

ANALYSIS OF STONE FROM THE SCOTTISH HILL FORT CRAIG PHADRIG

INTRODUCTION

Craig Phadrig is one of the most famous hill forts to be found in Scotland. It lies two (2) miles west of Inverness at a height of 550 feet on a hilltop. The hilltop is covered with scrub, trees and other vegetation. The fort overlooks the narrows at the east end of the Beaully Firth from the south west. It has been described in several places such as in "A Guide to Prehistoric Scotland", by Richard Feacham (B.T. Batsford Ltd., London 1963). A more detailed description is to be found in The Inverness Scientific Society, Archaeological Notes, Vol. 8, pp. 90-93, 1912-13.

The hill-forts of Scotland according to Feacham were in their simplest form a palisade or stockade constructed of a heavy timber fence set firmly in a trench. A higher step in the development was a simple stone wall, the inner and outer face of which was built of carefully laid blocks and the space between was filled by rubble or stone. Walls packed with stones were often built around a shelter of stout timbers. Feacham quotes Williams, who about two-hundred years ago wrote: "Immediately on the inside of this wall there are ruins of vitrified buildings". This aforementioned vitrification introduces the fact that a considerable number of wooden constructions were set on fire by accident or purpose. This generated considerable heat and when conditions were favorable the stone and materials would melt or sinter. The silicate rock which had been exposed to this intense heat was in earlier times considered to be of volcanic origin and thus confused with lava.

The walls of Craig Phadrig are to a large extent vitrified and much of the walls are sticking to the rock of the hill indicating that at least part of the wall had been in fluid state and the material in physical properties such as thermal expansion similar to the rock. A substantial amount of heat energy must have been generated because the wall is in most places about nine feet wide and of considerable height.

A piece (~ 300 g) of the vitrified wall material from the hill fort, Craig Phadrig, has been made the subject of a chemical and physical investigation for the purpose of reaching an understanding of the materials and methods which were utilized in the construction of the hill fort.

Composed of and its origin and thermal history it is necessary to perform chemical analysis, study it microscopically, and correlate these data with known phase equilibria. A research program was therefore initiated. This program was to encompass the following:

1. Microscopy
 - (a) Optical microscopy
 - (b) Electron microscopy
2. X-Ray diffraction to determine mineral type and degree of vitrification.
3. X-Ray fluorescence for chemical analysis
4. Differential thermal analysis

The data obtained were then to be discussed in the light of known melt behavior of minerals, i.e. in their relationship to phase equilibria.

DESCRIPTION OF THE STONE

The stone, at first inspection, appears to be a dark piece of material which evidently once had been subjected to intense heat. The stone could, at a first glance, very easily be confused with volcanic matter because of the many open blisters or bubbles. The inside of some of the bubbles are covered with a shiny, glassy substance. The dark material is here and there broken by lighter colored areas indicating sub-surface extensions.

For a better understanding of the material the stone is composed of and its origin and thermal history it is necessary to perform chemical analysis, study it microscopically and correlate these data with known phase equilibria. A research program was therefore initiated. This program was to encompass the following:

1. Microscopy
 - (a) Optical microscopy
 - (b) Electron microscopy
2. X-Ray diffraction to determine mineral type and degree of vitrification.
3. X-Ray fluorescence for chemical analysis
4. Differential thermal analysis

The data obtained were then to be discussed in the light of known melt behavior of minerals, i.e. in their relationship to phase equilibria.

EXPERIMENTAL WORK AND RESULTS

1. Microscopy:

The first step in the investigation was to study the stone microscopically. For that reason it was important to have a representative cross section because the rough surface alone would not tell what the whole piece was made of. Therefore a slice, 47 X 70 X 3 mm, was cut out from the stone with a diamond saw. It should be pointed out that the material was very easy to cut and did not have any tendency to chip or break up under the pressure of the saw. An enlargement of a color photograph of each side of the piece is seen in Figures 1 and 2. The first one is against a white background so that the extent of some of the bigger bubbles can be realized. The other picture is against a black background which improves some of the contrast. Figure 3 shows a further enlargement of an area from Figure 2. The photographs have a slightly more yellowish tinge than the real stone. The pictures reveal the presence of at least three different materials distributed over five main areas. Figure 4 shows, for simplicity, the outlines of the piece with the different areas indicated in Roman numerals. Arabian numerals indicate areas where electron microscopy has been performed. The whole piece was also carefully studied with optical microscopy, both high and low magnification. The inside of the bubbles were best studied with a stereomicroscope at relatively low magnification (30X). The result of higher magnification revealed only more tiny bubbles without significantly adding additional information. The essential points of interest are to be found in Figure 1-3. Below are discussed the findings in the different areas complemented with the microscopic data.

Area I - The upper white portion appears to consist of three phases; a crystalline white material interspaced by a darker material and the whole mass penetrated by a glassy matrix. The darker material seems to be of the same type as the one found in Areas II and IV. The larger bubbles are located in the dark section. The white portion is full of small bubbles or so called seeds. The insides of the bubbles are smooth and shiny and without any deposit. Evidently the bubbles, which are round, originate in the vitreous mass.

Area II - This dark portion is penetrated by a great number of bubbles of all sizes. Here and there the dark material is mottled by dots of white material. The inside of the bubbles are shiny but not smooth and show flakiness. Some of the bubbles seem to have united and formed larger entities. This must have occurred while the mass had been soft and during cooling with increasing viscosity. It can be concluded from the preservation of the shape. A difference in vapor pressure between the bubbles, which had to be very close, must have caused the collapse of the parting wall.

Area III - The yellow-green segment, which cuts across the piece, is more devitrified than Area I but more glassy than Area II. The area is heavily streaked by the dark material. Numerous small distorted and coalesced bubbles can be found throughout. The flattened form of the bubbles in comparison with the rest points towards the fact that this part did completely solidify later than any other part. Inside a number of bubbles a white material can be seen in the form of fine fibers and particle agglomeration. The fiber must have been formed from a molten glass.

Area IV - This lower part of the black mass is more homogeneous than the upper black portion. Numerous round bubbles and coalesced bubble formations can be seen. A number of partly devitrified glass fibers can be observed adjacent to and inside the bubbles.

Area V - This area is similar to Area I but shows a more reddish color indicating higher iron content. The inside of a number of bubbles rust color can be seen.

Electron Microscopy:

There is of certain interest to study the boundaries of fusion between the different areas. Optical microscopy is not capable to resolve well details. Electron microscopy is much more powerful. A two-stage replica technique was utilized for this purpose. Figures 5-8 show part of the boundaries at the points indicated in Figure 4.

Point 1 is situated between Areas III and IV (Figure 5). The magnification of this electron micrograph as well as all subsequent micrographs is 6400 times. The boundary can be seen. A number of small bubbles or cavities are noted by the black spots. They belong to Area IV. The two areas are completely fused together. The texture, in particular of Area III, is surprisingly smooth and homogeneous.

Point 2, between Areas II and III, shows the boundary cutting across from top to bottom of Figure 6. The part with cavities belongs to Area II. The inter-diffusion zone is quite wide. Numerous crackings can be noted indicating earlier presence of strain between the two materials.

Point 3, between Areas III and V, (Figure 7) shows a rather wide landscape with big cracks. The material is not very homogeneous and phase separation is clearly visible (white dots).

