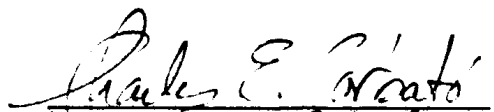


IDENTIFICATION BY  
X-RAY POWDER DIFFRACTION  
OF  
VARIOUS COPPER ARSENIDE MINERALS  
FROM  
KEWEENAW COUNTY, MICHIGAN

Presented in Fulfillment of Requirements  
For the Bachelor of Science Degree  
in  
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## INTRODUCTION

The purpose of the project was to analyze and describe by x-ray diffraction methods a set of copper arsenide minerals belonging to the Mineralogy Museum at The Ohio State University. The suggestion to initiate this study was made by Dr. Charles E. Corbato. Aside from questioning the accuracy of the previous labelling of these minerals, an additional incentive for research was to analyze the nature of a brown alteration product occurring on the majority of the samples. Prior to the x-ray examination, these specimens had been designated Algodonite, Domeykite, Mohawkite, or Whitneyite based on physical appearance. All samples were believed to be copper arsenides, of varying percentages of copper and arsenic. Due to the relative rarity of these minerals, there is only a small amount of literature published on the subject.

## COPPER ARSENIDES

### General History

Copper mining began in Keweenaw County, Michigan (see Figure 1) approximately 5000 years ago, and continued until 1969 (Min. of Mich. 1976 Bulletin 6). Native and copper-bearing minerals occur in volcanic and sedimentary rocks of the Keweenaw series of Late Precambrian age on the Keweenaw Peninsula. This area has not been severely metamorphosed, and aside from some minor tilting, folding, and faulting, the peninsula remains relatively unchanged. Copper arsenide minerals are nearly always found in fissures which intersect bedded deposits of native copper. The bulk of the samples analyzed are from the Mohawk Mine in Keweenaw County.

### Nomenclature

When it became evident that copper mining was going to be a primary industry in Michigan, several mineralogists proposed a system of classification for the various copper-bearing minerals. Between 1900 and 1903, Koenig recognized the existence of Algodonite, Domeykite, Mohawkite and Whitneyite, and described the minerals Stibio-Domeykite, Melanochalcite, Argentodomeykite, and Argentoalgonite. In addition to these names, other researchers described the minerals Keweenawite, Ledouxite, Mohawk-Algodonite, Mohawk-Domeykite, Semi-Whitneyite, and Gamma Domeykite. Previous to x-ray

based studies, this system of nomenclature was sufficient. Following substantial x-ray analysis, it appears that Algodonite and Domeykite are the only valid copper arsenide species present in the area. X-ray data verifies the presence of an alpha and beta polymorph of Domeykite. The beta Domeykite polymorph was not present in any of the specimens analyzed for this project. All other names previously assigned represented mixtures of Algodonite and Domeykite, arsenian copper, cobalt or nickel arsenides or silver.



## EXPERIMENTAL METHOD

### Sample Preparation

The unknown alteration product was removed from the surface of the specimens with a very soft typing brush. Since the alteration was a very fine powder, crushing and grinding was not necessary.

The previously identified specimens were fragmented with a hammer and pliers, then ground to a fine powder in a corundum mortar and pestle. Due to the metallic nature of these specimens, it was extremely difficult to prepare sufficient sample to fill the entire specimen holder.

### X-ray Diffractograms

X-ray patterns of 10 copper arsenide samples were obtained. Also analyzed was the brown alteration product common to all samples. In addition to these, one pattern was also run with an empty aluminum specimen holder. Since many of the patterns were believed to possess indicative reflections in the low to intermediate angle region, all the samples were run over a goniometer range of  $10^{\circ}$  to  $76^{\circ} 2\theta$ . The x-ray unit utilized in experimentation was a Philips x-ray generator and goniometer with the following experimental conditions:

power	35 kv/15 ma
radiation/filter	Cu/Ni
goniometer speed	$1^{\circ}/\text{min.}$

chart speed	30"/hr.
time constant	1 second
full scale	400 counts/second (scale factor = 8)
divergence and anti-scatter slits	1°
receiving slit	0.006"

## RESULTS

### Alteration Product

The x-ray pattern for the brown alteration product exhibited very broad, low intensity peaks. From the character of these reflections, the alteration product appears amorphous. The only recognizable peaks in this pattern are attributed to Domeykite, which was probably brushed off the specimens along with the powder. Other than the poor crystallinity of this substance, the character of the alteration product from this analysis remains uncertain.

