

X/ 69 36074

CASE FILE COPY

DETERMINATION OF THE DENSITY AND CHEMICAL
PROFILES OF GOVERNMENT-FURNISHED
CHARRED ELASTOMERIC ABLATOR MODELS

Contract No. NAS1-8212

by

Schwarzkopf Microanalytical Lab., Inc.

Woodside, New York

Distribution of this report is provided
in the interest of information exchange.
Responsibility for the contents resides
in the author or organization that prepared
it.

December 1968

PART I

Contract No. L64-9042 as specified in the work statement requests the analysis of various cuts of several ablation models. Specifically, it requests the determination of:

- 1) Total Carbon
- 2) Hydrogen
- 3) Total silicon and silicon carbide
- 4) Residue
- 5) "Free" oxygen
- 6) "Free" carbon
- 7) Density

In part I of this report, we will describe the chemical analyses performed 1 to 6 and some additional investigations not covered by this contract, but that we deemed essential to the understanding of the problem.

We will now describe the analytical methods employed:

Total carbon was obtained by combustion at 1100°C , using lead oxide as an additive. This included all carbide-carbon.

Total hydrogen was also obtained in this analysis.

Total non-carbide silicon was obtained by oxygen flask combustion with concentrated sulfuric acid as an absorbent and dehydrating agent. Silicon dioxide formed was filtered and weighed and then volatilized by treatment with hydrofluoric acid. This left a residue.

Residue. The resulting residue consisted of a) silicon carbide and b) metal oxides, especially oxides of iron, aluminum, and of sodium. A carbonate fusion, followed by acidification, dissolved both components. Silicon from SiC was determined colorimetrically by the molybdene blue method. It is shown in our Tables as SiSiC. Iron and aluminum were determined colorimetrically and by atomic absorption spectrophotometry.

The main component of the residue was Na. We checked for the presence of Li and K but only Na was present in sufficiently large amounts. We restricted the tests to Na. Since Na_2CO_3 was used in the fusion, this method was not suitable for the Na determination. Instead the residues from the determinations of free carbon, where no additive was used, and of free oxygen were analyzed for Na by atomic absorption spectrophotometry (AA).

"Free Oxygen" was determined by known techniques, that is by pyrolysis at 1000°C in a stream of N_2/H_2 followed by conversion into CO; then oxidation into CO_2 . Total oxygen was determined by difference because oxygen bound to silicon could not be reduced under present conditions.

"Free" carbon (non-carbide carbon) was more difficult to determine than it was stated in the work statement. Combustion at 900°C, without any additive, produced only incomplete recoveries. The combustion residue contained substantial amounts of free carbon.

Instead carbide-carbon was calculated from the amount of carbide-silicon. Free carbon was the difference between total carbon and carbide carbon.

To obtain a direct measure of free carbon and also resolve some interesting other problems which cropped up in the course of our work, we conducted two series of tests, called Series I and Series II - and we also extended the oxygen test series - called Series O, to include measurements of volatile fractions, carbon and silicon.

This part of our work - Series I, II and the extended series O, have not been requested in the work statement, but we felt strongly that without this additional investigation our results may not have significance. We also thought that all possible information should be extracted from elementary analyses. We showed in these tests some of the properties of the test material when exposed to chemical treatments such as combustion, heating in nitrogen, reaction with HF. We especially examined the volatility and the state of oxidation of silicon. Some of the problems which still remain may deserve further and more detailed investigation.

The preparation of layers of material (cuts) to be examined and the measurement of Density were carried out by the AVCO corporation, Lowell, Mass. as a sub-contractor. The results have already been submitted by us and will appear in this report as Part III.

Analytical Results

Part I

Chemical Analysis

The analyses requested in this contract are given for

Model	II	in Tables:	I	and	VII, VIII
Model	IV		IX	and	XV, XVI
Model	VI		XVII	and	XXIV, XXV
Model	VII		XXVI	and	XXVIII

The following comments can be made:

TABLE I - Carbon - free and total, reach a minimum in cut 11-9, then carbon increases to cut 5 and decreases again to cut 1.

Hydrogen is present only in cuts 15-10. In the cuts 9 - 1, a trace may be present but the amount found is near or equal the precision of the method.

Free oxygen is found only in cut 15 (virgin material) none was found in cut 14 in several tests, a small amount of oxygen was found in cut 13, 12. All other cuts did not have free oxygen.

Included in this Table is the column, Volatility, which is derived from Series O. We see that cuts 14-10 contain volatile fractions in decreasing amounts. This shows that in these cuts pyrolysis was incomplete during the charring heat treatment to which they had been exposed. Fractions 8 - 1 have been completely charred and do not contain either hydrogen, oxygen or volatile material.

The non-carbide silicon content is the highest in cuts 6 - 1. However, this table does not show us what form of silicon is present. We will see that only a small part is present as SiO_2 while considerable amounts, sometimes the main part, is present in a lower state of oxidation, e.g. as SiO or SiOSi .

It is remarkable that we find considerable differences in the amount of residue present. The highest amounts are found in cuts 12 - 9 and again in 3 - 1.

From Table VII and also in the last column of Table I we can see that SiC was found in significant amounts only in cuts 1 - 5. Some may be present in cuts 11 - 12.

The main metallic component of the residue is sodium. This may have its origin in the catalyst General Electric SRC - 04. The Na content is highest in cuts 12 - 9 and then falls off in both directions. As the material supposedly was of uniform composition before the charring heat treatment, we have to assume that sodium dispersed by melting or evaporation and concentrated in fractions 13 - 9.

Table IX shows similar patterns to Table I. The carbon content is at its lowest in cuts 9 and 10, reaches a higher point in cut 4 and falls off to cut 1. Hydrogen is found in cuts 15 - 10 but the pyrolysis may have been less complete because we find a considerable amount of hydrogen in cut 12 (5.4%) while in Table I cut 12 has only 1.7% H.

Free oxygen is also spread out. It is definitely present in small amounts up to cut 11.

The volatility is also much greater in this model. Cut 12 contains 58.4% volatile as compared to 15 in Table I.

Non carbide silicon follows the pattern already discussed. More will be said in the later pages of this report.

The residue is the highest in 12 - 8. We do not see any concentration in cuts 1 - 3.

Silicon carbide is quite low.

A substantial component of the residue is sodium. Again the highest concentration is in the cuts 11 - 8.

Table XVII shows a similar pattern

Carbon is the lowest in cuts 9 - 8 and has a second peak in cut 4. Cut 2 is particularly low in carbon. 4 analyses agree with this low value.

Hydrogen is present in cuts 15 to 10. A small amount, within limits of the experiment, could be present in 10.

Free oxygen is present in 15 to 12. In 11 no free oxygen was found; in 10 a small amount.

Volatile fractions are found until cut 10. In 9 and 8 only very small fractions are still volatile.

Non carbide silicon increases irregularly with a high in cuts 9 to 6 and in cut 2 while the other cuts are low.

The residue is the highest in cuts 11 to 9.

Sodium is the highest in cuts 10 to 8 and SiC in 11 to 9, 6, 4, 3 and 1.

Very little can be deducted from analyses of model VII which broke repeatedly during cutting. Cut 5 is the virgin material.

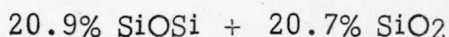
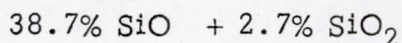
	Model II/15	Model IV/15	Model VI/15	Model VII/5	Average
Volatile%	76.8	76.3	76.5	76.5	76.5
non volatile	23.2	23.7	23.5	23.5	23.5
% free oxygen	3.0	2.5	2.4	2.2	2.5
Non volatile					
%C	5.2	4.4	4.6	4.6	4.7
%H	-	-	-	-	-
%Weight loss (HF)	16.6	17.0	16.7	17.6	17.0
Residue	1.3	2.2	1.2	1.3	1.5
weight loss calc.as Si	7.8	7.9	7.8	8.2	7.9
weight loss calc.as O	8.9	9.1	8.9	9.4	9.1

Table XXVIII

	Volatile fraction (average)			atom %
	total	non volatile	volatile	
%C	30.5	4.7	25.8	
%H	6.3	-	6.3	
%Si	33.8	7.9	25.9	0.925
%Free O	2.6	-	2.6	
%O _{Si}	24.6	9.1	15.5	0.97

$$\frac{O}{Si} = \frac{0.97}{0.925} = 1.049$$

1.049 corresponds to



Calculation I seems more realistic than calculation II. It would require the presence in the volatile fraction of 2.7% volatile SiO₂. This could be an experimental error or it could be a radical $\text{Si} \begin{smallmatrix} \text{OR} \\ \text{OR} \end{smallmatrix}$ present in the virgin material which would be volatile.

This could correspond to the dimethoxy component of the preparation.

We noted the carbon content of the non volatile fraction. We feel that the carbon has its origin in the phenolic portion of the mixture. This component seems to pyrolyze more easily than the siloxanes. On heating under nitrogen the siloxanes are volatilized without decomposition while the phenolics are pyrolyzed losing hydrogen and oxygen (found as free oxygen) and leaving the carbon behind.