Point 4, between Areas I and II, (Figure 8) shows the wide dark line of separation between materials. The upper portion of Area I is very smooth and homogeneous. Chatter marks from the diamond saw are visible.

Area I - High quartz, high potassium feldspar, some sodium feldspar, low calcium feldspar, lowest content of iron and magnesium oxide.

Area II - Lowest quartz, high potassium feldspar, moderate calcium feldspar, highest iron and moderate magnesium content. Least crystalline structure.

Area III - Relatively high quartz content, substantial amount of potassium feldspar, high calcium feldspar, intermediate iron content and substantial amount of magnesium oxide. Mainly crystalline.

Area IV - In comparison with Area II, Area IV had less potassium feldspar, higher calcium feldspar, lower iron and was slightly better crystallized.

X-RAY ANALYSIS

X-ray diffraction and X-ray fluorescence spectrometry of the various areas showed that the material is essentially a mixture of finegrained crystalline to glassy plagioclase feldspar with an excess of quartz. This is typical in many respects of basalt rock of various proportions of calcium, potassium, sodium feldspars and magnesium bearing pyroxene. The results for the different areas are given below:

Area I - High quartz, high potassium feldspar, some sodium feldspar, low calcium feldspar, lowest content of iron and magnesium oxide.

Area II- Lowest quartz, high potassium feldspar, moderate calcium feldspar, highest iron and moderate magnesium content. Least crystalline structure.

Area III-Relatively high quartz content, substantial amount of potassium feldspar, high calcium feldspar, intermediate iron content and substantial amount of magnesium oxide. Mainly crystalline.

Area IV- In comparison with Area II, Area IV had less potassium feldspar, higher calcium feldspar, lower iron and was slightly better crystallized.

CHEMICAL ANALYSIS

The chemical analysis was performed with X-ray fluorescence. The results are shown in Table I. of Area III and the third of Area IV. The temperature range was from room temperature to slightly above 1100°C. The material in Area I showed at 550°C an endotherm peak indicating the presence of free quartz. A gradual softening of the glass phase occurred from around 1000°C. Heating tests proved that TABLE I of the stone has the lowest melting point. DTA of the black material from Area IV did not show any peaks slightly above 1100°C. The material in Area III is very hard to melt. The DTA could not establish the melting point. At 720°C there is

Result of Chemical Analysis

<u>Area</u>	<u>% K₂O</u>	<u>% MgO</u>	<u>% CaO</u>	<u>% Fe₂O₃</u>	<u>% Al₂O₃</u>	<u>% SiO₂</u>
I	4.0	1.0	0.5	1.6	11	80-85
II	3.2	4.6	1.7	4.2	12	60-65
III	2.5	4.2	3.6	2.5	10	70-75
IV	2.7	-	2.4	2.3	10	75-80

DIFFERENTIAL THERMAL ANALYSIS

Differential thermal analysis (DTA) were run on three specimens, one of Area I, another of Area III and the third of Area IV. The temperature range was from room temperature to slightly above 1100°C . The material in Area I showed at 580°C an endotherm peak indicating the presence of free quartz. A gradual softening of the glass phase occurred from around 1000°C . Heating tests proved that this part of the stone has the lowest melting point. DTA of the black material from Area IV did not show any peculiarities and melting occurs slightly above 1100°C . The material in Area III is very hard to melt. The DTA could not establish the melting point. At 720°C there is a endothermal peak of unknown origin.

in the form of quartz is one of the main components. The piece was very inhomogeneous. The vitreous portion, i.e. amount of glass, varied strongly. Most of the material had devitrified, i.e. crystallized. Figure 9 shows the phase diagram for the portion of the system $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ relevant to the present case. The lines within the diagram are isotherms, i.e. lines for equal melting temperature. The eutectic (lowest melting) line of interest is indicated with red. This line has been chosen because the plagioclase in all the present cases has been found to be in equilibrium with silica (quartz). The temperature range is from 1062°C to 1366°C . In the present case the compositions were further modified by potassium, iron, etc. This will shift these temperatures up or down somewhat. It should be pointed out that when any portion of the stone is melted and rapidly cooled glass is formed. Slow cooling promotes crystallization. Some feldspars, in particular albite, resist strongly crystallization after having been melted and prefer to stay in the glassy state. It is concluded that the inside of the wall of the fort should be found to be more crystalline than the outside because of its slower cooling rate.

DISCUSSION:

The discussion of the above results can be done in several ways. On one side there are the obvious facts of chemical composition and the state of the material. On the other side there must be sources of raw material within reasonable distance and the method used in creating the vitrified wall.

The results showed that the stone studied was a mixture of silicates and silica. The silicates were mainly feldspars of several different compositions of plagioclase type such as anorthite and andesine. The iron content varied somewhat but was relatively low. Silica in the form of quartz is one of the main components. The piece was very inhomogeneous. The vitreous portion, i.e. amount of glass, varied strongly. Most of the material had devitrified, i.e. crystallized. Figure 9 shows the phase diagram for the portion of the system $\text{CaO-Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ relevant to the present case. The lines within the diagram are isotherms, i.e. lines for equal melting temperature. The eutectic (lowest melting) line of interest is indicated with red. This line has been chosen because the plagioclase in all the present cases has been found to be in equilibrium with silica (quartz). The temperature range is from 1062°C to 1368°C . In the present case the compositions were further modified by potassium, iron, etc. This will shift these temperatures up or down somewhat. It should be pointed out that when any portion of the stone is melted and rapidly cooled glass is formed. Slow cooling promotes crystallization. Some feldspars, in particular albite, resist strongly crystallization after having been melted and prefer to stay in the glassy state. It is concluded that the inside of the wall of the fort should be found to be more crystalline than the outside because of its slower cooling rate.

The origin of the gases forming the bubbles depends on the raw materials used in forming the wall. Entrapped air must account for some but the other likely sources are carbonates, chemically bound water in clays and chemically reduction of iron oxide from a higher oxidation state to a lower. Silicate melts and glasses are known to dissolve gases. When supersaturated they release these gases gradually at points on solid matters, such as sandgrains.