### Previously Identified Specimens

It was possible to designate over 94% of the 196 recorded reflections to specific mineral species. There were a total of ten peaks which are unidentifiable. Each specimen contains the identical unknown peak. This reflection occurs at approximately  $45^{\circ} 2\theta$  in all the previously identified samples, but was not present in the x-ray pattern of the alteration product. A method of investigation to ascertain the identity of this peak will be discussed after the individual presentation of each pattern.

### Sample 56

Aside from two Quartz peaks, this sample consists en-

tirely of a mixture of Algodonite and Domeykite. Every possible Algodonite peak within our goniometer range is present. The thirteen most intense Domeykite peaks comprise the remainder of the x-ray data. From the observed information, this sample resembles a relatively balanced mixture of Algodonite and Domeykite with a minimal amount of Quartz.

PREVIOUS LABEL: Domeykite

SUGGESTED LABEL: Mixture of Algodonite and  
Domeykite with Quartz

#### Sample 1218

Other than the presence of the second and third most intense reflections of Algodonite, the other reflections are attributable to Domeykite. The most intense Algodonite peak has been covered by the third most intense reflection of Domeykite. The Domeykite peaks in this sample are extremely sharp and strong, while the Algodonite peaks are quite weak.

PREVIOUS LABEL: "Mohawkite"

SUGGESTED LABEL: Domeykite with a Small Amount  
of Algodonite

#### Sample 2053

The three most intense peaks of Algodonite, and the first seventeen reflections of Domeykite comprise this sample. The Domeykite peaks are exceptionally strong and well defined, while the Algodonite peaks are well defined, but of moderate intensity. This sample closely resembles sample #1218, with perhaps a slight increase in Algodonite.

PREVIOUS LABEL: "Mohawkite"

SUGGESTED LABEL: Domeykite with Partial  
Algodonite Phase

Sample 5095

Quartz, Domeykite, and Algodonite are present in this sample. All three of the constituents peaks are very sharp. The Quartz and Domeykite reflections are of exceptionally high intensity. The Algodonite peaks have a moderately high intensity, but begin to acquire a somewhat broader nature as  $2\theta$  increases. Since four of the five possible Algodonite peaks appear, exhibiting a relatively strong nature, this sample cannot be defined as containing trace Algodonite. A mixture of the three constituents seems to present a reasonable description.

PREVIOUS LABEL: Domeykite

SUGGESTED LABEL: Mixture of Domeykite,  
Algodonite, and Quartz

Sample 10099

This sample was quite deficient in copper arsenide peaks. The majority of this specimen is Calcite and Ankerite. There is also some Algodonite and Quartz, as well as a Chlorite group mineral present. The Calcite and Ankerite peaks are very well defined and extremely strong. The Algodonite peaks are very broad with moderate intensity. The Chlorite and Quartz peaks are of moderately low intensity, yet exhibit a sharp character. Although the Ankerite is described by only

one peak, the assumption is made with relative certainty for several reasons: (1) Besides the peak observed (at  $30.80^\circ 2\theta$ ), with a ten scale intensity reflection, Ankerite exhibits no other reflections above an intensity of one. (2) The literature describes the abundance of Ankerite in copper arsenide veins, and its intimate association with Calcite. The Chlorite group mineral is assumed due to the unusual location of a peak at  $12.45^\circ 2\theta$ , which is indicative of some of the Chlorite group minerals.

PREVIOUS LABEL: Algodonite

SUGGESTED LABEL: Calcite and Ankerite with  
Algodonite, Quartz and Chlorite

#### Sample 10100

This sample resembles sample 10099, but contains increased amounts of Algodonite and Quartz. The Calcite and Ankerite peaks exhibit extreme intensity with a fairly sharp character. The Algodonite reflections represent all five possible peaks within our goniometer range, but the intensity and definition of peaks are weak to moderate. The Quartz peaks are of moderate intensity and sharp character, while the Chlorite peaks are somewhat well defined, but of relatively low intensity.

PREVIOUS LABEL: Algodonite

SUGGESTED LABEL: Mixture of Algodonite, Ankerite,  
Calcite and Quartz with a Small  
Amount of Chlorite

Sample 10102

All three constituents in this sample exhibit very sharp, moderate intensity peaks. Domeykite and Ankerite are present, while Algodonite is absent in this specimen. The third mineral is Niccolite, a nickel arsenide. Both reflections by which Niccolite is defined are of substantial nature. Previous literature describes the intergrowth of Niccolite with Domeykite in the copper arsenide veins of Keweenaw County (Mohawk Mine). This past work has been confirmed by x-rays. The first and third most intense peaks of Niccolite are present, while the second most intense is masked by a major Domeykite peak.