No conclusions can be drawn from the results of the analyses of cuts 15 of the series I and series II. We have already mentioned that recoveries of carbon and silicon are incomplete in these tests.

From our mode of analyses and the behaviour of the virgin material, the following picture of charring is suggested: At first, siloxanes are volatilized and phenolics pyrolyzed. The siloxanes penetrate the upper layer up to cut 11 where they are completely pyrolyzed. During this process, gases are formed that make the material porous and even may cause more or less deep cracks. Cut 11 has the lowest density because of the evolution of gas. In this cut practically all silicon has been converted to SiO₂ and no oxidation (D₂) occurs during combustion.

PART II

Additional work (not included in work statement)

We mentioned that in the course of our investigation, we found out that the charred ablation models gave incomplete and inconclusive results when the analyses were performed in strict compliance with the work statement.

We carried out the requested analyses and the results are given in Part I of this report. We also determined "free carbon" as requested in the work statement (by combustion at 900°C) and these results figure as Combustion I ($\%C_1$) in Tables VI, XIV, XII of the Serie II and also in Tables VII, XVI, XXV.

The following problems were encountered:

1. Free carbon:

By combusting at 900°C , only a portion of free carbon (non carbide-carbon) is burned. A sizable amount of carbon, depending on the model and the cut, is obtained in a second combustion after an intermediary treatment with HF. We must mention again that neither combustion at 900°C nor HF treatment will attack SiC . The additional free carbon is given in the tables as C_2 .

2. Volatility

Cuts 9 to 15 yielded variable amounts of volatile fractions when heated under nitrogen to 1000°C . Obviously, the volatility increased greatly with the cut number. The amount of volatiles is given in Table I, IX, XVII of Part I.

The volatility did not affect the results of "Total carbon" or "Total non carbide-silicon". Combustion with PbO as additive was complete. The "total silicon" analysis by oxygen flask combustion and gravimetric determination of SiO_2 was not affected.

However the combustion analysis without additive even as performed in Serie II (as will be shown later) in two steps gave incomplete recoveries of carbon because in the intermediary step of HF treatment carbon was lost (this will also be discussed later).

To illustrate the incomplete recovery of carbon in cuts 12 to 15 the following table compares "total carbon" with C_1 and C_2 of Serie II.

TABLE XXVI

Model	Cut	$\%C_1$	$\%C_2$	$\%C_1 + C_2$	% total carbon
II	15	29.0	0	29.0	30.4
	14	28.8	0.7	29.5	31.6
	13	25.3	0	25.3	27.7
	12	20.8	0.6	21.4	24.1
IV	15	29.2	0	29.2	32.0
	14	29.6	0	29.6	33.4
	13	28.6	0	28.6	30.9
	12	27.6	0	27.6	30.2
VI	15	29.6	0	29.6	30.7
	14	29.1	0.5	29.6	31.3
	13	28.4	0.5	28.9	29.1
	12	27.8	0.7	28.5	27.4

The difference between "total" and $C_1 + C_2$ cannot be attributed to silicon carbide because very little Si_{SiC} (silicon in the Na_2CO_3 fusate) is found and therefore little SiC is present in these fractions.

Similarly complete recovery of silica as combustion residues is not always possible. Not affected was the analysis for "total non carbide silicon" and "carbide silicon", because both derived from the same analysis by oxygen flask combustion. Here the sample is burned in a closed flask filled with oxygen and concentrated H_2SO_4 as absorbent. All the vapors pass through the hot flame. SiO_2 becomes anhydrous with the concentrated H_2SO_4 but silicon carbide remains unburned. After elimination of SiO_2 by treatment with HF the remaining residue is fused with Na_2CO_3 and Si_{SiC} is determined in the fusate by the molybdenum blue colorimetric procedure. This analysis is not effected by the volatility of the sample and has been used by us for the analysis of volatile silanes, etc.

3. Oxygen uptake and oxidation state of silicon

After combustion of cuts 1 to 11 (samples without volatile material) we find that the combustion residue weighs more than the loss of carbon indicates. If we deduct the weight of the carbon found from the starting weight, there is a gain. This is caused by oxidation of the combustion residue and we call it oxygen uptake. (D_O). The only component which is present in the residue in substantial amounts is silicon and we consider the oxygen uptake to be a measure of the oxidation state of silicon. It is of significant value that should lead to an interpretation of the state of oxidation of the silicon present, e.g. SiO_2 , SiO or $SiOSi$, etc. We felt that this information should be extracted from our experiments.

4. Composition of the volatile fraction

Cuts 12 to 15 contain increasing amounts of volatile fractions that volatilize at $1000^\circ C$ under a stream of N_2 , the conditions required for oxygen analysis. The elementary analysis of the remaining ^{non}volatile fractions is performed in Series O and gives us, by difference with "totals" the composition of the volatile fractions.

5. Another interesting and unsettled aspect of the problem is to distinguish between various forms of "free" (non carbide) carbon. The starting virgin material contains carbon as a component of siloxane, methoxy silanes and also phenolic carbon.

We have had no occasion to analyze the various components separately and to study their behavior under conditions of pyrolysis or oxidation as they occur during the charring test and also in our analytical procedures. Such experiments would have been helpful in the interpretation of our results especially to explain the carbon found in the non-volatile residues of cuts 12 to 15. We have some evidence that there is a difference in stability of siloxanes and phenolics and that it is phenolic carbon that is present in the non volatile fraction of cut 15. The siloxanes on the other hand seem to volatilize without pyrolysis. A more detailed study of this phenomenon should be of value.

These were the main problems we encountered in our investigation. To try to solve them at least partly, we performed Series I, II and O which we will now discuss. Each series is a whole sequence of analyses, all carried out with the same weighed starting material.

Series I comprised the following steps:

1. treatment with hydrofluoric acid, determination of the weight loss
2. combustion, determination of carbon, hydrogen and combustion residue
3. determination of D_O
4. treatment with hydrofluoric acid, determination of weight loss
5. determination of the "final" residue
6. dissolving the residue in HCl for the analysis of Na, Fe, Al

The treatment with HF (step I) affects by

- a. volatilization - all silica (SiO_2)
- b. hydrolysis - ether type linkages such as $Si \begin{array}{l} \diagup OR \\ \diagdown OR \end{array}$ e.g. di methoxy silanes or siloxanes

SiO_2 and RH are both volatilized, causing losses both of SiO_2 and C. Losses of C occur in cuts with volatile fractions only, where charring did not cause complete pyrolysis. In cuts 1 to 9 and practically in 10 and 11, the loss of weight after HF treatment is strictly SiO_2 .

In step 2 "free carbon" is burned. We obtain practically all the "free carbon". Carbon left in the combustion residue is small. In this combustion we observe an oxygen uptake (D_O): the residue weighs more than the difference between starting material and "free carbon" because SiO_2 is formed. It is volatilized in Step 4. Deducting D_O shows that before oxidation² the oxygen/silicon ratio of this fraction is roughly 1/1 (e.g. O/Si = 1.1/1). The excess of oxygen may indicate the presence of some SiO_2 or may be characteristic of the end-group of the siloxane polymer. We attempted to calculate the SiO_2 of this fraction by assuming an oxygen-silicon ratio of 1/1 (Si-O) and 1/2 (Si-O-Si) for the second component. (Tables II, X, XVIII). The results of Series I are found in tables III for model II

XI	"	IV
XIX	"	VI

We compared the results with those of tables II, X AND XVIII.

Series II comprised the following steps.

1. combustion I - determination of carbon (C_1), hydrogen and combustion residue
2. calculation of oxygen uptake D_{O1}
3. treatment with hydrofluoric acid, determination of the weight loss $(HF)_1$
4. combustion II determination of carbon (C_2) and combustion residue
5. calculation of oxygen uptake D_{O2}
6. treatment with hydrofluoric acid, determination of the weight loss $(HF)_2$
7. determination of the final residue
8. dissolving the residue in HCl for the analysis of Na, Fe, Al

This series differs from series I by the first step, combustion I, afterwards it follows the sequence of series I. Combustion I represents the determination of "free C" in accordance with the work statement. The results are given separately

in Table VIII for model II, Table XVI for model IV, table XXV for model VI.

By starting with a combustion we achieve better recoveries and better agreement with the "Totals". We can also compare the weight loss of Step 3 (HF)₁ with the weight loss of Step 1, in Series I.

In Series II a combustion and oxygen uptake had preceded the treatment with HF causing an increase in SiO₂ and a weight loss. We were trying to find a correlation between D_O and (HF)₁. The results of this test series are given for:

Model	II	in table	VI
Model	IV	"	XIV
Model	VI	"	XXII

Series O comprises the following steps:

1. determination of free oxygen by pyrolysis in a stream of nitrogen.
Determination of CO₂ as a measure of free oxygen
2. determination of the weight loss, this is the volatile fraction
3. a) treatment with HF₁, weight loss
b) combustion, carbon, hydrogen, residue
c) determination of D_O
d) treatment with HF, weight loss
e) final residue
f) dissolution of residue and analysis of Na

An alternate step 3 followed the sequence of Series II starting with combustion and continuing with a to f as above. Sometimes a third combustion and a third treatment with HF was necessary to clear the residue of all free carbon.