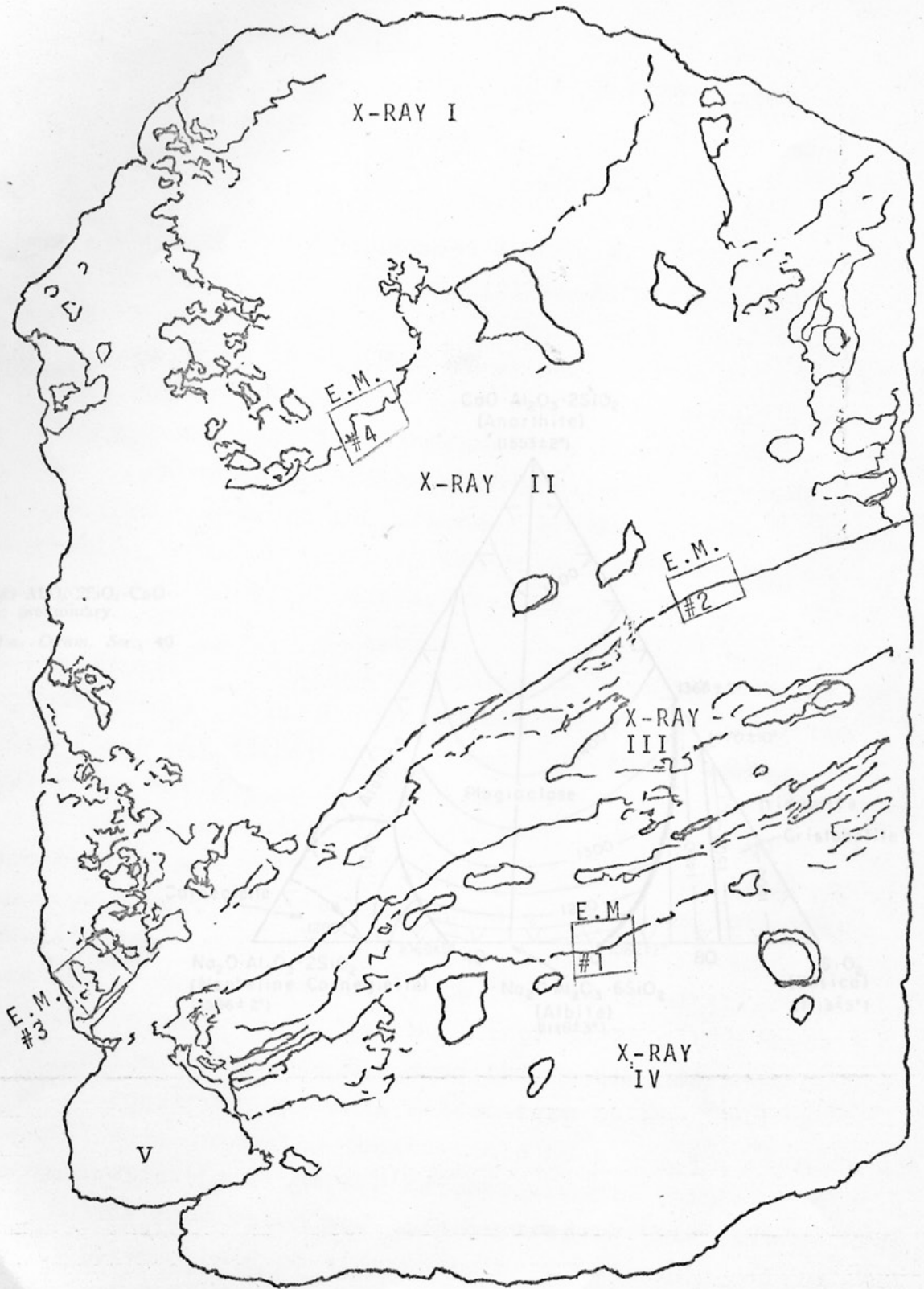
The raw materials used in building the fort must have come from the nearest practical point, in other words the hill Craig Phadrig itself. The hill is composed of red sandstone and the associate minerals, such as iron ore. The stones, rocks and minerals must have varied in sizes but from what appears from the piece investigated partly fine grained with pieces at least a few centimeters long intermingled with rather big stones. This accounts for the inhomogeneity of the present piece.

The temperature must have been rather high to be able to melt the material as can be concluded from the phase diagram (Figure 9). A guess would be over 1200°C . The duration of the fire can only be concluded from the depth of vitrification towards the center of the wall.

The age of the piece cannot be concluded from the investigation but it is likely that some carbon from the fire or fires remain in the wall. A carbon -14 determination should be tried.

The above introductory study of the remains of the hill fort Craig Phadrig has shown that certain minerals have been formed during a fire, the temperature of which is above 1200°C and must have been very extensive in size. Such a fire is very likely to be done intentionally for the purpose of making a strong vitrified structure.

PICTISH ROCK



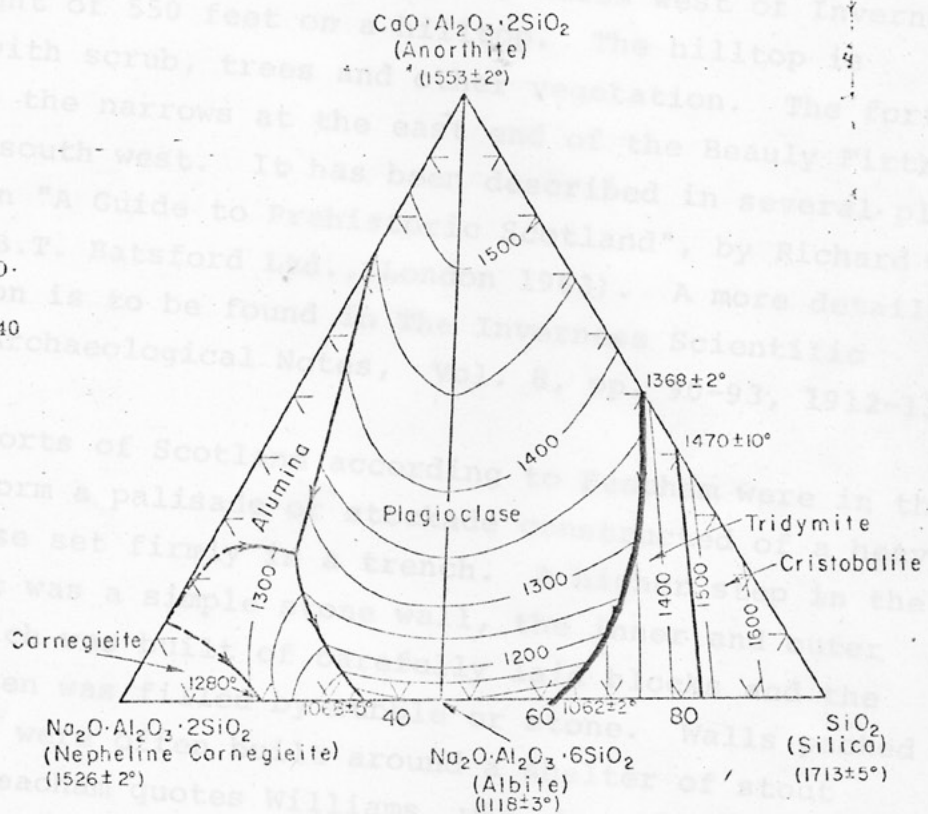
X-RAY ANALYSIS -- I to IV

FIGURE 4

E.M. REPLICAS -- # 1 to 4

CaO-Al₂O₃-SiO₂ (cont.)

