϵ , their $(He/A)_{rad}$ ratio remains fairly constant despite over an order of magnitude variation in radiogenic helium and argon content. Whereas the chief factor producing the spread observed in the (N_2/A_{air}) ratio for the Sacramento Valley gases was a highly variable nitrogen content, the Green River gases, which demonstrate an even greater range in (N_2/A_{air}) ratios, have more uniform nitrogen content, but over an order of magnitude variation in air argon content. Thus, these gases may represent either (1) reservoirs of highly variable V^*/V^* , (2) reservoirs into which air argon from sources other than saturated sea water was introduced, (3) reservoirs in which varying degrees of diffusive disequilibrium exist, or (4) samples having incorporated air argon owing to varying levels of contamination.

Samples 12 and 13 were selected to represent gases from a present-day geosynclinal environment.

Samples 18-20 are from Lea County, New Mexico. The first two gases are produced from Permian sandstones. Sample 18 comes from a reservoir directly overlying the reservoir of sample 19 and is stratigraphically separated from it by about 1000 feet of section. The other gas occurs in a Permian carbonate. The similarity in the $(He/A)_{rad}$ ratio, the (N_2/A_{air}) ratio, and ϵ for these samples from the sandstone reservoirs may be a reflection of a similar source. The gas from the limestone reservoir appears to be distinctly different in these parameters from the other two gases.

Sample 23 from western New York and samples 25-27 from Pennsylvania represent Paleozoic gases from the Appalachian petroleum province. These gases contain the highest $(He/A)_{rad}$ ratios found in any of the samples; they range from 26.2 to 134. Such a high ratio is quite surprising in these gases because of their relatively great age, low V^*/V^* , and proximity to orogenic activity, which may have been more effective than average in releasing radiogenic argon. All of these features point toward a low $(He/A)_{rad}$ ratio.

On the other hand, it is possible that some distillation mechanism has been particularly operative in the production of these gases and

has selectively enriched the gas phase in helium. The low value of V^*/V^* may in reality point to the removal or absence of air argon from the system. If the high value of R did result from a distillation mechanism operating on an originally normal $(He/A)_{rad}$ ratio, there should exist somewhere a complimentary phase having a correspondingly low value of R . It is also possible that the sources of the western Appalachian gases are characterized by a low K/U ratio. Whereas such a ratio might be expected to occur in impure limestones, the fact that most of the Appalachian gases occur in stratigraphic traps, involving sandstone lenses surrounded by impervious shales, seems to exclude this possibility. In no way does this region demonstrate a $(He/A)_{rad}$ ratio to be expected by a simple degassing of a chondritic mantle.

Samples 11 from the Sexson field, Kansas, 22 from a wildcat well in San Juan County, New Mexico, 24 from the Keyes field in Oklahoma, and 29-32 from the West Panhandle field, Texas, were selected as representative high helium natural gases. They range between 0.5 and over 6 per cent helium with $(He/A)_{rad}$ ratios ranging from 11.1 to 23.3. Such values of R are in no way compatible with a large increase in the concentration of uranium and thorium over potassium as compared with average rocks. As stated elsewhere, it is the authors' opinion that high helium wells result from the favorable interaction of several processes operating on normal rock types having average U, Th, and K contents. Some of these high helium reservoirs, such as those of the Texas Panhandle field, appear to be closely related to buried Precambrian granite and granite wash, which may have been the source of the helium [Cotner and Crum, 1935]. In other areas, such as San Juan County, New Mexico, no such correlation with basement rock is obvious [Hinson, 1947]. In many cases, however, the high helium reservoirs are stratigraphically low in areas containing several reservoir horizons. This would be expected if helium, having been liberated from the basement, rose through the overlying sediments until it became incorporated into the first reservoir it encountered. Numerous exceptions to the occurrence of high helium gases in low stratigraphic horizons exist. Rogers [1921] found that in the mid-continent region it may be that certain intermediate horizons, or even the highest

producing zone, contain the largest percentage of helium. It is still not possible to give a rigid explanation of the processes by which certain reservoirs became highly enriched in helium.