We compared the weight loss of 3 a with the weight loss of Series I, Step 1 and found good agreement in the cuts 1 to 9 where no volatile fractions are involved. In the cuts 10 to 15 there is also a correlation, if we take into account the volatile portion eliminated before the HF treatment, in other words if we add % volatile to the weight loss of 3 a.

Next we calculated the composition of the volatile fractions in cuts 11 to 15. We found that the volatile fractions have roughly 1/1 Si/O ratio.

The results of Series O are found for

Model II	in table	IV and V
Model IV	"	XII and XIII
Model VI	"	XX and XXI

Analysis of the virgin material (model VI, cut 15, IV, cut 15, VI cut 15 and VII, cut 5)

This material has not been exposed to the effect of heat and its composition is somewhat though not completely known from the composition given in the work statement given to us and here are the results:

Table XXVII gives the "totals"

Model	Cut	%C	%H	%Si	free	%O total	O _{Si}	%Residue
II	15	30.4	6.4	33.5	3.1	27.9	24.8	1.8
		30.6	6.2	33.7	2.9	27.5	24.6	2.0
IV	15	30.9	6.2	34.2	2.5	26.5	24.0	2.2
VI	15	30.7	6.4	34.1	2.4	26.5	24.0	2.2
VII	5	31.1	6.1	33.6	2.2	27.7	25.2	1.5
Average		30.5	6.3	33.8	2.6	27.2	24.6	2.0
Composition of residue:				Na	0.55	0.50	0.56	
				Fe	0.03			
				Al	0.05			
				Si	0.30		0.43 SiC	

Calculation of D_O

Si: 33.8 1.21 atom %
 O_{Si} : 24.6 1.54 atom %

$$D_O = 2 \times 1.21 - 1.54 = 0.88 \text{ expressed as } \%O = 14.08$$

Calculation I - a mixture of SiO_2 and SiO

$$\%SiO = D_O \times 44 = 0.88 \times 44 = 38.7$$

$$\%SiO_2 = \left(\frac{\%Si}{28} - D_O \right) \times 60 = (1.21 - 0.88) \times 60 = 19.8$$

Calculation 2

$$\%SiOSi = \frac{D_O}{3} \times 72 = 0.29 \times 72 = 20.9\% \text{ SiOSi}$$

$$\%SiO_2 = \left(\frac{\%Si}{28} - \frac{2 D_O}{3} \right) \times 60 = 37.8\%$$

TABLE XXVIII

Composition of the non volatile and volatile fractions

The following table gives the composition of the non volatile fractions (Series O)

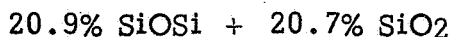
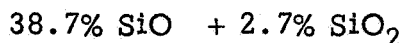
	Model II/15	Model IV/15	Model VI/15	Model VII/5	Average
Volatile%	76.8	76.3	76.5	76.5	76.5
non volatile	23.2	23.7	23.5	23.5	23.5
% free oxygen	3.0	2.5	2.4	2.2	2.5
Non volatile					
%C	5.2	4.4	4.6	4.6	4.7
%H	-	-	-	-	-
%Weight loss (HF)	16.6	17.0	16.7	17.6	17.0
Residue	1.3	2.2	1.2	1.3	1.5
weight loss calc.as Si	7.8	7.9	7.8	8.2	7.9
weight loss calc.as O	8.9	9.1	8.9	9.4	9.1

Table XXVIII

	Volatile fraction (average)			atom %
	total	non volatile	volatile	
%C	30.5	4.7	25.8	
%H	6.3	-	6.3	
%Si	33.8	7.9	25.9	0.925
%Free O	2.6	-	2.6	
%O _{Si}	24.6	9.1	15.5	0.97

$$\frac{\text{O}}{\text{Si}} = \frac{0.97}{0.925} = 1.049$$

1.049 corresponds to



Calculation I seems more realistic than calculation II. It would require the presence in the volatile fraction of 2.7% volatile SiO₂. This could be an experimental error or it could be a radical $\text{Si} \begin{smallmatrix} \text{OR} \\ \text{OR} \end{smallmatrix}$ present in the virgin material which would be volatile.

This could correspond to the dimethoxy component of the preparation.

We noted the carbon content of the non volatile fraction. We feel that the carbon has its origin in the phenolic portion of the mixture. This component seems to pyrolyze more easily than the siloxanes. On heating under nitrogen the siloxanes are volatilized without decomposition while the phenolics are pyrolyzed losing hydrogen and oxygen (found as free oxygen) and leaving the carbon behind.

No conclusions can be drawn from the results of the analyses of cuts 15 of the series I and series II. We have already mentioned that recoveries of carbon and silicon are incomplete in these tests.

From our mode of analyses and the behaviour of the virgin material, the following picture of charring is suggested: At first, siloxanes are volatilized and phenolics pyrolyzed. The siloxanes penetrate the upper layer up to cut 11 where they are completely pyrolyzed. During this process, gases are formed that make the material porous and even may cause more or less deep cracks. Cut 11 has the lowest density because of the evolution of gas. In this cut practically all silicon has been converted to SiO₂ and no oxidation (D₂) occurs during combustion.

Above cut 11 oxidation is prevented by the evolution of large amounts of reducing gas, e.g. H_2 , CO or CH radicals. Therefore, we find Si as SiO or SiO_2 or other lower Si oxides. Due to the higher temperature and the presence of oxygen in the environment, oxidation occurs at the surface and Si is mostly oxidized.

We have already discussed the pattern of distribution of silicon carbide and of sodium. Silicon carbide seems to be found in the middle layers as well as near the surface. Sodium also is concentrated in the middle layers. Is it possible that the combination of carbon and silica formed in the layers 11 produces a barrier to heat and oxidation and tends to contribute to the stability of the material?

Other Cuts

Interesting deductions can be made from the analyses of the other cuts containing volatile fractions but at present we refer to the tables showing the composition of non-volatile and volatile fractions. The first result is that the ratio of silicon to oxygen in the volatile fractions is nearly 1 : 1 and the fact that volatile fractions do occur in cuts 14, 13 and 12 and small amounts even in 11. Free oxygen has vanished nearly immediately while hydrogen is still present. All this points out that the phenolics are already pyrolyzed in cut 14 and siloxanes are pyrolyzed gradually. Hydrogen and volatility are indicative of incompletely pyrolyzed siloxanes.

The completely pyrolyzed cuts 1 to 10 have been quantitatively analyzed in Series I and II and again interesting evaluations can be made. We refer to the tables where Series I and II are compiled. We cannot at present decide whether calculation I or II comes nearest to the reality. Further experimentation would be necessary. In some of the samples the material which was available to us was extremely small, e.g. in model II, cut 1 we had a total of 1 mg. sample. Not all of the sample which was cut off was recovered. Fortunately we were able to run this analysis on our ultra micro apparatus and reasonably good results were obtained. We could, however, not perform more than Series II which was used to calculate total silicon, carbon, etc.

Wherever the sample was insufficient we have noted it in the tables.

PART III

In this part we report the preparation of layers of material to be analyzed. This work was performed in sub-contract by AVCO Corp., Lowell, Massachusetts, and we have already reported, on Sept. 24, 1968 (letter to LRC-William E. Rew).

Models II, IV, VI were successfully layered. Model VII was found to have a fractured char cup. As a result, attempts to layer the specimen in accordance with instructions in the work statement were unsuccessful. Only 5 layers were obtained. These attempts are described in greater detail below. Photographs made and included with out letter of Sept. 24 are part of this report. The photographs were made to show the result of one attempt to set the char cup in epoxy resin in the hope of being able to partition it successfully and to illustrate the type of damage observed by us prior to the initial layering attempt. These photographs show also that the char was not uniform horizontally, dark portion on the outside and lighter portion on the inside. This condition was present in all four models 2, 4, 6 and 7.

The results for models 2, 4, 6 and 7 are presented in Tables I through IV respectively. Each specimen was basically cylindrical. Therefore most layer volume calculations were straight forward. However, equations for the volumes of spherical segments (one base and two bases) had to be applied to the first few layers of Models 2, 4 and 7 because these specimens were rounded on the end. Also, a prism shaped chip had to be removed from Model 2 beginning with layer 5, before layering could continue. Consequently, an adjusting calculation was necessary for subsequent layers. The equations used with the exception of cylindrical volume are given as footnotes at the bottom of each table. The following describes briefly the difficulties encountered with Models 6 and 7.

When the outer diameter of these specimens was turned down to 1.50 inches (Models 2 and 4 were treated similarly) to expose the char region of interest, the char region of Model 6 was observed to be cleaved by a fissure extending across the surface of the char and down through the char layer. Model 7 was fractured more severely. Two large cracks penetrated the char from the surface down through the char but, more significantly, the char cap was almost totally separated from a zone just above the virgin region because of a break extending horizontally through the specimen.