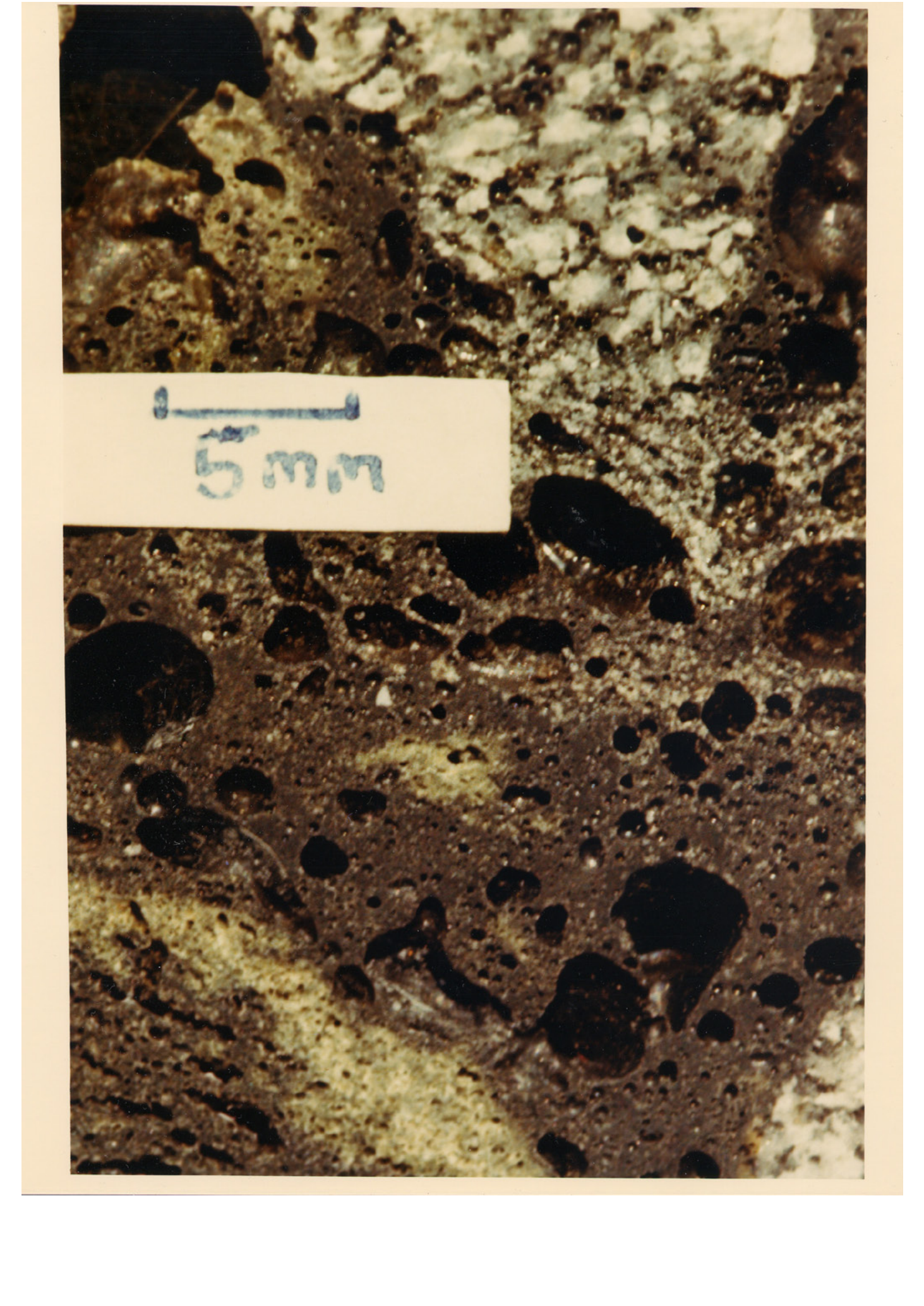
9. System Na₂O·Al₂O₃·2SiO₂-CaO·Al₂O₃·2SiO₂-SiO₂; preliminary.
 F. Schairer, *J. Am. Ceram. Soc.*, 40
 32 (1957).







5 mm

A photomicrograph showing a mineral specimen with a complex, porous, and crystalline texture. The specimen is divided into two main regions: a lighter, more crystalline upper portion and a darker, more porous lower portion. A white rectangular scale bar is positioned horizontally across the middle of the image, with the text "5mm" written in blue ink below it. The overall appearance is that of a mineralized rock or sediment with varying degrees of crystallinity and porosity.

5mm

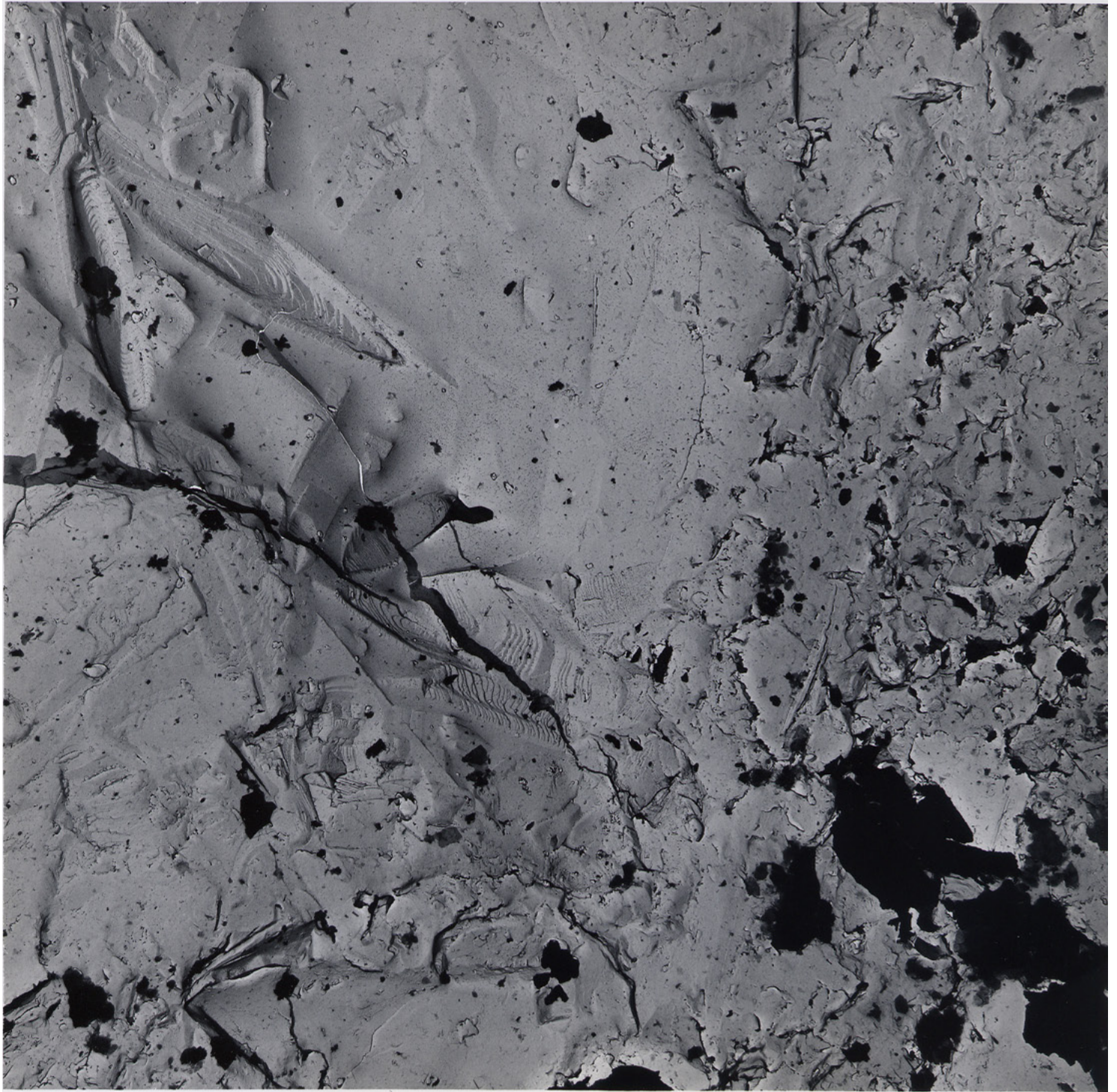


Figure 5a

PICTISH ROCK
(Area I)

