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CHEMICAL ANALYSIS FOR THE GASBUGGY EVENT

GENERAL CHEMISTRY TECHNICAL NOTE 266

John H. Hill

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GENERAL CHEMISTRY TECHNICAL NOTE NO. 266

CHEMICAL ANALYSIS FOR THE GASBUGGY EVENT

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ABSTRACT

This report is a compilation of chemical analyses of the pre-shot rock taken from the Gasbuggy site.

INTRODUCTION

This work was done in support of the Plowshare Division's effort to document the pre-shot environment of the Gasbuggy site. The data were used to predict the production and distribution of radionuclides and to correlate with the mineralogical analysis.

Results of the various analyses may be found in the appendix. Pulverized samples were used for all determinations excepting free and bound H_2O .

SAMPLING AND ANALYSIS

Samples of core were taken from test hole GB-1. Test hole GB-1 is at the following coordinates of the New Mexico State Coordination System, Central Zone: N 2,067,481.54; E 218,800.91. It is 187.79 ft N, $55^{\circ} 51' 23''$ W of the emplacement hole GB-E. The emplacement hole, GBE, is at the following coordinates: Longitude W $36^{\circ} 40' 40.4141''$; Latitude N $107^{\circ} 12' 30.2540''$ (New Mexico State Coordinate System, Central Zone, N 2,067,376.14; E 218,956.33). Elevations of GB-1 and GB-E are 7,203.6 ft. and 7,203.1 ft. respectively. Approximately six inches of core was taken for each sample at the depths shown in Table I. These depths are corrected to the density log.

Table I

Sample No.	Sample Depth
P-19	4121.1 - 4121.7
P-24	4095 - 4095.7
P-47	3945.7 - 3946.1
L-14	4280.3 - 4280.8
L-15	4278.0 - 4278.4
L-17	4272.1 - 4272.4
L-19	4266.1 - 4266.6
L-22	4258.4 - 4258.8
L-24	4252.6 - 4253.8
L-26	4246.7 - 4247.3
L-28	4243.8 - 4244.6
L-29	4240.1 - 4240.7
L-31	4234.7 - 4235.3
L-32	4231.8 - 4232.3
L-35	4224.9 - 4225.2
L-37	4219.8 - 4220.3
L-38	4217.6 - 4218.1

The coring was done with conventional drill rigs using air cooled bits. Cores were taken from the core barrel, wrapped in Saran Wrap and aluminum foil and sealed with paraffin at the drill site. Samples were opened and prepared for analysis at Livermore.

Sample L-14 was turned (dry) on a lathe to remove any surface contamination left from the coring operation. Sample L-15 was cut with a watercooled diamond wheel to remove the surface contamination and to obtain samples for thin sections. The analysis for free water indicated that sample L-15 did not pick up an appreciable amount of water in the cutting process. Therefore, the remaining samples were wet sawed to obtain thin sections and remove the cored surface. The clean portion of each sample was then crushed in a chipmunk crusher. Chunks taken from the crusher were used for the free and bound water analyses. The remainder of each crushed sample was cored and quartered to obtain about 75 grams of sample for the other chemical analyses. The 75 gram samples were pulverized in the tungsten carbide unit of a Bleuler rotary mill. The GBL composite was prepared by blending equal weighed portions of powder from each of the L series samples. The GBP composite was prepared likewise from the P series samples.

Possible sources of contamination are as follows:

1. Water lost during coring. This would tend to cause results for free water to be low by an indeterminate amount.
2. Water gained from wet sawing. This would tend to cause high results for free water. A comparison between the results for samples L-14 and L-15 indicates that there was no detectable contamination from this source.
3. Brass from the diamond wheel. Care was taken to remove any surface that showed rub marks. However, Cu, Pb, Zn, Sn and Fe are possible contaminants.
4. Iron from the chipmunk crusher. This is probably low as compared to the total Fe content of the rock.
5. Tungsten and cobalt from the tungsten carbide unit of the Bleuler mill. This probably accounts for an appreciable amount of the W and Co found in the pulverized sample. When more accurate

W and Co analyses are required, a separate sample can be ground in an iron or alumina container.

6. Carbon from the tungsten carbide unit of the Bleuler mill. This should be negligible as compared to the carbon content of the sample.

Elemental analyses were obtained by several techniques. A survey analysis of major and minor metallic constituents was obtained by emission spectroscopy. Spark source mass spectroscopy was used to determine trace elements. Chemical methods were used for accurate analysis of major and minor constituents and to analyze trace elements which could not be determined by the other techniques. The accuracy of the analytical results is approximately as follows:

Emission Spectrographic Methods

Major constituents; $\pm 20\%$ of the concentration

Minor constituents; $\pm 50\%$ of the concentration

Spark Source Mass Spectrographic

In general, results are within a factor of 2 times the concentration of the element (+2 X concentration, $-1/2$ X concentration.)