To try to make it possible to layer successfully models 6 and 7, a collar was designed, fabricated and used to enclose the specimen uniformly. This technique was successfully applied with Model 6. However, during the third layer cut on Model 7, the entire cap separated from the specimen and broke into three large pieces and one smaller piece. Photographs 1 and 2 illustrate respectively the appearance of the pieces broken from the char cap and the appearance of the specimen after separation of the cap during machining.

After this occurrence, we called you, and with your permission reassembled the char pieces and set them in an epoxy resin in such a way that layering could be continued without being contaminated by resin. Photograph 3 best illustrates the result.

Unfortunately, the attempt to layer the bonded char cap met with failure because the char itself did not have sufficient strength to hold together under shear forces of layering. As a result, the upper surfaces of each piece separated from its bonded epoxied portion.

We hoped that we could yet obtain four or five layers for density information and therefore bonded each of the segments to an aluminum block. The bonding held, but again, each segment broke away from itself. At this point, time considerations did not permit us to try again. We had three layers from the char surface. We obtained two more from the residual portion of Model 7 - one just below where the char cap broke away and the other in the virgin region.

TABLE I

MODEL II

Cut	TOTALS									
	% Total C	Free %C	%H	% O free	% Volatile under N ₂	%Si	Total % O	%O _{Si}	% Residue	%Si _{SiC}
1	20.7	20.0*	i.s.	i.s.	i.s.	39.5	35.7	35.7	4.8	2.*
2	20.0	19.3	0.2	i.s.	i.s.	40.6	33.4	33.4	6.5	1.80
3	22.5	21.6	0.2	0	0	40.4	32.0	32.0	5.8	1.8
4	22.2	21.8	0.1	0	0	40.3	34.6	34.6	3.2	0.9
5	23.9	23.4	0.2	0	0	40.1	32.8	32.8	3.5	1.05
6	22.5	22.4	0.1	0	0	40.0	34.7	34.7	2.9	0.3
7	21.2	21.0	0.2	0	0	37.6	38.4	38.4	2.9	0.4
8	20.5	20.4	0.1	0	0	38.0	39.2	39.2	2.3	0.1
9	19.0	18.84	0.2	0	1.2	37.5	39.6	39.6	3.8	0.3
10	18.9	18.8	0.7	0	2.8	36.7	39.2	39.2	4.6	0.3
11	19.2	18.9	1.09	0	2.6	35.0	39.7	39.7	5.0	0.5
12	22.8	22.5	1.7	0.8	15.1	33.4	36.6	35.8	5.8	0.7
13	27.7	27.6	4.9	0.6	44.2	33.9	31.6	31.0	2.0	0.15
14	30.1	30.0	6.1	0	64.2	33.5	28.3	28.3	2.1	0.3
15	30.2	30.1	6.4	3.0	76.8	33.5	28.2	25.2	2.0	0.3

* - estimated, sample insufficient

TABLE II

MODEL II

Attempt of Interpretation of Silicon & Oxygen (O_{Si})

Cut	%Si	%O _{Si}	D _O	Calculation I		Calculation II	
				%SiO	%SiO ₂	%SiOSi	%SiO ₂
1	39.5	35.7	0.59	26.0	49.2	14.2	60.6
2	40.6	33.4	0.81	35.6	38.4	19.8	54.0
3	40.4	32.0	0.90	39.6	32.4	21.6	50.4
4	40.3	34.6	0.72	31.7	43.2	17.3	57.6
5	40.1	32.8	0.81	35.6	37.2	19.4	53.4
6	40.0	34.7	0.71	31.7	42.6	17.3	57.0
7	37.6	38.4	0.28	12.3	63.6	6.5	69.6
8	38.0	39.2	0.27	11.9	65.4	6.5	70.8
9	37.5	39.6	0.20	8.8	68.4	4.8	72.6
10	36.7	39.2	0.17	7.5	68.4	4.1	72.0
11	35.0	39.7	0	—	75.0	—	75.0
12	33.4	35.8	0.14	6.2	63.0	3.6	65.4
13	33.9	31.0	0.48	21.1	43.8	11.5	53.4
14	33.5	28.3	0.63	27.7	34.2	15.1	46.8
15	33.5	25.2	0.83	36.5	22.2	20.2	38.4

TABLE III

MODEL II

Analysis of Series I

Cut	Volatile	(HF) ₁ * %W.L.	Calc.as Si.	D _O Atom %	D _O Table II	%C	%C Table I	% Silicon		%SiO ₂ Table II Calc.II	DC	D Si
								(HF) ₂	(HF) ₁ +(HF) ₂	Table I		
2	0	56.2	26.2	0.67	0.81	16.9	19.3	14.2	40.4	40.6	-2.4	0
3	0	60.1	28.0	0.66	0.90	20.6	21.6	11.2	39.2	40.4	-1.0	-1.2
4	0	61.1	28.5	0.56	0.72	20.8	21.8	10.3	38.8	40.3	-1.0	-1.5
5	0	60.9	28.4	0.50	0.81	22.4	23.4	10.0	38.4	40.1	-1.0	-1.7
6	0	61.3	28.6	0.43	0.71	23.2	22.4	9.1	37.7	40.0	+0.8	-2.3
7	0	60.2	28.1	0.28	0.28	21.5	21.0	9.4	37.5	37.6	+0.5	0
8	0	57.4	26.8	0.25	0.27	19.1	20.4	12.1	38.9	38.0	-1.3	+0.9
9	1.2	57.9	27.0	0.06	0.20	18.1	18.8	9.7	36.7	37.5	-0.7	-0.8
10	2.8	59.9	28.0	0.09	0.17	17.4	18.8	9.6	37.6	36.7	-1.4	+1.1
11	2.6	63.5	29.6	0	0	18.5	18.9	5.1	34.7	35.0	-0.4	-0.3

* W.L = weight loss

The following cuts, 12 - 15, contain large volatile fractions. This table cannot be continued.

TABLE IV

MODEL II

Analysis of Series O

Cut	% Volatile	% Free Oxygen	HF loss	HF loss Series I
1	0	0	N.D.*	
2	0	0	N.D.*	56.2
3	0	0	60.0	60.1
4	0	0	56.5	61.1
5	0	0	56.1	60.9
6	0	0	60.5	61.3
7	0	0	59.3	60.2
8	0	0	57.5	57.4
9	1.2	0	55.4	57.9
10	2.8	0	59.3	59.9
11	2.6	0	65.0	63.5
12	15.1	0.8	**	**
13	44.2	0.6		
14	64.2	0		
15	76.8	3.0		

* Sample insufficient

** The Table is cut here as the volatile fraction obscures the picture.

TABLE V

MODEL II

Analysis of Series O (continued)

Calculation of the volatile fraction in cut 12, 13, 14, 15Cut 12

Totals		% Non volatile	Volatile %	Atom %
%C	22.5	13.2	9.3	
%H	1.7	—	1.7	
% Free O	0.8	—	0.8	
% Si	33.4	30.8	2.6	0.09
% O _{Si}	35.8	35.2	0.6	0.04
Res.	5.8	5.8	—	
Total			15.0	
Found volatile			15.1	

Cut 13

Totals		%Non volatile	Volatile %	Atom %
%C	27.6	8.6	19.0	
%H	4.9	—	4.9	
% Free O	0.6	—	0.6	
%Si	33.9	16.1	17.8	0.64
% O _{Si}	31.0	18.3	12.7	0.80
Res.	2.0	2.0	—	
Total			55.0	
Found Volatile			55.8	

Cut 14

Totals		%Non Volatile	Volatile %	Atom %
% C	30.0	7.9	22.1	
% H	6.1	—	6.1	
% Free O	0	—	0	
% Si	33.5	12.0	21.5	0.77
% O _{Si}	28.3	13.9	14.4	0.90
Res.	2.1	1.8	—	
Total			64.1	
Found Volatile			64.2	

TABLE V (continued)

Cut 15

Totals		%Non volatile	Volatile %	Atom %
%C	30.1	5.2	24.9	
% H	6.4	—	6.4	
% Free O	3.0	—	3.0	
% Si	33.5	7.8	25.7	0.92
% O	25.2	8.9	16.3	1.02
Res. ^{Si}	3.5	1.3	—	
Total			76.3	
Found Volatile			76.8	