USD Electron Micrograph #110970-14
Mag.: X 6,000 Date 8/19/71
Prep.: Two stage carbon replica

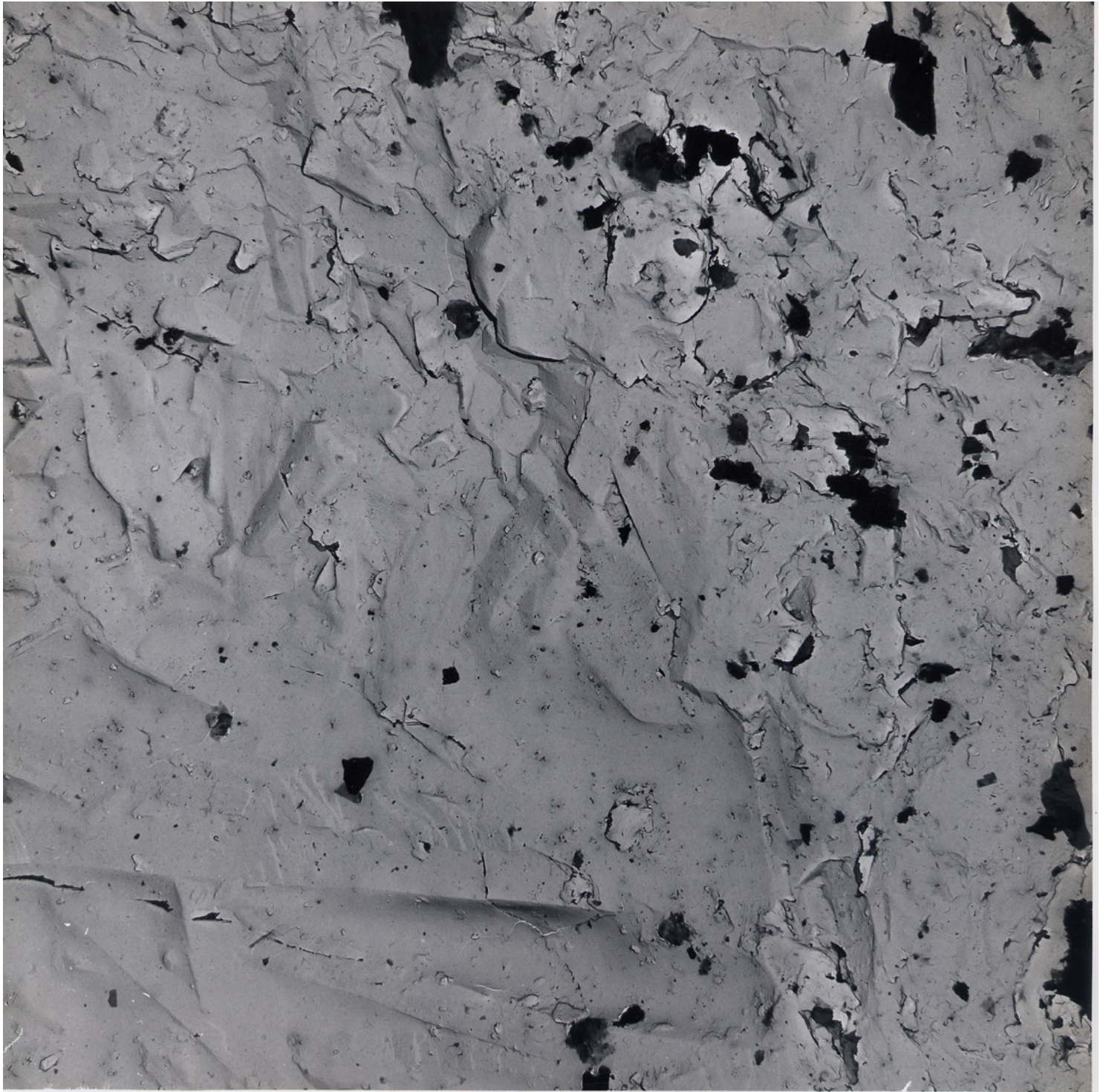


Figure 5b

PICTISH ROCK
(Area I)

USD Electron Micrograph #110970-15
Mag.: X 6,000 Date 8/19/71
Prep.: Two stage carbon replica