PREVIOUS LABEL: Algodonite

SUGGESTED LABEL: Domeykite with Niccolite and  
Ankerite

Sample 10103

Algodonite, Calcite, Quartz, and a Chlorite group mineral are present in this sample. The Algodonite reflections exhibit tremendous intensity with very broad peaks. By far, these are the most intense Algodonite peaks recorded in this experiment. The Calcite and Chlorite peaks are well defined, but of very low intensity. The single Quartz peak is of extremely low intensity, but exhibits moderately sharp definition. This sample contains the most distinct Algodonite composition recorded.

PREVIOUS LABEL: Domeykite

SUGGESTED LABEL: Algodonite with Small Amounts  
of Calcite, Chlorite and Quartz

Sample 10105

This powder sample exhibits the eighteen most intense reflections of Domeykite possible in our goniometer range. One Algodonite peak and two Quartz peaks are present also. Overall, these Domeykite reflections are the sharpest, most intense recorded. The Domeykite peaks are so strong that three of them do not even appear on the power diffraction file card. These three were calculated by Dr. Corbato as possible reflections for Domeykite at extremely low intensities. The method and procedure for calculation is described in Table 1. Both the Quartz and Algodonite peaks exhibit very low intensity reflections. The Quartz peaks were fairly sharp, while the Algodonite peak was very broad and poorly defined. The most intense Algodonite peak was covered by a major Domeykite peak.

PREVIOUS LABEL: "Mohawkite"

SUGGESTED LABEL: Domeykite with Small Amounts  
of Quartz and Algodonite

Sample 10106

This is the most definitive pattern measured. The only constituent present in this specimen is Domeykite. All peaks are very sharp and extremely intense. The fifteen most intense reflections are visible in this sample. This specimen



approaches purity more so than any other. K-alpha-one and K-alpha-two peaks are extremely well resolved here.

PREVIOUS LABEL: "Whitneyite"

SUGGESTED LABEL: Domeykite

### Discussion of Unidentifiable Peak

The various methods by which identification of the unknown reflection at approximately  $45^\circ 2\theta$  (2.01 Angstrom d spacing) will be provided now. This presentation is aimed mainly at elimination of the same methods in further research. One of the major obstacles in identification is the inability to define a mineral by one peak. It was inferred that this reflection is the highest, or very nearly the highest intensity reflection for the particular species.

One method of identification was using the powder diffraction search manual to identify a mineral by the peak. Another method was to review previous literature regarding the occurrence of other minerals with Algodonite and Domeykite. Much of the literature referred to the occurrence of arsenian copper with Domeykite and Algodonite. After checking the powder data file for arsenian copper, it was clear that this was not the unknown peak. Contamination was another factor considered. Some of the possible methods of contamination were:

- 1) Part of the pliers (Fe) used to break the sample entering the specimen holder
- 2) Abrasion of the mortar and pestle ( $Al_2O_3$ ) used to

crush the specimen

3) Specimen holder causing reflection (A1)

All of these possibilities were eliminated after checking the x-ray patterns for each of the substances. In addition, the specimen holder was x-rayed at the indicated values of  $2\theta$  where the reflection occurred, revealing no peaks.

Native copper was another possibility ruled out after consulting the x-ray powder data file. The samples were investigated for a magnetic constituent, but there was so little magnetic material present that elimination of this factor was possible. A direct or inverse proportionality between the character of the unknown peak and the absence or presence of any of the minerals was considered and found wanting. At the termination of this research, this peak remains unidentified, but all the samples have been retained and placed in the Mineralogy Museum to aid in further research.

SUMMARY

The original intent was to analyze and describe the unknown alteration product by x-ray diffraction methods, and to determine the accuracy of the previous labels on these specimens. Since the brown alteration product was termed an amorphous substance, the bulk of remaining research was spent determining the correct mineral composition of the samples. It was clear that many of the labels would be changed due to the invalidity of the names "Whitneyite" and "Mohawkite." Other than the one unidentifiable peak, the remainder of the specimens were analyzed and described with sufficient accuracy to initiate the re-labelling of these samples.