TABLE VI

MODEL II

Analyses - Series II

wt	Combustion I		Do ₁ Atom%	(HF) ₁		Combustion II		(HF) ₂		C ₁ + C ₂	%C Table I	Do ₁ + Do ₂	Do Table II	Si ₁ + Si ₂	Si Table II
	(%C), %H	%Res.		%W.L.	calc. % Si	(%C) _v	Do ₂ % Atom%	W.L.	calc. as Si						
1	14.6	0	0.1	62.7	29.2	6.1	0.70	21.9	10.2	20.7	20.0	0.80	1.s.	39.4	39.5
2	11.1	0.2	0.27	62.0	28.9	8.1	0.57	25.7	12.0	19.2	19.3	0.84	0.81	40.9	40.6
3	14.1	0.2	0.31	65.9	30.7	8.2	0.62	24.4	11.4	22.3	21.6	0.93	0.90	42.1	40.4
4	15.3	0.1	0.21	66.2	30.9	6.7	0.48	19.6	9.1	22.0	21.8	0.69	0.72	40.0	40.3
5	16.4	0.08	0.17	64.2	30.0	7.4	0.58	21.3	10.0	23.8	23.4	0.75	0.81	40.0	40.1
6	16.6	0.0	0.20	65.2	30.4	5.8	0.50	19.5	9.1	22.4	22.4	0.70	0.71	39.5	40.0
7	14.6	-	0.09	63.3	29.7	7.0	0.22	16.4	7.7	21.6	21.0	0.31	0.28	37.4	37.6
8	13.5	0.18	0.14	63.7	29.7	6.4	0.05	18.6	8.7	19.9	20.4	0.19	0.27	38.4	38.0
9*	12.6	0.19	0.07	66.8	31.2	4.8	0	11.8	5.5	17.4	18.8	0.07	0.27	36.7	37.5
10*	13.8	0.7	0.1	61.4	28.7	4.4	0	12.7	5.9	18.2	18.8	0.1	0.17	34.6	36.7
11*	18.7	1.1	0	70.8	33.0	0.3	0	2.8	1.2	19.0	18.8	0	0	34.2	36.7

* - volatile fractions are present

TABLE VII

MODEL II

Analysis of Residues

Cut	Determination of Silicon Carbide and Metallic Impurities					
	% Residue Totals	Series I	Series O	%Si(SiC) [*]	Calc. as SiC	%Na %Fe %Al
1	4.8		N.D.**	2.0 [*]	3.0	N.D.**
2	6.5	7.5	N.D.**	1.8	2.6	0.5
3	5.8	5.4	6.1	1.8	2.6	0.03
4	3.2	3.8	2.9	0.9	1.3	0.03
5	3.5	3.0	2.5	1.05	1.5	0.03
6	2.9	2.9	3.1	0.3	0.4	0.013
7	2.9	2.9	3.5	0.4	0.6	0.02
8	2.3	2.7	3.3	0.1	0.1	0.03
9	3.8	3.9	4.7	0.3	0.4	0.04
10	4.6	3.4	5.9	0.3	0.4	0.09
11	5.0	6.3	6.0	0.5	0.7	0.03
12	5.8	6.0	6.6	0.7	1.0	0.04
13	2.0	2.0	1.8	0.15	0.2	0.04
14	2.1	3.1	2.0	0.3	0.4	0.01
15	2.0	3.0	1.3	0.3	0.4	0.03

* estimated

** sample insufficient

TABLE VIII

MODEL II

"Free Carbon" by combustion at 900°C (incomplete recovery)

Cut	% C
1	14.6
2	11.1
3	14.1
4	15.3
5	16.4
6	16.6
7	14.6
8	13.5
9	12.6
10	13.8
11	18.7
12	20.8
13	25.3
14	28.8
15	29.0

TABLE IX

MODEL IV

TOTALS

Cut	%TotalC	Free %C	%H	%O free	Volatile Under N ₂	%Si	Total %O	%O _{Si}	%Residue	%Si, SiC
1	26.27	25.7	-	-	-	35.7	37.1	37.1	1.5	-
2	26.2	26.1	-	-	-	36.0	35.7	35.7	2.25	0.5
3	27.0	26.8	-	-	-	37.1	33.5	33.5	2.5	0.5
4	27.2	27.2	-	-	-	37.4	34.3	34.3	1.1	0.2
5	25.6	25.4	-	-	-	38.5	34.1	34.1	2.0	0.5
6	22.4	22.2	-	-	-	40.3	35.3	35.3	2.1	0.5
7	21.9	21.8	0.10	-	-	41.2	34.8	34.8	2.1	0.3
8	20.2	20.0	0.30	-	-	41.1	35.0	35.0	3.5	0.5
9	18.7	18.4	0.20	-	1.3	39.9	36.3	36.3	5.1	0.7
10	18.9	18.8	0.60	1.6	1.8	38.3	38.3	36.7	4.0	0.4
11	21.0	20.8	1.10	1.8	8.0	33.0	39.7	37.9	5.3	0.5
12	30.2	30.2	5.4	1.7	58.4	33.5	27.7	26.0	3.2	0.1
13	31.1	31.0	6.2	1.9	70.5	31.7	28.6	26.7	2.5	0.4
14	31.5	31.4	6.6	2.6	73.0	34.2	25.4	22.8	2.4	0.38
15	31.1	31.0	6.4	2.5	76.3	34.2	26.2	24.0	2.4	0.31

TABLE X

MODEL IV

Interpretation of Silicon and Oxygen (O_{Si})

Cut	%Si	%O _{Si}	D _O	Calculation I		Calculation II	
				%SiO	%SiO ₂	%SiOSi	%SiO ₂
1	35.7	37.1	0.23	7.0	64.8	3.6	68.4
2	36.0	34.4	0.34	15.0	57.6	7.9	64.8
3	37.1	33.5	0.55	24.2	46.8	13.0	58.2
4	37.4	34.3	0.54	23.8	48.0	13.0	58.6
5	38.5	34.1	0.60	26.4	46.8	14.2	58.8
6	40.3	35.3	0.67	29.5	46.2	15.8	60.0
7	41.2	34.8	0.76	33.4	42.6	18.0	58.2
8	41.1	35.0	0.75	33.0	43.2	18.0	58.2
9	39.9	36.3	0.59	26.0	50.4	14.4	61.8
10	38.3	36.7	0.44	19.4	55.8	10.8	64.2
11	33.0	37.9	0	-	70.9	-	70.9
12	33.5	26.0	0.76	34.3	25.2	18.7	40.8
13	31.7	26.7	0.59	26.0	32.4	14.4	43.8
14	34.2	22.8	1.01	44.4	12.6	25.2	31.2
15	34.2	24.0	0.94	41.4	16.8	22.3	36.0

$$D_O = \frac{\%Si}{28} \times 2 - \frac{\%O_{Si}}{16}$$

$$\text{calc. I} \begin{cases} \%SiO = D_O \times 44 \\ \%SiO_2 = \left(\frac{\%Si}{28} - D_O \right) \times 60 \end{cases}$$

$$\text{calc. II} \begin{cases} \%SiOSi = \frac{D_O}{3} \times 72 \\ \%SiO_2 = \left(\frac{\%Si}{28} - \frac{2D_O}{3} \right) \times 60 \end{cases}$$

TABLE XI

MODEL IV

Analysis of Series I

Cut	Volatile *	(HF) ₁ %W.L.	Calc.as Si	%C	Table IX %Free C	D Atom %	D _O Tbl. X	% Silicon (HF) ₂ (HF) ₁ +(HF) ₂		Tbl. IX	%SiO ₂ Tbl. X Calc. II	D C	D _{Si}
1	i.s.	i.s.	i.s.	i.s.	25.7	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.	i.s.
2	-	59.8	27.9	26.1	26.1	0.74	0.69	11.2	39.1	37.2	64.8	-2.9	+1.9
3	-	60.9	28.4	25.4	26.8	0.42	0.56	8.8	37.2	37.1	58.2	-1.4	-
4	-	59.3	27.7	27.2	27.2	0.50	0.54	9.3	37.0	37.4	58.6	-	-0.4
5	-	58.7	27.4	25.9	25.4	0.43	0.60	9.0	36.4	38.5	58.9	+0.5	-2.1
6	-	60.0	28.0	22.2	22.2	0.30	0.67	9.9	37.9	40.3	60.0	-	-2.4
7	-	51.4	24.0	20.1	21.8	0.45	0.76	15.2	39.2	41.2	58.2	-1.7	-2.0
8	-	48.7	22.7	18.5	20.0	0.25	0.75	15.8	38.5	41.1	58.2	-1.5	-2.6
9	-	52.1	24.3	17.1	18.4	0.13	0.59	14.0	38.3	39.9	61.8	-1.3	-1.6
10	-	58.7	27.4	17.4	18.8	0	0.44	8.0	35.4	38.3	64.2	-1.4	-2.9

*i.s. insufficient sample

The following cuts, 11 - 15, contain large volatile fractions. Therefore this table is not continued.

TABLE XII

MODEL IV

Analysis of Oxygen

Cut	%Volatile	%Free Oxygen	HF Wt. loss	H.F. W.L. Table XI
1				
2				
3	-	-	61.0	60.9
4	-	-	57.2	59.3
5	-	-	55.6	58.7
6	-	-	55.6	60.0
7	-	-	49.3	51.4
8	-	-	47.1	48.7
9	1.3	-	48.7	52.1
10	1.8	1.6	54.9	58.7
11	8.0	1.8	62.0	66.5
12	58.4	1.7		
13	70.5	1.9		
14	73.0	2.6		
15	76.3	2.5		

TABLE XIII

MODEL IV

Calculation of volatile fractions in cuts 11 - 15.