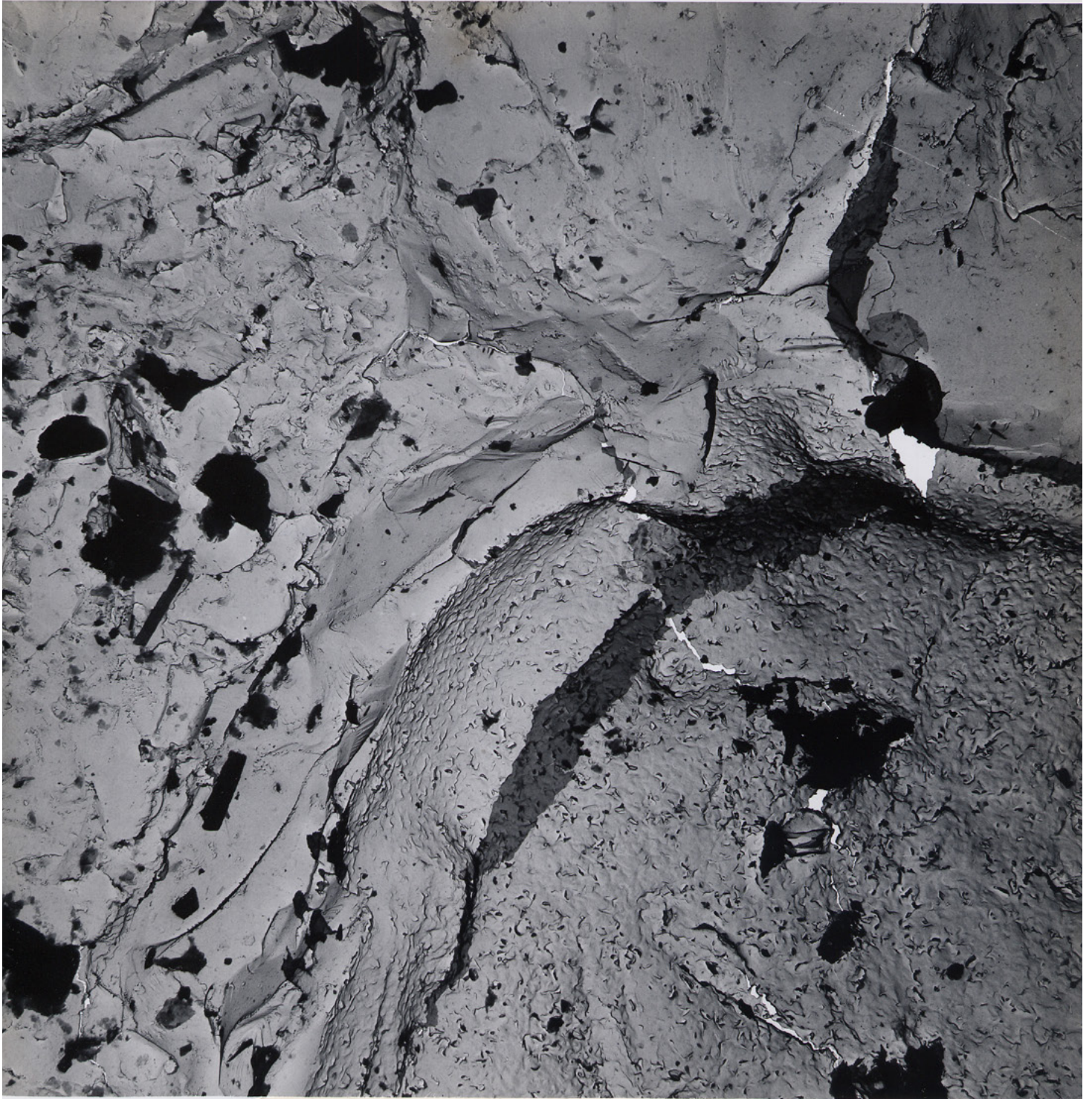


Figure 6a

PICTISH ROCK
(Area 2)

USD Electron Micrograph #110970-16
Mag.: X 6,000 Date 8/19/71
Prep.: Two stage carbon replica

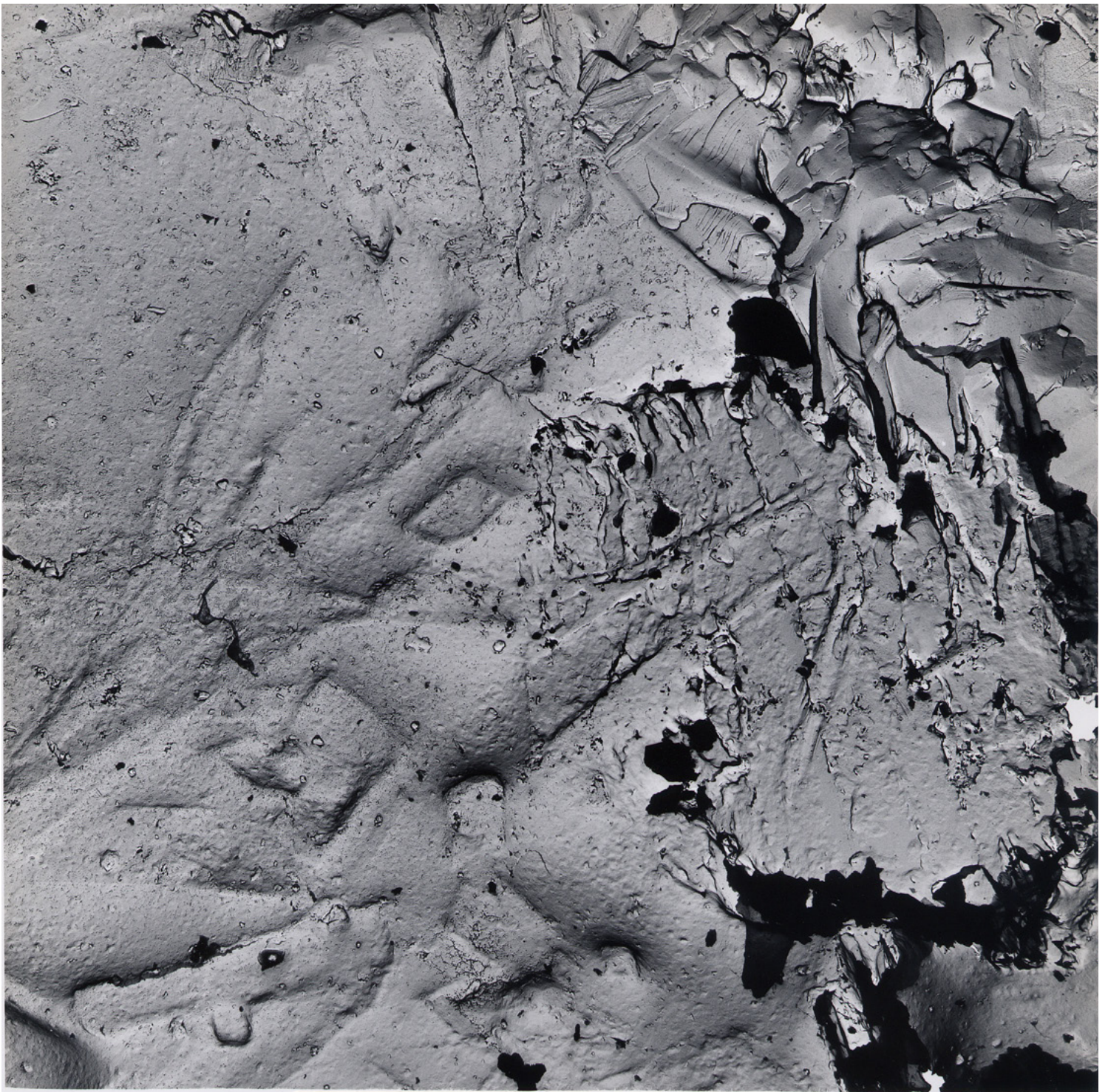


Figure 6b

PICTISH ROCK
(Area 2)

USD Electron Micrograph #110970-18
Mag.: X 6,000 Date 8/19/71
Prep.: Two stage carbon replica