The alkali metals are an exception. Results for the alkali metals may be high by a factor > 2 because their oxides are more volatile than the oxides of most other metals.

Chemical Methods

Major and minor constituents; $\pm 2\%$ of the concentration or better.

Trace elements; $\pm 5\%$ of the concentration or better.

CO₂ from CO₃; $\pm 5\%$ of the concentration.

Total C; $\pm 5\%$ of the concentration.

Total S; $\pm 5\%$ of the concentration.

Total H; $\pm 5\%$ of the concentration.

Fe⁺²/Fe⁺³; The Fe⁺²/Fe⁺³ ratio is determined on a pulverized rock sample which is dissolved in a hydrochloric-hydrofluoric acid mixture. Results obtained by this technique are

probably within 5% of the true ratio for rocks which are free of organic matter and sulfides. However, both the organic matter and the sulfide in the Gas Buggy rock can reduce Fe^{+3} to Fe^{+2} during sample preparation. This reaction will cause the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio to be high by an indeterminate amount.

Free H_2O ; The relation of the free water content of the sample to the content of the in situ rock is uncertain. An indeterminate amount of H_2O is probably lost in the coring process. There was probably a small addition of free H_2O in the wet sawing operation. Gain or loss in crushing is probably negligible. The free water was determined by heating the sample to 110°C in a vacuum line. The H_2O was collected and weighed. The accuracy of this analytical method is about $\pm 5\%$ of the free H_2O found in the sample.

Bound H_2O ; The bound water content of the sample should not change appreciably during sampling operations. After the free water was removed and measured, the bound water was determined by heating the samples to 1000°C in a vacuum line. The H_2O was collected and weighed. This technique has an accuracy of about $\pm 5\%$ of the bound H_2O concentration in samples which are free of hydrocarbons. The reaction of hydrocarbons in the Gasbuggy samples with metal oxides at 1000°C would produce H_2O . This indeterminate error would bias the results high.

It is conventional to classify the carbon content of rocks into a carbonate fraction and a "hydrocarbon" fraction. In the Gasbuggy samples, this "hydrocarbon" fraction consists of material with a very high C/H ratio. The H_2 to H_2O balance in the Gasbuggy samples is evidence supporting this conclusion. The free and bound H_2O account for almost all of the H_2 present in these samples. Therefore, there is very little H_2 present as hydrocarbon.

Results for the solvent extraction of two samples are additional evidence of a high C/H ratio in the "hydrocarbon" fraction. The % C in the "hydrocarbon" fraction of a sample is the difference between the % total C and the % carbonate C. This difference is 0.58% C and 0.56% C for samples

L-14 and L-38 respectively. However, only 0.01% and 0.03% of soluble hydrocarbons were extracted from samples L-14 and L-38 respectively. Thus, the soluble hydrocarbon in either sample contains < 5% of the C present in its "hydrocarbon" fraction. The extractions were made using 50g portions of sample in a Soxhlet extractor. Toluene, ether, and carbon tetrachloride were used as solvents. The results cited above were obtained with carbon tetrachloride, the best of the three solvents.

APPENDIX

GASBUGGY
CHEMICAL ANALYSIS

Sample No.	CO ₂ ^{**}	Total C	Total H	Free H ₂ O	Bound H ₂ O	Fe ⁺² /Fe ⁺³	Loss on
	%	%	%	%	%		Ignition
L-14*	3.72	1.59	0.40	1.48	2.42	3.12	7.62
L-15	3.60	1.67	0.45	1.72	2.43	3.68	7.80
L-17	3.01	1.54	0.45	1.55	2.65		
L-19	2.66	1.52	0.47	1.56	2.64	3.27	6.99
L-22	3.83	1.65	0.41	1.64	--	2.53	7.70
L-24	8.54	2.38	0.20	1.11	1.13	2.24	10.64
L-26	7.06	1.62	0.33	1.29	1.78		
L-28	6.96	2.47	0.26	1.31	1.36		
L-29	3.57	1.45	0.36	1.51	2.13		
L-31	4.34	1.60	0.39	1.14	2.15		
L-32	8.63	2.40	0.30	1.23	1.78		
L-35	3.30	1.79	0.56	1.63	2.99		
L-37	4.09	1.51	0.36	1.35	2.06		
L-38	2.24	1.17	0.40	1.75	3.23		
GBL-Comp	4.64	1.74		0.88***		2.93	
P-19	6.96	2.16	0.32	0.86	1.29	6.12	
P-24	0.25	0.44	0.33	0.91	1.56	1.95	
P-47	0.52	0.33	0.28	0.98	1.38	2.73	

Basis - Total sample

* Turned on a lathe to remove cored surface. All others wet sawed

** By acid evolution - CO₂ only.

*** Loss with air drying at 110°C - Pulverized sample

On all samples except GBL-Comp, the free and bound H₂O analyses were done by vacuum extraction using chunk samples from the chipmunk crusher. The H₂O which evolved at 110°C was collected, weighed and reported as free H₂O. The H₂O which evolved between 110°C and 1000°C was collected, weighed and reported as bound H₂O.