Cut 11

<u>Totals</u>		<u>Non-volatile</u>	<u>Volatile</u>	<u>Atom %</u>
%C	20.9	18.1	2.8	
%H	1.1	—	1.1	
%Free O	1.8	—	1.8	
%Si	33.0	31.4	1.6	0.058
%O _{Si}	37.9	35.8	0.9	0.058
Res.	5.3	6.7	—	
Total		92.0	8.2	
Found-volatile			8.0	

Cut 12

<u>Totals</u>		<u>Non-volatile</u>	<u>Volatile</u>	<u>Atom %</u>
%C	30.2	7.8	22.4	
%H	5.4	—	5.4	
%Free O	1.7	—	1.7	
%Si	33.5	14.5	19.0	0.68
%O _{Si}	26.0	16.3	9.7	0.6
Res.	3.2	3.0	—	
			58.2	

Cut 13

<u>Totals</u>		<u>Non-volatile</u>	<u>Volatile</u>	<u>Atom %</u>
%C	31.0	9.1	21.9	
%H	6.2	—	6.2	
%Free O	1.9	—	1.9	
%Si	31.7	9.2	22.5	0.8
%O _{Si}	26.7	10.6	16.1	1.0
Res.	2.5	1.4	—	
Total			68.6	
Found volatile			70.5	

Cut 14

<u>Totals</u>		<u>Non-volatile</u>	<u>Volatile</u>	<u>Atom %</u>
%C	31.4	5.0	26.4	
%H	6.6	—	6.6	
%Free O	2.6	—	2.6	
%Si	34.2	9.8	24.4	0.87
%O _{Si}	22.8	11.2	11.6	0.73
Res.	2.4	1	—	
Total			71.6	
Found Volatile			73.0	

TABLE XIII (continued)

Model IV

Cut 15

<u>Totals</u>		<u>Non-volatile</u>	<u>Volatile</u>	<u>Atom %</u>
%C	30.9	4.4	26.5	
%H	6.2	-	6.2	
%Free O	2.5	-	2.5	
%Si	34.2	7.9	26.3	0.94
%O _{Si}	24.0	9.1	14.9	0.93
Res.	2.2	2.2	—	
Total			76.4	
Found volatile			76.3	

TABLE XIV'

Com b u s t i o n I			Do ₁ Atom%	MODEL IV			-Analyses Series II (HF) ₁			C ₁ C ₂	%C Table IX	Do ₁ Do ₂	Do Table X	Si ₁ + Si ₂	Si Table IX	
Cut(%C) ₁	%H	%Res		(HF) ₁	%W.L. Calc.Si	Combust ₁ II(%C) ₂	Atom%	W.L. as Si ₁ calc.	%Res							
1	21.2	-	78.4	0	62.7	29.3	4.5	0.28	13.7	6.4	1.5	25.7	0.28	0.23	35.7	35.7
2	20.0	-	79.5	0	57.0	26.6	5.7	0.12	17.3	8.0	1.5	25.7	0.12	0.34	34.6	36.0
3	19.8	-	81.8	0.10	63.9	29.8	6.0	0.38	16.3	7.6	1.7	25.8	0.48	0.57	37.4	37.1
4	21.1	-	80.8	0.12	61.8	28.8	6.3	0.40	17.7	8.2	1.5	27.4	0.52	0.54	37.0	37.4
5	18.5	-	83.5	0.13	61.8	28.8	6.6	0.38	19.0	8.9	2.1	25.1	0.51	0.60	37.7	38.5
6	16.3	-	85.8	0.14	66.1	30.9	6.5	0.25	15.2	7.1	1.9	22.8	0.39	0.67	38.0	40.3
7	15.0	0.1	89.2	0.28	65.2	30.1	6.0	0.22	19.0	8.8	3.1	21.0	0.50	0.75	38.9	41.2
8	15.7	0.5	91.8	0.50	73.5	34.3	3.5	0	11.7	5.4	1.2	19.2	0.50	0.75	39.7	41.1
9*	16.3	0.2	90.5	0.44	78.5	36.6	2.5	0.31	2.9	1.3	2.0	18.8	0.75	0.59	37.9	39.9
10*	18.2	0.6	85.0	0.34	74.0	34.6	0.5	-	9.6*	4.5	1.3	18.7	0.34	0.44	39.1	38.8
11*	20.9	1.1	75.5	0	75.5	30.0	****	-	6.7**	3.1	5.0***	20.9	0	0	33.1	33.0

**** these cuts contain small volatile fractions**

**** 3% volatile**

*** weight loss during combustion 7.2%, W.L. (HF), was corrected

The table was discontinued

TABLE XV

MODEL IV

Analysis of Residues

Determination of Silicon carbide and metallic impurities

Cut	Totals	% Residue		Series O	%Si (SiC)	Calc.as SiC	% Na	% Fe	%Al
1	1.5-	i.s.*	1.5	i.s.	0.6	0.8	0.11	0.2	0.1
2	2.2	1.1	1.5	i.s.	0.5	0.7	0.1	0.03	0.05
3	2.5	1.5	1.7	1.2	0.5	0.6	0.1	0.08	0.15
4	1.1	1.5	1.5	1.6	0.2	0.25	0.1	0.06	0.06
5	2.0	3.0	2.1	2.2	0.5	0.6	0.2	0.02	0.16
6	1.9	1.4	2.1	2.2	0.5	0.6	0.4	0.06	0.07
7	2.1	3.0	3.1	3.3	0.3	0.4	0.53	0.08	0.08
8	3.5	2.9	1.2	2.9	0.5	0.6	0.66	0.02	0.2
9	5.1	2.9	2.0	5.5	0.7	0.85	1.13	0.02	0.04
10	4.0	3.5	1.3	7.6	0.4	0.5	1.20	0.08	0.10
11	5.3	4.0	0	6.0	0.5	0.6	1.13	0.02	0.04
12	3.2	3.0	0	1.0	0.1	0.1	0.32	0.01	0.01
13	2.5	3.0	0	1.0	0.4	0.5	0.13	0.10	0.05
14	2.4	2.0	0	0.6	0.3	0.4	0.12	0.02	0.03
15	2.4	2.5	0	2.2	0.3	0.4	0.55	0.02	0.05

* - insufficient sample

TABLE XVI

MODEL IV

"Free Carbon" by combustion at 900°C (incomplete recovery)

Cut	%C
1	21.2
2	20.0
3	19.8
4	21.1
5	18.5
6	16.3
7	15.0
8	15.7
9	16.3
10	18.2
11	20.9
12	27.6
13	28.6
14	29.6
15	29.2

TABLE XVII

MODEL VI

TOTALS

Cut	%Total C	%free C	%H	%free O	Volatile under N ₂	%Si	Total % O	%O _{Si}	% Res.	%SiSiC
1	18.6	18.2	0	0	0	38.2	41.9	40.9	1.4	0.9
2	13.5	13.3	0	0	0	41.4	44.1	44.1	1.0	0.5
3	24.7	24.1	0	0	0	38.0	35.3	35.3	2.1	1.3
4	28.0	27.4	0	0	0	36.6	33.3	33.3	2.2	1.5
5	25.9	25.7	0	0	0	37.2	34.9	34.9	2.1	0.5
6	22.2	21.7	0	0	0	39.7	35.8	35.8	2.4	1.1
7	20.0	19.8	0	0	0	40.8	37.3	37.3	1.9	0.4
8	18.0	17.8	0	0	0.5	40.4	38.6	38.6	3.2	0.5
9	18.0	17.6	0	0	1.4	39.1	39.1	39.1	4.0	1.0
10	19.9	19.8	0.3	0.6	2.9	35.2	40.4	39.8	4.4	0.6
11	26.1	25.8	2.2	0	22.9	31.2	36.9	36.9	3.8	0.8
12	27.4	27.3	5.5	1.1	52.0	33.2	30.5	29.4	3.6	0.3
13	29.1	29.0	6.0	0.8	70.2	34.5	28.8	28.0	1.7	0.2
14	31.3	31.2	6.4	1.5	74.0	32.3	28.3	26.8	1.8	0.2
15	30.7	30.5	6.4	2.4	76.5	34.1	26.7	24.3	2.2	0.4

TABLE XVIII

MODEL VI

Calculation of D_O Attempts of Interpretation of Silicon and Oxygen (O_{Si})

Cut	%Si	%O _{Si}	D_O atom %	CALCULATED AS			
				Calculation I %SiO	Calculation I %SiO ₂	Calculation II %SiOSi	Calculation II %SiO ₂
1	38.2	41.9	0.11	4.8	75.0	2.9	77.4
2	41.4	44.1	0.20	14.4	76.8	5.0	80.4
3	38.0	35.3	0.51	22.4	51.0	12.2	61.2
4	36.6	33.3	0.54	23.8	46.2	13.0	57.0
5	37.2	34.9	0.48	21.1	51.0	11.5	60.6
6	39.7	35.8	0.60	26.4	49.2	14.4	61.2
7	40.8	37.3	0.59	26.0	52.2	14.4	63.6
8	40.4	38.6	0.47	20.7	58.2	11.5	67.2
9	39.1	39.1	0.36	15.8	62.4	8.6	69.6
10	35.2	39.8	0	0	75.0	0	75.0
11	31.2	34.7	0.05	2.2	63.6	1.4	64.2
12	33.2	29.4	0.54	23.8	28.6	13.0	49.2
13	34.5	28.0	0.71	31.2	31.2	17.3	45.0
14	32.3	26.8	0.64	28.2	31.6	15.1	43.8
15	34.1	24.3	0.92	40.5	13.2	22.3	36.0