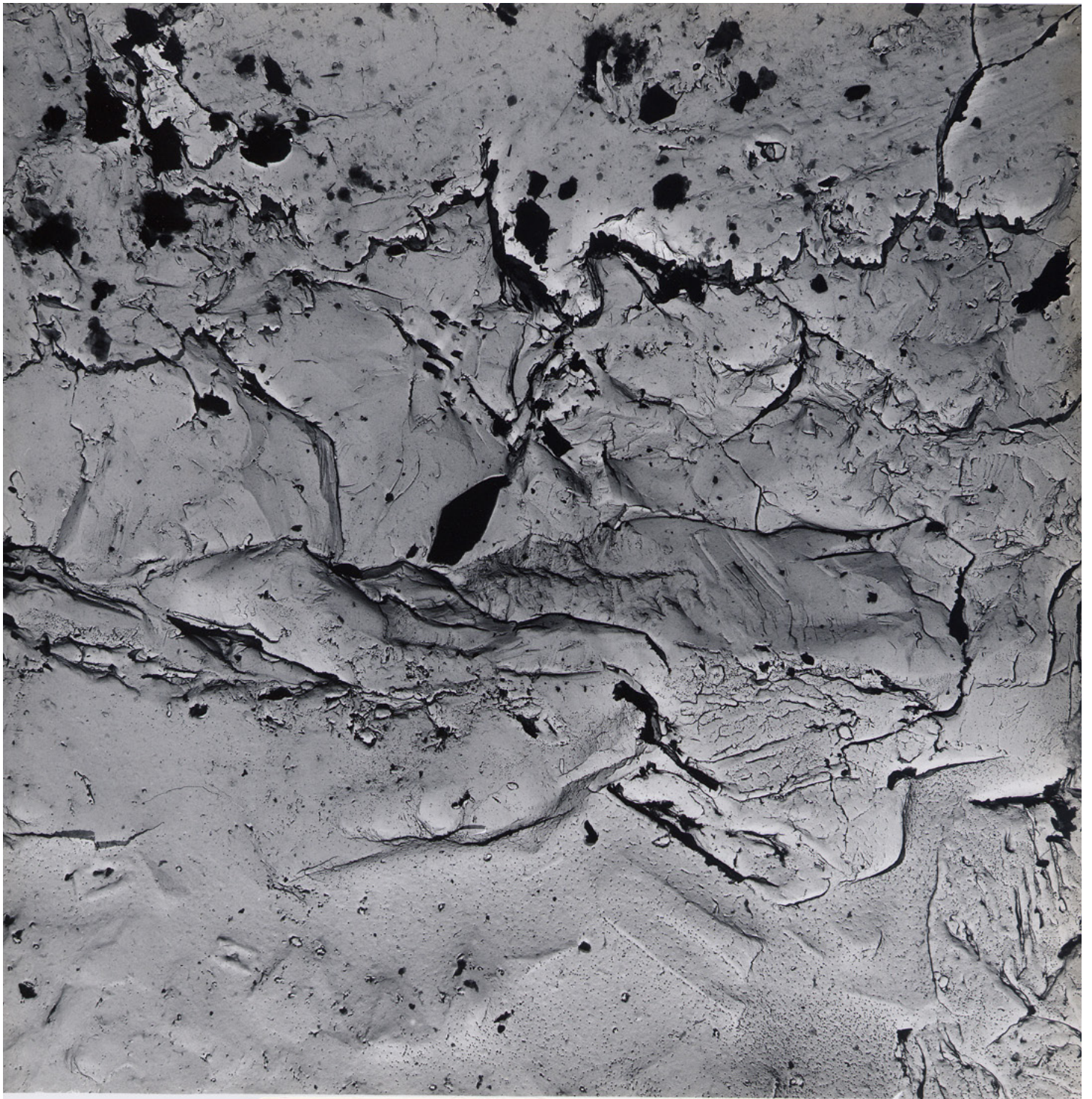


Figure 6c

PICTISH ROCK
(Area 2)

USD Electron Micrograph #110970-17
Mag.: X 6,000 Date 8/19/71
Prep.: Two stage carbon replica

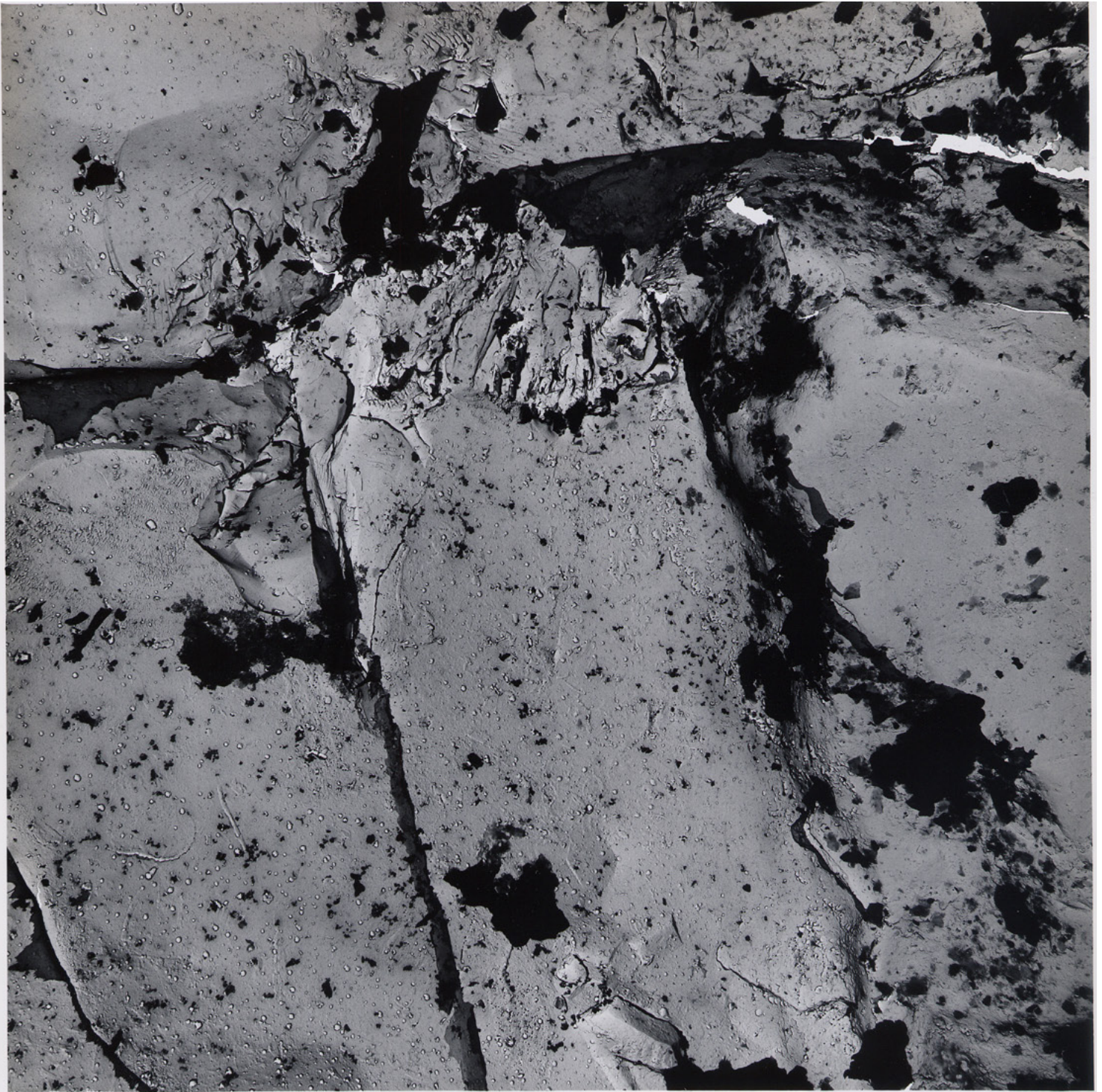


Figure 7

PICTISH ROCK
(Area 3)

USD Electron Micrograph #111170-2
Mag.: X 6,000 Date 8/19/71
Prep.: Two stage carbon replica