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Table 1

SYMBOLS USED ON FIGURES AND TABLES

<u>SYMBOL</u>	<u>EXPLANATION OF SYMBOL</u>
A	Algodonite
An	Ankerite
C	Calcite
Cl	Chlorite Group Mineral
D	Domeykite (Alpha)
N	Niccolite
Q	Quartz
U	Unidentified Peak
r.t.	All d-spacing calculations from tables by Dr. R. T. Tettenhorst
c.e.c.	This refers to theoretical reflections for Domeykite calculated by Dr. C. E. Corbato. These values were not listed in powder data file due to the low nature of their intensities. Dr. Corbato calculated these theoretical d-spacings with crystal system and cell dimension data from:  Padera, K. 1952, Acad. Tcheque Sci. Bull. International Classe Sci., Math. Nat., Med., V. 52, P. 53-68.

NOTE: Numbers enclosed in parentheses of second and fourth columns of tables indicate relative intensity.























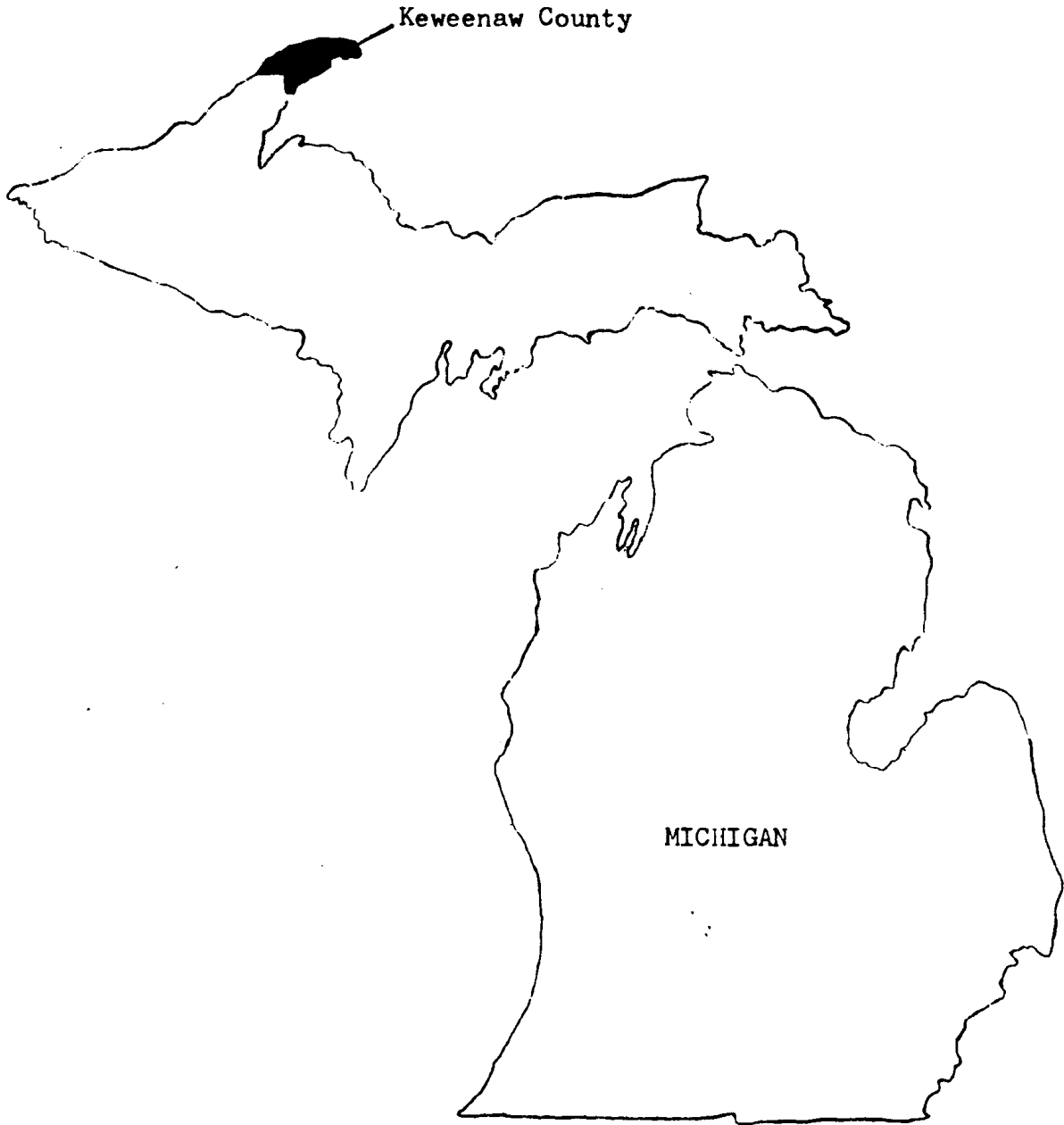
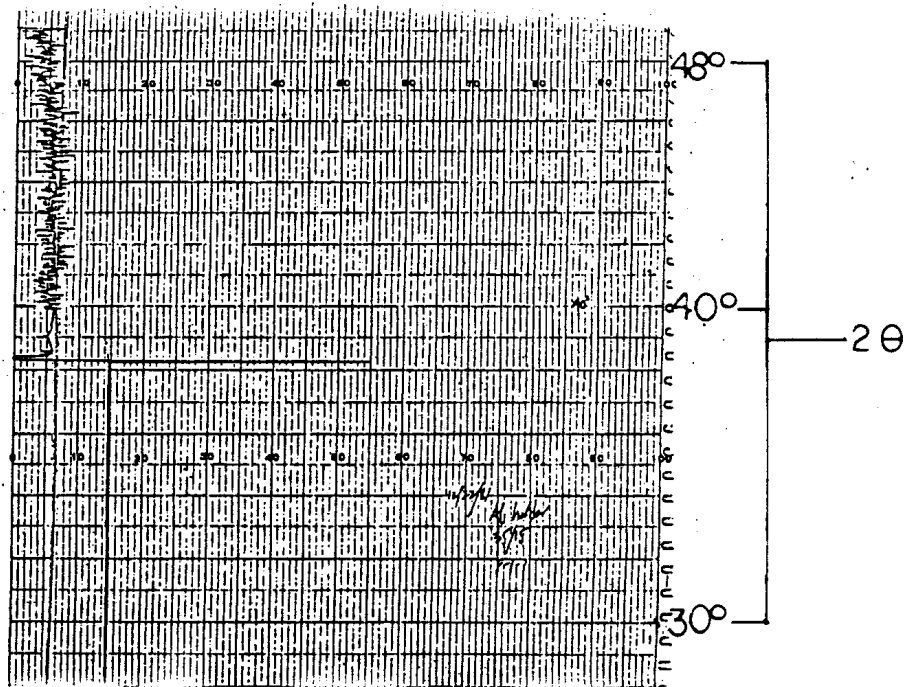