TABLE XIX

MODEL VI

Analyses of Series I

Cut	% Volatile	% Wt. (HF), % Si	% C	% C Table XVII	DO atom %	DO Table XVIII	(HF) ₂	% Silicon (HF) ₂ + (HF) ₁	% Silicon Table XVII	% SiO ₂ Table XVIII Calc. II	D _C	D _{Si}
1	0	73.9	19.3	18.2	0.12	0.11	3.8	38.3	38.2	77.4	+1.1	+0.1
2	0	73.2	13.6	13.5	0.03	0.20	5.9	40.1	41.4	80.4	+0.3	-1.3
3	0	65.3	22.9	24.1	0.46	0.51	8.5	39.0	38.0	61.2	-1.2	+1.0
4	0	58.8	26.6	27.4	0.60	0.54	9.8	37.2	36.6	57.0	-0.8	+0.6
5	0	59.4	25.5	25.7	0.41	0.48	9.4	37.1	37.2	60.6	-0.2	-0.1
6	0	58.6	21.8	21.7	0.35	0.60	9.6	36.9	39.7	61.2	+0.1	-2.8
7	0	51.5	19.4	19.8	0.40	0.59	16.3	40.3	40.8	63.6	-0.4	-0.5
8	0.5	42.7	19.3	17.8	0.42	0.47	19.3	39.3	40.4	67.2	+1.5	-1.1
9	1.4	48.9	18.1	17.6	0.19	0.36	18.1	40.9	39.1	69.6	+0.5	+1.8
10	2.9	60.9	18.8	19.8	0	0	6.2	34.6	35.2	75.0	-1.0	-0.6
11	22.9											

This table is discontinued. The large volatile fraction results in incomplete recoveries. The volatile fractions are discussed elsewhere.

TABLE XX

MODEL VI

Analysis of Oxygen

Cut	% volatile	% free oxygen	%HF W.L.*	HF W.L. Table XIX
1	0	0	0	73.9
2	0	0	0	73.2
3	0	0	62.2	65.3
4	0	0	60.8	58.8
5	0	0	57.7	59.4
6	0	0	51.0	58.6
7	0	0	46.1	51.5
8	0.5	0	40.1	42.7
9	1.4	0	46.7	48.9
10	2.9	0.6	57.7	60.9
11	22.9	0	51.8	73.3
12	52.0	1.1	33.0	78.2
13	70.2	0.8	20.0	85.2
14	74.0	1.5	17.4	85.2
15	76.5	2.4	15.9	32.7

* - W.L. = weight loss

TABLE XXI

MODEL VI

Analysis of Series O

Calculation of the volatile fraction in Cut 10,11,12,13,14,15

Cut 10	Total	% non volatile	% volatile	atom %
%C	19.7	17.2	2.5	
%H	0.3	0.0	0.3	
% free O	0.6	0.0	0.6	
%Si	35.2	34.2	1.0	0.04
%O _{Si}	39.8	37.5	2.3	0.08
Residue	4.4	4.4	<u>0.0</u>	
Total			6.7	
found			2.9	
Cut 11	Total	% non volatile	% volatile	atom %
%C	25.9	14.6	11.3	
%H	2.2	0.0	2.2	
%free O	0.0	0.0	0.0	
%Si	31.2	27.8	3.4	0.12
%O _{Si}	36.9	31.7	5.2	0.32
Residue	3.8	3.8	<u>0.0</u>	
Total			22.1	
found			22.9	
Cut 12	Total	% non volatile	% volatile	atom %
%C	27.2	9.3	17.9	
%H	5.5	0.0	5.5	
% free O	1.1	0.0	1.1	
% Si	33.2	17.6	15.6	0.56
%O _{Si}	29.4	20.2	9.2	0.58
Residue	3.6	3.6	<u>0.0</u>	
Total			49.3	
found			52.0	

TABLE XXI (continued)

Cut 13	Total	%non-volatile	%volatile	atom %
%C	29.0	5.9	23.1	
%H	6.0	0.0	6.0	
%free O	0.8	0.0	0.8	
%Si	34.5	10.0	24.5	0.9
%O _{Si}	28.0	11.5	16.5	1.0
Residue	1.7	1.7	0.0	
Total			<u>70.9</u>	
found			70.2	
Cut 14	Total	%non-volatile	% volatile	atom %
%C	31.2	5.3	25.9	
%H	6.4	0.0	6.4	
% free O	1.5	0.0	1.5	
%Si	32.3	8.1	24.2	0.9
%O _{Si}	26.8	9.3	17.5	1.1
Residue	1.8	1.8	0.0	
Total			<u>75.5</u>	
found			74.0	
Cut 15	Total	%non-volatile	% volatile	atom %
%C	30.6	4.6	26.0	
%H	6.4	0.0	6.4	
%free O	2.4	0.0	2.4	
%Si	34.1	8.1	26.0	0.9
%O _{Si}	24.3	9.3	15.0	0.9
Residue	2.2	2.2	0.0	
Total			<u>75.8</u>	
found			76.4	

TABLE XXII

Comparison of carbon content of

a.) Non volatile fraction, Series O

b.) Series I

Cut	Series I %C	Series O % C
10	18.8	17.2
11	14.8	14.6
12	9.7	9.3
13	6.4	5.9
14	5.9	5.3
15	5.0	4.6

TABLE XXII

Comparison of carbon content of

a.) Non volatile fraction, Series O

b.) Series I

Cut	Series I %C	Series O % C
10	18.8	17.2
11	14.8	14.6
12	9.7	9.3
13	6.4	5.9
14	5.9	5.3
15	5.0	4.6

TABLE XXIII

MODEL VI

Analyses of Series II																		
Cut	Combustion I		Do_1 atom %	$(\text{HF})_1$		Combustion II		$(\text{HF})_2$		C_1 +	C_2	%C Table XVII	Do_1 +	Do_2	Do Table XVII	Si_1 +	Si_2	Si Table XVII
	$(\% \text{C})_1$	%H %Res.		%W.L.	calc. as Si	$(\% \text{C})_2$	Do_2 atom %	%W.L.	calc. as Si % Res.									
1	14.9	0	0.12	75.4	35.2	3.1	0.15	8.7	4.1	18.0	18.2	0.27	0.11	39.3	38.2			
2	10.8	0	0.04	81.3	38.0	2.9	0.15	7.3	3.4	13.7	13.3	0.19	0.20	41.4	41.4			
3	17.4	0	0.04	65.6	30.6	6.6	0.42	16.3	7.6	24.0	24.1	0.46	0.51	38.2	38.0			
4	19.9	0	0.06	62.6	29.2	7.3	0.44	19.0	8.8	27.2	27.4	0.50	0.54	38.0	36.6			
5	17.8	0	0.07	61.9	28.9	7.8	0.38	17.8	8.3	25.6	25.7	0.45	0.48	37.2	37.2			
6	15.8	0	0.12	62.2	29.0	7.2	0.28	18.3	8.5	23.0	21.7	0.40	0.60	37.5	39.7			
7	13.2	0	0.20	53.2	24.8	5.2	0.25	32.1	15.1	18.4	19.8	0.45	0.59	39.9	40.8			
8*	13.3	0	0.37	64.6	30.1	5.6	0.04	19.7	9.2	18.9	17.8	0.41	0.47	39.3	40.4			
9*	16.9	0	0.47	79.9	37.3	1.6	0	5.0	2.3	18.5	17.6	0.47	0.36	39.6	39.1			
10*	19.2	0.3	0.13	71.7	33.5	0.1	0	6.7	3.1	19.3	19.8	0.13	0	36.6	35.2			

* - The table is discontinued because volatile fractions produce incomplete recoveries.

The cuts 12-15 are given in Tables XX, XXI and XXII.