These gases contain between 50 and 200 ppm of atmospheric argon. A comparison between the A^{40}/A^{36} ratio as given by *Wasserburg, Czamanske, Faul, and Hayden* [1957] and by this paper (sample 31, Table 2) shows a much greater enrichment in radiogenic argon for our analysis. This is most likely due to atmospheric contamination in the older analysis. All of the Texas Panhandle gases now have similar A^{40}/A^{36} ratios, and this is believed to be a regional characteristic. All of the high helium gases have (N_2/A_{air}) ratios of an order of magnitude or more higher than the atmospheric value.

Sample 22 was observed to have a minimum possible value of $(A^{40}/A^{36})_{rad}$ of 1.9×10^6 . This value is larger than the maximum value predicted by *Gerling, Levskii, and Afanasyeva* [1956] by a factor of 2.4 and, therefore, adds additional evidence [*Wasserburg and Bieri*, 1958; *Signer and Nier*, 1959] against the presence of a long-lived isomer of K^{38} .

Samples 16, 17, 34, and 35 were chosen to include carbon dioxide gases in the survey. The Bueyeros field gases, which are over 99.8 per cent CO_2 , show the lowest $(He/A)_{rad}$ ratios of any gas analyzed. They also contain less than 0.5 ppm atmospheric argon, and have ϵ 's of 0.98–0.99. The Farnham Dome gases contain approximately 99.3 per cent CO_2 . They also have quite low $(He/A)_{rad}$ ratios and high values of ϵ . Both these gas fields occur in areas containing carbonate rock and Tertiary basaltic intrusives and lavas. Geologic evidence, as well as carbon isotopic data which will be discussed later in this report, suggests that the CO_2 was derived from the decomposition of carbonate rocks during metamorphism by the basalt. Under such conditions, it is possible that most of the original gases and liquids in the near-by sediments were driven off before the carbon dioxide accumulation. This would explain the high purity of the CO_2 and the extremely low atmospheric argon content of the gases. Since the molten basalt might cause a relatively higher release of radiogenic argon, compared to radiogenic helium, than results from low temperature diffusion, we could expect such an environment to yield low values of $(He/A)_{rad}$.

Sample 40 from Texas and sample 41 from Alberta, Canada, were included to represent gases from carbonate reef environments. They show no indication of an abnormally high $(He/A)_{rad}$ ratio as might be expected from pure carbonate sources. Sample 41 contains 12.2 per cent H_2S .

CARBON ISOTOPES

Isotopic analyses were made on some of the carbon compounds contained in the gases. The results are shown in Table 3. The isotopic composition of the carbon is given in terms of its delta (δ) value relative to the Chicago standard, PDB [*Craig*, 1953].

Most of the California samples were run only as total gas; however, since they generally contained less than 0.1 per cent CO_2 , and very little ethane, propane, etc., the total gas carbon is very nearly equal to the methane carbon. Several of the Texas Panhandle and the Keyes, Oklahoma, high helium gases were also run only as total gas. A comparison with samples 29 and 30 from the Texas Panhandle area, in which both total carbon and methane carbon were run, indicates that about a 1–2 per mil difference may be expected between total gas and methane carbon for this suite, with the methane having the lighter carbon. The remainder of the natural gases were analyzed for methane carbon, and in some cases an additional analysis of total gas carbon was made. The carbon dioxide well gases were analyzed for CO_2 carbon only. Carbon dioxide was analyzed from all natural gas samples containing more than 0.2 per cent CO_2 with the exception of sample 24. All of the methane analyses give delta values between -57.6^* and -29.2 per mil. Both these extreme values are from wells within the Sacramento Valley gas fields of California. Usually individual gas-producing districts possess a much narrower range in methane carbon composition. This is exemplified by samples 8–10 and 36–39 from the Green River area and samples 29–33 from the Texas Panhandle. The methane carbon from the Green River suite lies between -38.5 and

* Although this analysis for sample 5 refers to total gas carbon, it is from a gas essentially free of CO_2 and other hydrocarbons; therefore, it undoubtedly is within a few tenths of a per mil of the methane value.