GASBUGGY
D/H RATIOS

	8/18/67 10/13/67 11/11/67			
	Total	D in H	D in H	D in H
	<u>%</u>	<u>ppm</u>	<u>ppm</u>	<u>ppm</u>
L-14	0.40	164	159	
L-15	0.45	157		168
L-19	0.47	167	167	
L-22	0.41	159		171
L-24	0.20	158		162
L-28	0.26	160		170
L-31	0.39	153	160	
L-35	0.56			170
H ₂ standard		145 ± 5	150 ± 5	166 ± 5

The following procedure was used to determine the D/H ratios. The sample was placed in a vacuum line which was evacuated to remove extraneous gases. The sample was then ignited in an oxygen atmosphere at 1000°C and H₂O was collected. The H₂O was reduced to H₂ with hot U. The H₂ was analyzed in a mass spectrometer.

Analyses shown for 8-18-67 were obtained from samples which were pumped hard on a vacuum line prior to collection of H₂O. Therefore, the H₂ collected came primarily from bound H₂O and hydrocarbons which decomposed on heating.

Analyses shown for 10-13-67 are from samples which were pumped as little as possible prior to collection of H₂O. The H₂ determined represents most of the free H₂O together with the bound H₂O and hydrocarbons which decomposed on heating.

The analyses for 11-11-67 are duplicates of those shown 8-18-67. However, on 11-10-67, a large amount of D₂ gas was run in the mass spectrometer resulting in a high deuterium background.

GASBUGGY
CHEMICAL ANALYSIS

	<u>L-14*</u>	<u>L-15</u>	<u>L-19</u>	<u>L-22</u>	<u>L-24</u>	<u>P-19</u>	<u>P-24</u>	<u>P-47</u>
SiO ₂	63.20	63.94	65.82	64.38	65.86	65.06	74.51	77.31
Al ₂ O ₃	12.36	12.58	12.55	12.01	5.26	6.85	11.46	10.74
Fe ₂ O ₃ (Total Fe)	4.49	4.16	4.64	4.89	2.76	9.20	2.13	2.28
CaO	4.08	4.16	3.00	3.78	9.60	3.24	1.18	1.16
MgO	2.62	2.50	2.25	2.82	2.21	2.19	0.91	0.62
MnO	0.05	0.04	0.04	0.04	0.15	0.19	0.04	0.02
Na ₂ O	2.30	2.32	2.30	2.16	1.90	1.94	2.54	2.44
TiO ₂	0.92	0.86	1.00	1.04	0.60	0.84	0.94	0.80
K ₂ O	1.86	1.80	1.78	1.60	1.22	1.28	2.08	1.92
BaO	0.09	0.09	0.09	0.07	0.05	0.05	0.10	0.06
SrO	0.05	0.04	0.04	0.04	0.09	0.02	0.04	0.02
SO ₃ (Total S)	0.84	1.30	2.35	1.55	0.15	0.80	1.35	0.13
P ₂ O ₅	0.15	0.15	0.12	0.17	0.13	0.16	0.07	0.07
ZrO ₂	0.16	0.15	0.13	0.15	0.08	0.02	0.04	0.02
Total C	1.59	1.67	1.52	1.65	2.38	2.16	0.44	0.33
CO ₂ (From CO ₃ ⁼)	3.66	3.65	2.57	3.80	7.11	5.97	0.42	0.47
Loss on drying at 110° C	0.58	0.68	0.62	0.62	0.64	0.34	0.48	0.44
Loss on Ignition	6.94	6.94	6.18	6.80	9.94	8.32	2.78	2.42

Basis - sample dried at 110° C, all results are wt. %.

*Turned on a lathe to remove cored surface, all other samples were wet sawed.