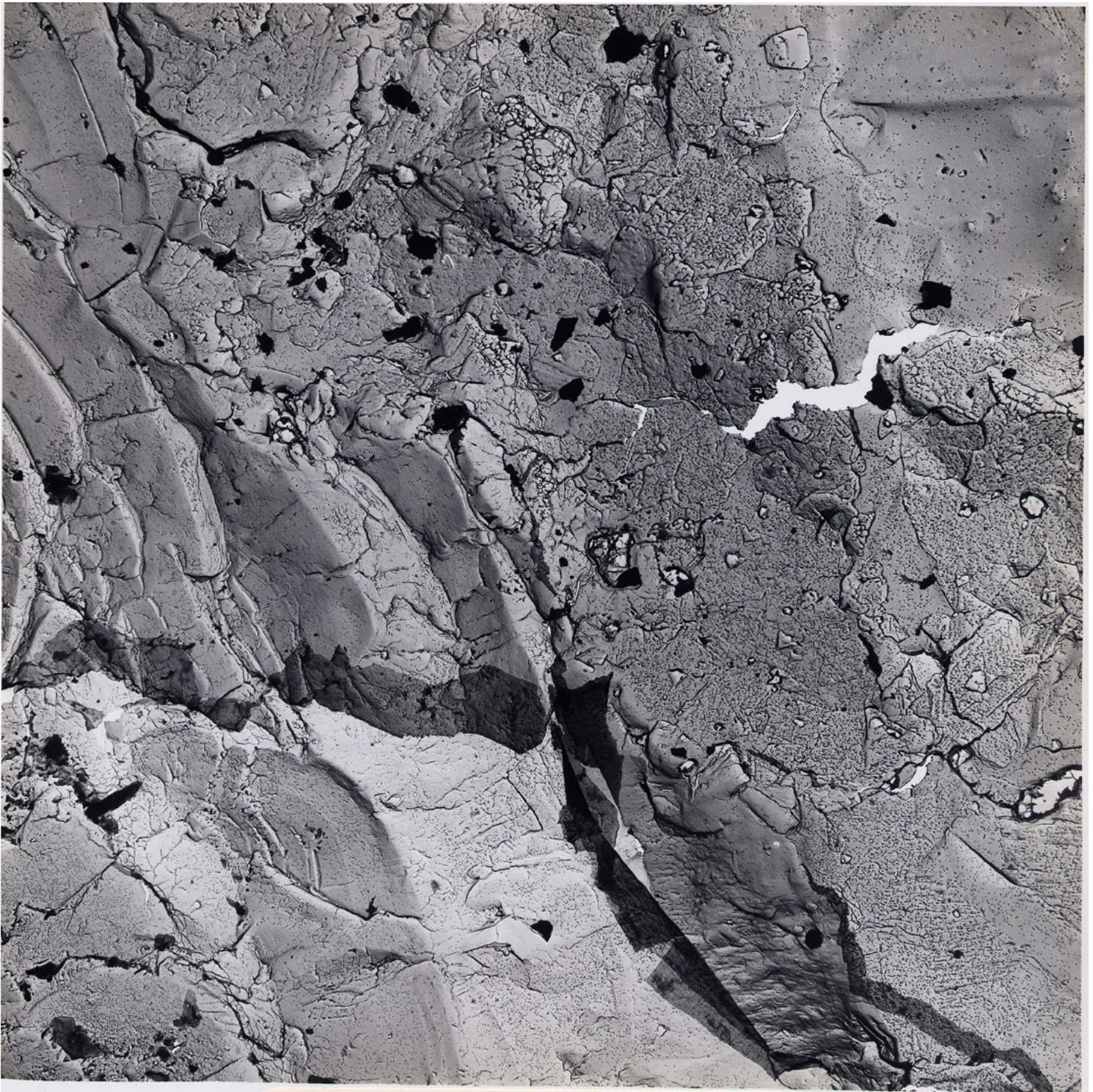


Figure 8

PICTISH ROCK
(Area 4)

USD Electron Micrograph #111170-8
Mag.: X 6,000 Date 8/19/71
Prep.: Two stage carbon replica

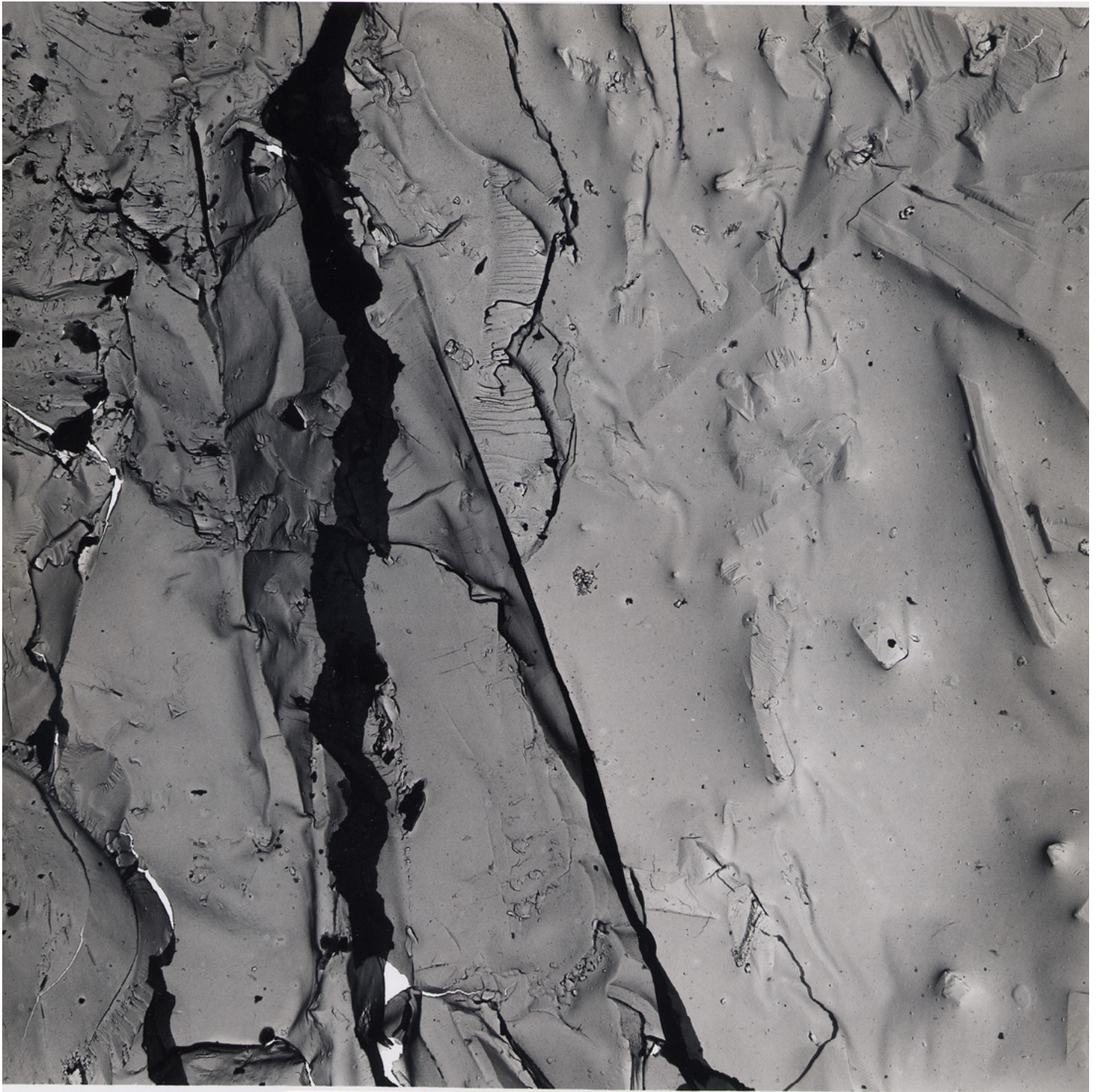


Figure 8a

PICTISH ROCK
(Area 4)

USD Electron Micrograph #111170-7
Mag.: X 6,000 Date 8/19/71
Prep.: Two stage carbon replica