—43.5 per mil, and the total carbon from the Texas Panhandle gases suggests an even narrower range.

These results are similar to the observations made by *Silverman and Epstein* [1958] and *Wasserburg, Czamanske, Faul, and Hayden* [1957], who found that methane has the lightest carbon found in nature. The exact mechanism by which methane is produced is not known at present. It is probable that some breakdown of organic matter, either by bacterial or inorganic processes, results in the liberation of methane. It was noted by *Silverman and Epstein* [1958] that natural gas carbon is generally lighter than associated petroleum, and that this in turn is lighter than the organisms from which it is supposedly derived. *Rosenfeld and Silverman* [1959] have found an unusually high fractionation between methanol and the methane which is produced from it by anaerobic bacterial decomposition. The methane is about 8 per cent enriched in C^{13} relative to the methanol. Further investigation of the origin of methane is required before a more specific discussion of its C^{13}/C^{12} ratio can be made.

An analysis was made of a sample of gas collected by Louis Gordon from a gas-seep over the head of the north fork of Scripp's Canyon off the coast of southern California near La Jolla. The delta value for this sample was -44.2; it falls in the same general range as the well methanes. K. O. Emery (personal communication) considers this gas to be a seep from a subsurface source.

In those gases where total methane and CO_2 carbon were analyzed, it was possible to calculate approximate ranges of the δ value for the higher hydrocarbons. Because small uncertainties in the known δ values are greatly increased in such a calculation, it can only be concluded that the δ value of the higher hydrocarbons is generally 5-15 per mil greater than the methane.

If we consider the carbon dioxide gases, we see that they are often associated with stratigraphic sections also containing carbonate rock and igneous intrusives and lavas. *Lang* [1959] found that the C^{13}/C^{12} ratios of several CO_2 gases lay within the range of carbon in marine limestones. This is in agreement with the theory that the CO_2 comes from the non-equilibrium dissociation of carbonate during

contact metamorphism. The results from the two CO_2 fields studied in this report are in agreement with the work of Lang.

The isotopic composition of the oxygen from three of the carbon dioxide wells was also determined. Mitchell No. 4, Farnham Dome No. 2, and Farnham Dome Equity gave values of δ_{CO_2} relative to PDB of -23.0, -20.2, and -20.3 per mil respectively. Such values might be expected either for CO_2 produced by the high temperature decomposition of marine carbonate or possibly by CO_2 in equilibrium with certain reservoir waters at appropriate temperatures. In the first case, if fractionation of only a few per mil occurred between the carbonate and CO_2 during such high temperature processes as contact metamorphism, we would obtain values of δ_{CO_2} close to those of marine carbonate, i.e., -20 to -10 per cent [*Clayton and Epstein*, 1958; *Engel, Clayton, and Epstein*, 1958] recomputed relative to the acid extracted PDB standard. In the second case, we see that although the δ value is too low to represent CO_2 in equilibrium with normal marine water at room temperatures such values might result from equilibration with light waters or at elevated temperatures. [*Epstein and Mayeda*, 1953].

At least traces of carbon dioxide are observed in nearly all natural gases, and gases ranging in composition up to almost pure CO_2 have been found. Some literature [*Lang*, 1959; *Miller*, 1937] has been published on the origin of high carbon dioxide gases; however, no detailed work has been done on the CO_2 in ordinary petroleum gases. Here, the CO_2 generally makes up between a few hundredths of a per cent and a few per cent of the total gas.

The δ values for all the CO_2 analyses are seen to lie between -21.9 and +12.8. In every case, the CO_2 carbon is considerably heavier than that of the coexisting methane or total gas. This is a remarkable regularity which must have important genetic significance.