GASBUGGY
EMISSION SPECTROGRAPHIC ANALYSIS

<u>GBP-Comp</u>	<u>Wt. %</u>
Fe	4.5
Cu	0.0005
Ni	0.001
Cr	0.007
Al	7.00
Pb	0.001
Sn	<0.001
Zn	0.01
Co	0.01
Mn	0.03
Mo	<0.005
Ag	<0.0001
V	0.01
Mg	1.50
Ca	2.50
Ti	0.50
Bi	<0.001
Na	1.50
K	1.50
Sr	0.03
Ba	0.08
B	0.003

GASBUGGY

GBL-COMP

CHEMICAL

	<u>Wt. %</u>	<u>Wt. ppm</u>
B		19
Li		28.5
SiO ₂	64.02	
Al ₂ O ₃	10.10	
CaO	4.26	
MgO	2.46	
TiO ₂	1.08	
MnO	0.05	
Na ₂ O	2.12	
K ₂ O	2.34	
Fe ₂ O ₃ (total Fe)	4.44	
N	0.06	
SO ₃ (total S)	2.01	
C (total C)	1.74	
CO ₂ (from CO ₃ ⁼)	4.64	
P ₂ O ₅	0.29	
Fe ⁺² /Fe ⁺³		Ratio 2.93
Loss on drying at 110°C	0.88	

Basis - total sample

EMISSION SPECTROGRAPHIC

	<u>Wt. ppm</u>
Ag	2
B	80
Ba	500
Be	2
Co	60
Cr	50
Cu	2
Mo	<10
Ni	30
Ga	15
Pb	40
Sn	< 3
Sr	200
V	100
Zn	50
Sc	12
Y	30
La	75
Ce	100
Nd	50
Yb	7

ANALYTICAL REPORT

Material SHALELRL Sample No. GBL-COMP

Z	Weight %	Weight PPM	Z	Weight %	Weight PPM
* 1. H	± X2**	± X2**	50. Sn	±	2 ± X2**
* 2. He	±	±	51. Sb	±	0.6 ±
* 3. Li	±	±	52. Te	±	±
* 4. Be	±	±	53. I	±	0.6 ±
* 5. B	±	±	55. Cs	±	23 ±
* 6. C	±	±	56. Ba	±	845 ±
* 7. N	±	±	57. La	±	48 ±
* 8. O	±	±	58. Ce	±	79 ±
9. F	±	146 ±	59. Pr	±	10 ±
11. Na	3.86 ±	±	60. Nd	±	40 ±
12. Mg	2.21 ±	±	61. Pm	±	±
13. Al	9.26 ±	±	62. Sm	±	3 ±
14. Si	29.92 ±	Chemical Analysis ±	63. Eu	±	0.8 ±
15. P	±	355 ±	64. Gd	±	4 ±
16. S	0.40 ±	±	65. Tb	±	0.3 ±
17. Cl	±	77 ±	66. Dy	±	4 ±
19. K	8.26 ±	±	67. Ho	±	0.3 ±
20. Ca	4.81 ±	±	68. Er	±	1 ±
21. Sc	±	51 ±	69. Tm	±	0.3 ±
22. Ti	0.41 ±	±	70. Yb	±	0.9 ±
23. V	±	83 ±	71. Lu	±	0.1 ±
24. Cr	±	90 ±	72. Hf	±	0.7 ±
25. Mn	±	820 ±	73. Ta	±	0.8 ±
26. Fe	5.39 ±	±	74. W	±	506 ±
27. Co	±	104 ±	75. Re	±	2 ±
28. Ni	±	184 ±	76. Os	±	±
29. Cu	±	42 ±	77. Ir	±	±
30. Zn	±	116 ±	78. Pt	±	±
31. Ga	±	36 ±	79. Au	±	±
32. Ge	±	2 ±	80. Hg	±	1 ±
33. As	±	14 ±	81. Tl	±	0.5 ±
34. Se	±	9 ±	82. Pb	±	46 ±
35. Br	±	1 ±	83. Bi	±	0.6 ±
37. Rb	±	252 ±	84. Po	±	±
38. Sr	±	380 ±	85. At	±	±
39. Y	±	30 ±	86. Rn	±	±
40. Zr	±	930 ±	87. Fr	±	±
41. Nb	±	14 ±	88. Ra	±	±
42. Mo	±	32 ±	89. Ac	±	±
43. Tc	±	±	90. Th	±	4 ±
44. Ru	±	0.3 ±	91. Pa	±	±
45. Rh	±	±	92. U	±	1 ±
46. Pd	±	0.3 ±	93. Np	±	±
47. Ag	±	0.4 ±	94. Pu	±	±
48. Cd	±	1 ±	95. Am	±	±
49. In	±	0.09 ±	96. Cm	±	±
	±	±		±	±
	±	±		±	±

Method of Analysis:

Spark Source Mass Spectrograph

* Not Analyzed for

All Other Blanks < 1 wt. PPM

** See Text

Analytical Lab. LRL

Lab. Sample No. _____

Date: 8-22-67Signed: R. D. Carver

ACKNOWLEDGEMENT

The data presented in this report represents the combined effort of many people. The samples were sawed and crushed by Al Horn of the Plowshare Division. Riley Carver of the Radiochemistry Division provided the spark source mass spectrographic analysis. Most of the remaining work was done by members of the Analytical Chemistry Section.

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