TABLE XXIV

MODEL VI

Analyses of Residues
Determination of Silicon Carbide and Metallic Impurities

Cut	Totals	% Residue Series I	Series II	Series O	%Si (SiC)	Calc.as SiC	%Na	%Fe	%Al
1	1.4	0.9	2.0	i.s.*	0.9	1.3	0.1	0.02	0.04
2	1.0	1.1	0.9	i.s.*	0.5	0.7	0.1	0.02	0.03
3	2.1	0.8	1.6	2.8	1.3	1.9	0.1	0.03	0.07
4	2.2	1.3	1.7	2.7	1.5	2.1	0.2	0.06	0.02
5	2.1	1.5	1.8	2.1	0.5	0.7	0.2	0.03	0.05
6	2.4	3.5	3.0	2.3	1.1	1.6	0.2	0.06	0.08
7	1.9	1.1	2.1	2.0	0.4	0.6	0.25	0.05	0
8	3.2	2.2	3.3	3.5	0.5	0.7	0.6	0.05	0.07
9	4.0	5.0	4.1	4.3	1.0	1.5	1.1	0.08	0.12
10	4.4	4.6	4.6	6.8	0.6	0.9	1.4	0.04	0.06
11	3.8	4.0	3.5	3.1	0.8	1.2	0.4	0.05	0.09
12	3.6	3.1	2.9	1.6	0.3	0.4	0.6	0.03	0.05
13	1.7	1.2	1.9	0.8	0.2	0.3	0.2	0.02	0.05
14	1.8	1.5	1.6	0.8	0.2	0.3	0.2	0.02	0.01
15	2.2	1.5	1.5	1.2	0.4	0.6	0.4	0.03	0.09

* - insufficient sample

TABLE XXV

MODEL VI

"Free Carbon" by combustion at 900°C (incomplete recovery)

Cut	% C
1	14.9
2	10.8
3	17.4
4	19.9
5	17.8
6	15.8
7	13.2
8	13.3
9	16.9
10	19.2
11	22.8
12	27.8
13	28.4
14	29.1
15	29.6

TABLE XXVI

MODEL VII

Cut	Totals									
	%Total C	%Free C	%H	%free O	Volatile under N ₂	%Si	% O total	%O _{Si}	% residue	% Si ₂ SiC
1	13.3	i.s.	0	0	0	36.6	43.2	43.2	6.9	i.s.
2	17.6	17.4	—	—	—	40.4	39.1	39.1	3.0	0.5
3	20.3	20.3	—	—	1.0	40.6	38.1	38.1	1.0	0.15
4	29.3	29.2	5.8	0.5	67.6	33.2	29.3	28.8	2.4	0.3
5 (virgin)	31.1	31.0	6.1	2.2	76.5	33.6	27.4	25.2	1.5	0.3

Calculation of D_O and attempts of interpretation of the Si/O_{Si} ratio

Cut	CALCULATED					AS	
	%Si	%O _{Si}	D _O atom %	Calculation I %SiO	Calculation I %SiO ₂	Calculation II %SiO _{Si}	Calculation II %SiO ₂
1	36.6	43.2	0	0	79.8	0	79.8
2	40.4	39.1	0.44	19.4	60.0	10.8	68.4
3	40.6	38.1	0.50	22.0	57.0	11.5	67.8
4	33.2	28.8	0.58	25.5	36.6	13.7	48.6
5 (virgin)	33.6	25.2	0.83	36.5	22.2	20.2	38.4

TABLE XXVII

MODEL VII

Series I

Cut	%volatile	(HF) ₁ %W.L. calc.as Si	%C Table XXVI	%C Table XXVI	Do atom % Table XXVI	(HF) ₂ (HF)+(HF) ₂ Table XXVI	% Silicon (HF) ₂ Table XXVI	%SiO ₂ Table XXVI calc. II	D _C	D _{Si}
2	0	68.9	32.2	18.6	17.4	0.30	0.44	68.4	+1.2	-1.7
3	1.0	64.5	30.1	20.6	20.3	0.20	0.50	67.8	+0.3	-2.8
4*										

* This table is discontinued due to volatile fractions

Series II

Series II																
Cut	Combustion I				(HF) ₁		Combustion II		(HF) ₂		C ₁ + %Residue C ₂		%C	Do ₁ + Do ₂	(Si) ₁ , (Si) ₂	Si Table XXVI
	%C ₁	%H	%Residue	Do ₁ , atom %	%W.L.	calc. as Si	%C ₂	Do ₂ , atom %	%W.L.	calc. as Si	%Residue	C ₂	Table XXVI			
1	8.6	0	90.2	-0.08	63.7	30.0	4.7	-0.06	14.1	6.6	6.9	13.3	i.s.	0	36.6	i.s.
2	14.3	0	86.7	0.06	71.8	33.5	4.4	0	9.0	4.1	0.9	18.7	17.4	0.06	37.6	40.4
3	14.3	0	86.8	0.06	65.3	30.5	6.7	0.31	9.0	4.7	2.2	21.0	20.3	0.37	35.2	33.2

Series O

Cut	%volatile	%free O	HF weight loss series I	HF weight loss series I
1	i.s.	i.s.	i.s.	i.s.
2	1.0	1.0	68.9	68.9
3	1.0	0	64.5	64.5
4	67.6	0.5	47.6	47.6
5	76.5	2.2	43.3	43.3

* i.s. = insufficient sample

TABLE XXVIII

MODEL VII

Analysis of Residues

Cut	Residue	%Si _{SiC}	Calc. as SiC	%Na	%Fe	%Al	
1	6.9	i.s.*	i.s.	i.s.	0.05	0.1	
2	3.0	0.5	0.7	0.7	0.08	0.06	
3	1.0	0.15	0.2	0.2	0.3	0.25	
4	2.4	0.3	0.4	0.35	0.03	0.05	
5	1.5	0.3	0.4	0.35	0.03	0.06	

* = insufficient sample

PART III

TABLE I

Char Density as a Function of Depth for Model 2

Char Depth in.	Layer No.	Distance From Top Surface, in.	Thickness of Layer, in.	Volume, cc	Weight, g	Density g/cc
0.36	1	0.017	0.017	0.0280 ^a	0.0170	0.608
	2	.043	.026	.1668 ^b	.0969	.581
	3	.074	.031	.4145 ^b	.2079	.502
	4	.099	.025	.7256 ^b	.2417	.333
	5	.128	.029	.8162 ^c	.2774	.340
	6	.155	.027	.7599 ^c	.2840	.374
	7	.186	.031	.8724 ^c	.2774	.318
	8	.216	.030	.8443 ^c	.2720	.322
	9	.243	.027	.7599 ^c	.2534	.333
	10	.275	.032	.9005 ^c	.2635	.293
	11	.302	.027	.7598 ^c	.1343	.177
	12	.327	.025	.7019 ^c	.1476	.210
	13	.356	.029	.7703 ^c	.1887	.245
	14	.374	.018	.3327 ^d	.1014	.305
	15	.824	.025	.7239	.4312	.596

$$^aV = \frac{\pi h_1}{6} (3r_1^2 + h_1^2)$$

$$^bV = \frac{\pi}{6} h_2 (3r_1^2 + 3r_2^2 + h_2^2)$$

$$^cV = D^2 H - (\text{approx. } .02\text{cc})$$

$$^dV = D^2 H - (.07\text{cc})$$

PART III

TABLE II

Char Density as a Function of Depth for Model 4

Char Depth in.	Layer No.	Distance From Top Surface, in.	Thickness of Layer, in.	Volume, cc	Weight, g	Density g/cc
.28	1	0.021	0.021	0.0700 ^a	0.0390	0.557
	2	.043	.022	.2228 ^b	.1343	.603
	3	.064	.021	.6081	.1935	.318
	4	.085	.021	.6081	.2715	.446
	5	.109	.024	.6950	.3310	.476
	6	.132	.023	.6660	.1904	.286
	7	.152	.020	.5792	.2541	.439
	8	.174	.022	.6371	.2254	.354
	9	.198	.024	.6950	.1877	.270
	10	.219	.021	.6081	.1865	.307
	11	.243	.024	.6950	.1095	.158
	12	.267	.024	.6950	.2421	.348
	13	.291	.024	.6950	.1327	.191
	14	.315	.024	.6950	.1850	.266
	15	.803	.036	1.042	.6198	.594

$$^a V = \frac{\pi}{6} h_1 (3r_1^2 + h_1^2)$$

$$^b V = \frac{\pi}{6} h_2 (3r_1^2 + 3r_2^2 + h_2^2)$$

PART III

TABLE III

Char Density as a Function of Depth for Model 6

Char Depth inches	Layer No.	Distance From Top Surface, in.	Thickness of Layer, in.	Volume, cc	Weight, g	Density g/cc
.36	1	0.020	0.020	0.2896	0.1220	0.421
	2	.043	.023	.3330	.1753	.526
	3	.064	.021	.6081	.2096	.345
	4	.084	.020	.5792	.2350	.406
	5	.106	.022	.6370	.2586	.406
	6	.128	.022	.6371	.2196	.345
	7	.149	.021	.6081	.2281	.375
	8	.173	.024	.6950	.2019	.291
	9	.196	.023	.6660 ^c	.1855	.278
	10	.237	.041	.9776 ^c	.2636	.270
	11	.260	.023	.4995	.1080	.216
	12	.283	.023	.4440	.1059	.238
	13	.302	.019	.4814	.1783	.370
	14	.322	.020	.5792	.2094	.362
	15	.832	.037	1.071	.6411	.598

$$c_V = D^2 h - (.14cc)$$

TABLE IV

Char Depth inches	Char Density as a Function of Depth for Model 7				Weight, g	Density g/cc
	Layer No.	Distance from Top Surface, in	Thickness of Layer, in	Volume, cc		
.48	1	0.027	0.027	0.01885 ^a	0.0089	0.472
	2	.067	.040	.1305 ^b	.0378	.290
	3	.080	.013	.1903 ^b	.1095	.575
	4	.398	.044	1.274	.3563	.280
	5	virgin	.042	1.216	.7173	.590

$$a_V = \frac{\pi}{6} h_1 (3r_1^2 + h_1^2)$$

$$b_V = \frac{\pi}{6} h_2 (3r_1^2 + 3r_2^2 + h_2^2)$$