If we assume that the CH_4-CO_2 pairs were in isotopic equilibrium within a gas phase under certain conditions, and that subsequent to that time these values were 'quenched in,' we may calculate effective temperatures. Such temperatures were computed using the fractionation factor as calculated by *Craig* [1953]. These results are given in Table 3. Since the kinetics

of this exchange are completely unknown, we are unable to say under what conditions we would expect equilibrium to occur and be frozen in. The possible ranges in temperature which we might obtain, assuming equilibrium to have occurred at some time, are room temperature and the maximum temperature which these gases may have experienced. Some of the calculated temperatures range up to several hundred degrees centigrade. This is considerably in excess of the actual well temperatures. Since it is generally agreed that petroleum does not result through high temperature processes of formation, we conclude that some of these gases lie well outside the range to be expected from equilibrium considerations.

Although it is thus doubtful that complete isotopic equilibrium prevails, it is impossible to say whether the $\text{CH}_4\text{-CO}_2$ pairs represent a partial attainment of isotopic equilibrium. It is significant that in every case of unreasonable temperature, the δ_{CO_2} value appears to be lower than the expected equilibrium value. That is, if isotopic equilibrium were to be attained in those gases, δ_{CO_2} would have to become more positive. Thus, assuming only equilibrium processes to be operative between the CO_2 and the CH_4 , the observed δ values would represent the maximum value which they could have originally had. Although nine of the samples listed in Table 3 have values of δ_{CO_2} greater than -10 per mil and, therefore, may have possibly arisen by either the equilibrium or disequilibrium breakdown of marine carbonate rock, the other seven samples for which we have data give δ values too negative to represent such a source. If we assume that all the carbon dioxides once had δ values at least as negative as the lightest sample now observed (~ -20 per mil) and that the present spread resulted from later partial equilibration, we must look for other sources of carbon capable of yielding such values.

When CO_2 occurs in much smaller concentrations than CH_4 , any change toward equilibrium in the isotopic composition of the system would cause a much greater change in the $\text{C}^{13}/\text{C}^{12}$ ratio of the CO_2 than of the CH_4 . Thus, while such a process will affect the original δ_{CH_4} value only weakly, even partial attainment of equilibrium will tend to obscure any original value of δ_{CO_2} .

At present, it is not possible to explain uniquely

the genesis of the carbon dioxide found in petroleum.

CONCLUSIONS

All the natural gases studied exhibit values of R which indicate that they are of a common family and have obtained their radiogenic gases from rather average rock types. The variations in abundance of radiogenic helium and argon in these gases are due to the effects of leakage and entrapment, solubility, porosity, and age of the source rocks. Major differences in the abundances of He cannot be due to large variations (over a factor of 50) in the abundance of U and Th in the source rocks.

For many cases studied, only a small fraction of the N_2 present may be attributed to the incorporation of air.

The methane was found to have extremely light carbon as suggested by previous workers. In addition, it was found that the carbon isotopic composition of CO_2 was always heavier than in the coexisting CH_4 . This could not be reasonably attributed to complete isotopic equilibrium between these gaseous species.

It is possible that the concentration of atmospheric argon in a gas reservoir may be correlatable with the amount of reservoir water with which it was equilibrated.

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APPENDIX

Potassium and uranium in carbonates. Of the common rocks, limestones may exhibit wide variations in the content of trace elements such as potassium and uranium. For this reason, various carbonates of known uranium content were analyzed for potassium. The measurements were made with a Perkin-Elmer flame photometer. Samples of the carbonates weighing 1.02 gram were dissolved in HCl and evaporated to dryness. They were put into aqueous solution with 1 ml of 12 N HCl and diluted to 250 ml volume. The solutions were run on the flame photometer and the readings compared with those obtained on identically prepared $CaCO_3$ solutions of known potassium content. The results were highly reproducible, and at concentrations above 100 ppm the data are probably accurate to within 10 per cent of the values reported. The data are given in Table 6. Column 2 of this table gives the per cent of the $CaCO_3$ that is aragonite.

Samples of the Bikini atoll cores had been analyzed previously for uranium by Dr. M. S. Coops of the Radiation Laboratory, Livermore, California. The analyses were done using a neutron activation technique in which the Np^{239} was counted. Dr. Coops kindly provided us with these samples.

Some of the uranium analyses are the results reported by *Tatsumoto and Goldberg* [1959] using a colorimetric method. Dr. Goldberg generously provided us with some of these samples, and in addition made other uranium analyses reported here. Two samples of marbles analyzed for uranium by Dr. B. Doe are also included.

The analytical method used in each case is given in the table.

It is evident that in the carbonate rocks reported here the potassium content is widely variable. The Muschel Kalk had the highest value of 4,600 ppm and the Algal ls. and Leadville ls. the lowest values, 6 ppm. The high potassium contents seem to be commonly associated with sizable insoluble residues. The

marbles GMW-2 and F6-B are rich in phlogopite. It was found that the dissolution procedure was vigorous enough to dissolve about one-half this mica. The values reported for samples with potassic noncarbonate fractions will therefore tend to be intermediate between the values of the whole rock and the pure carbonate fraction. The weight per cent of insoluble residues is given in column 3.

The K/U ratio in pure limestones such as the Spergen fm. and the Leadville ls. may be as low as 25. This ratio is lower than that in average igneous rocks by a factor of 400, and would yield a value of R of 3×10^8 . This difference is due to the great decrease in the potassium

content since the uranium values remain roughly the same for these materials.

The marbles show a range in K content similar to that found in limestones. All of the marbles contained some dolomite. Sample GMW-2 contains phlogopite, the larger part being in the +80 sieve fraction. This effect is clearly seen in the results on the total rock and the -40 +80 sieve fraction. Of the two Franklin marbles, F6-B contains some phlogopite. Sample F6-A was taken in the mine and is from a lithology which contains some coarse biotite crystals. No biotite was observed in the sample analyzed.

Sample fd 7-3 is a white dolomitic marble

TABLE 6. Analytical Data of Potassium and Uranium in Carbonates

Samples	% Aragonite	Wgt. % Residue	ppm K	ppm U	K/U
LIMESTONES					
Buckhorn	59	10.2	321		
Buckhorn residue			2220		
Cretaceous Chalk	0	1.4	198	1.08 ²	188
Chicago Formation	Dol.	0.7	131	0.01 ²	13100
Basal Coquina	46	0.6	112	0.87 ²	147
Pr 2—Algal Isl.	0		6	1.41 ²	4.25
Muschel Kalk	0	17.1	4600		
Muschel residue			2900		
Oolites (0-03)	98	0.1	87	3.4 ¹	25.6
GMW-2 (-40+80), marble	0	4.1	1000		
GMW-2, total hand spec. crushed marble	0	7.1	2100		
fd 7-3, marble		43.2	≤5	0.083 ⁴	<60
fd 7-2, marble		<0.3	235	0.640 ⁴	390
F6-A Franklin Marble	0	<0.1	40	0.12 ²	333
F6-B Franklin Marble	0	1.6	384		
Leadville Limestone 32	0	0.4	58	0.28 ²	207
Leadville Limestone 82	0	0.4	6	0.24 ²	25
Leadville Limestone 128	0	0.3	20		
Spergen Formation	0	0.4	25	1.02 ¹	24.5
Calcite I	0	<0.1	≤5	<0.01 ²	
Calcite II	0	<0.1	≤5		
Calcite III	0	<0.1	9		
MODERN SHELLS					
1336	99	<0.1	102		
1337	100		74		
1338	100		38		
1339	100		54		
1345	99	<0.1	79		
1348	100	<0.1	35		
S-07 (B)	100		153	0.013 ¹	11.77×10^3
S-11	100	0.3	62	0.012 ¹	5.17×10^3
S-13	99	0.4	51	0.067 ¹	0.76×10^3
S-14	100		39	0.022 ¹	1.77×10^3
S-15			44	0.032 ¹	1.38×10^3
S-17		0.6	154	0.041 ¹	3.76×10^3

containing 65 per cent dolomite and 35 per cent diopside. The residue of this sample was found to contain 61 ppm of potassium. Sample fd 7-2 is a dolomitic marble containing 0.26 per cent graphite. These samples were given to us by Dr. B. Doe, who determined the uranium contents in the course of another investigation.

Samples of calcite spar were run for comparison. It is evident that these carbonates have extremely low levels of potassium as suggested by A. E. Engel (personal communication).

In order to determine whether any potassium is present in the original shell materials which constitute limestones as distinct from contributions from clay materials and detrital particles, analyses were made of modern and fossil shells and corals. The concentration of potassium in both modern shells and corals are roughly the same and range from 30 to 150 ppm. It follows that these materials contain a significant amount of this element when formed. Many of the purer limestones have K concentrations lying inside of this range. Some

inorganically precipitated CaCO_3 , such as the calcite spar, has virtually no potassium; however, the oolite sample gave a result comparable with the shells and corals. These data suggest that carbonates precipitated from sea water will have some potassium in chemical combination. On the other hand, it is possible that some potassic clays may be contained in all these precipitates.

Some well preserved fossil shells were analyzed for K. Samples I and II were large complete specimens which were carefully cleaned to eliminate any contamination. Sample III was taken from a glauconite-rich matrix and a small amount of contamination with this mineral could easily cause this high result, while it appears that under optimal circumstances the potassium content of shells may be preserved in fossils. The concentration levels are very low but it may be possible to utilize these materials for $\text{A}^{40}\text{-K}^{40}$ dating with the most modern techniques. Assuming complete retention for sample I, this would correspond to 2×10^{-8} cc STP/g of A^{40} . While this is readily measurable, the

TABLE 6. Continued

Samples	% Aragonite	Wgt. % Residue	ppm K	ppm U	K/U
FOSSIL SHELLS					
I	99	0.2	29		
II	100	0.3	27		
III Shell Fragments	99	0.7	201		
MODERN CORAL					
Coral I (0-04)	70		31	2.5 ¹	12.4
Coral II (0-05)	99	0.3	50	3.2 ¹	15.6
Bikini Corals:					
Tare, depth 4'	51	0.2	35	2.3-3.2 ³	12.5
13'	49	0.3	43	4.2-5.2	11.6
				2.2-3.2	
34'	89	0.1	60	6.5-8.1	8.2
63'	73	0.2	65		
90-1/2'	66	0.1	85	4.7-5.7	15.7
97'	51	0.6	63	3.1-4.0	12.4
				4.1-4.9	
Roger, depth 4'	66	0.5	46	3.3-4.1 ³	12.4
8'	62	0.5	67	4.3-5.1	14.3
23'	62	0.3	96	3.4-4.2	25.0
44'	97	0.2	43	6.1-7.5	6.3
FOSSIL CORAL					
1437 Reef Coral	99		63		

¹ M. Tatsumoto and E. D. Goldberg (Colorimetric) *Geochim. et Cosmochim. Acta*, 17, 201, 1959.

² B. O. Goldberg (Fluorescence) personal communication.

³ M. Coops (Neutron activation) personal communication.

⁴ B. Doe (Isotope dilution) Thesis, Calif. Inst. of Technology, 1960.

problem of correction for atmospheric argon would be formidable.

The shells appear to have a uranium concentration about 100 times smaller than the corals. The K/U ratios for the shells are much closer to the values for average igneous rocks than the corals which have ratios 1000 times smaller.

The ashed bones of 15 different modern vertebrates were also analyzed to investigate the possibility of dating appropriate fossil materials. The total range in concentration was

found to be from 400 to 3000 ppm. This is a much higher level than found in shells. If it is assumed that this potassium is in the apatite crystals rather than in fluids in the marrow, it may be possible to date well-preserved fossil bone of Cretaceous age.

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TABLE 7. Descriptive Data
LIMESTONES

<i>Buckhorn</i> , Mid-Pennsylvanian, Sulphur, Okla.		
<i>Cretaceous Chalk</i> , Campanian, Vigny, France		
<i>Chicago Formation</i> , Niagaran, reef core, Thornton, Ill.		
<i>Basal Coquina</i> , Devonshire Marine Isl., Grape Bay, Bermuda		
<i>Pr 2</i> , Mid-Eocene, Algal Isl., Puerto Rico		
<i>Muschel Kalk</i> , Mid-Triassic, Rorigliana, Italy		
<i>Oolites (0-03)</i> Bahama Bank about 1 mile S.E. of S. Pt. Cat Cay 79°15'W, 25°30.5'N water depth 3 feet (recent)		
<i>GMW-2 (-40+80 Mesh Fraction) Marble</i> , Balducci Quarry, Gouverneur, N. Y.		
<i>GMW-2, Marble, total hand spec.</i> , Balducci Quarry, Gouverneur, N. Y.		
<i>Fd7-3 Marble</i> , fetid limestone, shore of Sylvia Lake, N. Y.		
<i>Fd7-2 Marble</i> , graphitic, 900 level, shaft of No. 3 mine, Balmat, N. Y.		
<i>F-6A Marble</i> , New Jersey Zinc Mine, Franklin, N. J.		
<i>F-6-B, Franklin Marble</i> , Franklin, N. J.		
<i>LV-32</i> , Elk Creek Colo., zone 1	} Leadville Limestone	These samples are described by Engel and Engle. Ms. in preparation
<i>LV-32</i> , Barites Cabin, Colo., zone 2		
<i>LV-128</i> , Sweet Water Lake, Colo., zone 1		
<i>Spergen Formation</i> , Oolitic portion of the Spergen Formation, Mississippian, St. Genevieve, Missouri		
<i>Calcite I</i> , Iceland Spar		
<i>Calcite II</i> , Manhattan, Nev.		
<i>Calcite III</i> , Spar 611, Hockerville, Okla.		

SHELLS

- 1336 *Lodakia Orbicularis*, Belmont Isl., Queens Free Cave, Ferry Rd., Bermuda
 1337 *Laevicardium Laevigatum* (recent) (TM₂), Patorreef Lagoon, Bermuda
 1338 *Lodakia Orbicularis* (recent), Whalebone Bay, Bermuda
 1339 *Laevicardium Laevigatum* (Pleist.), Basal Devonshire, Marshall Isl., Bermuda
 1345 *Conus Californianus* (recent), Naval Base E. Santa Barbara, Calif.
 1348 *Conus Californianus* (Pleist.), Hilltop Quarry, San Pedro, Calif.
 S-07 (B) *Haliotis Corrugata*, La Jolla, Calif.
 S-11 *Littorine Planaxis*, La Jolla, Calif.
 S-13 *Acmea Limatula*, La Jolla, Calif.
 S-14 *Olivella Biplicata*, La Jolla, Calif.
 S-15 *Acanthina Spirata*, La Jolla, Calif.
 S-17 *Tetraclita squamose*, La Jolla, Calif.

FOSSIL SHELLS

- Fossil I* *Crassatellites Vadosus*, L. Maestrichtian, Ripky Formation, Coon Creek, Tenn.
Fossil II *Trigonia Stantonii*, Coon Creek, Tenn.
III Shell Fragments Mathews Landing Marl., Paleocene, Wilcox Co., Ala.

CORAL

- Coral I* (0-04) Key Largo Is. (*Diploria labysinthiformis*)
Coral II (0-05) Key Largo Is. (*Montastrea Annulasis*)
Bikini Coral taken at different depths
 1437 *Reef Coral* Pleistocene, Bermuda

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