Figure 1. Index map showing location of Keweenaw County, Michigan



Figure 2. X-ray diffractogram of specimen holder.



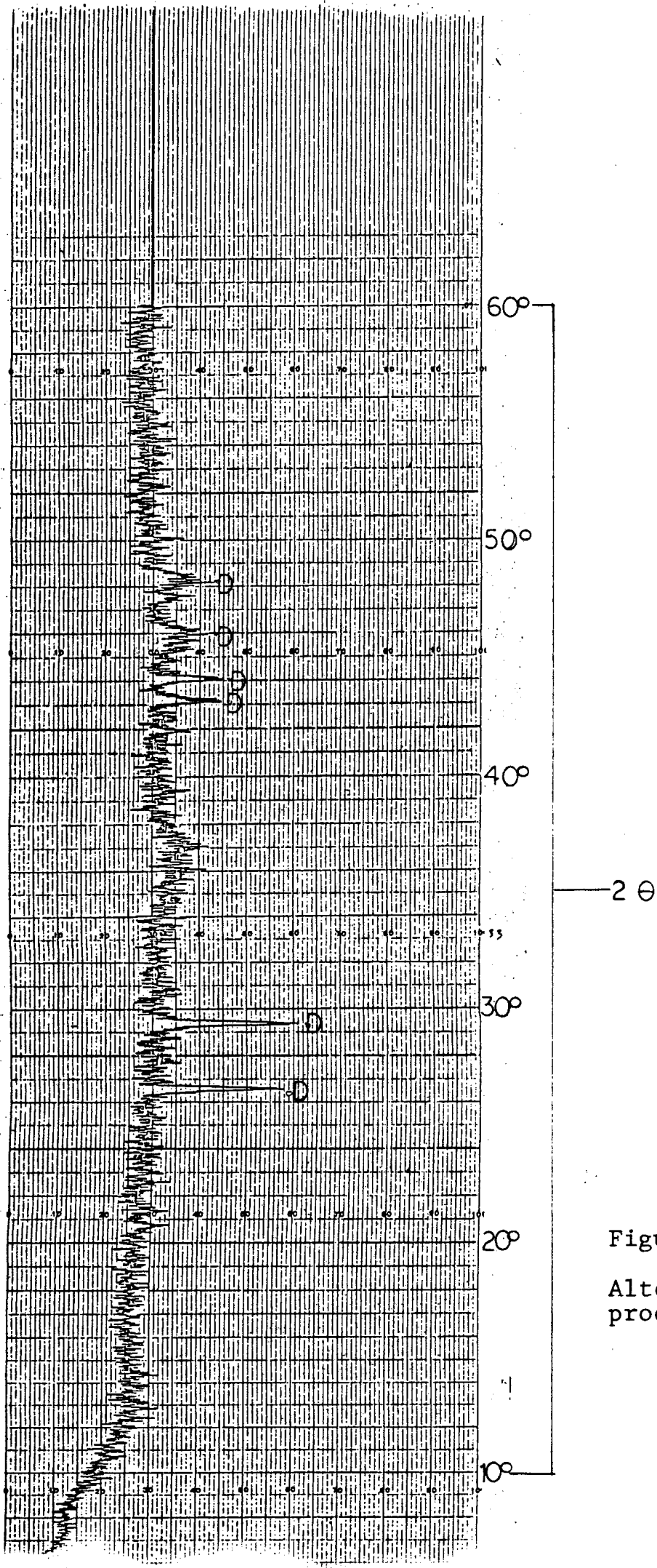


Figure 3.  
Alteration  
product

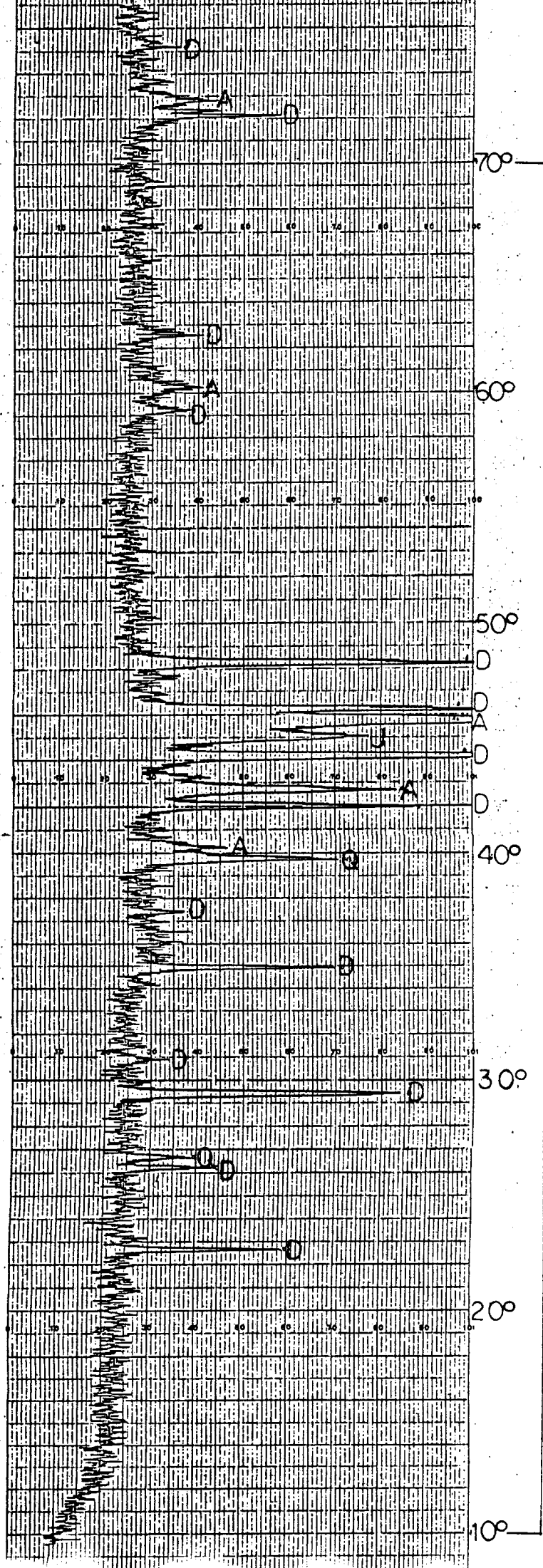


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#56

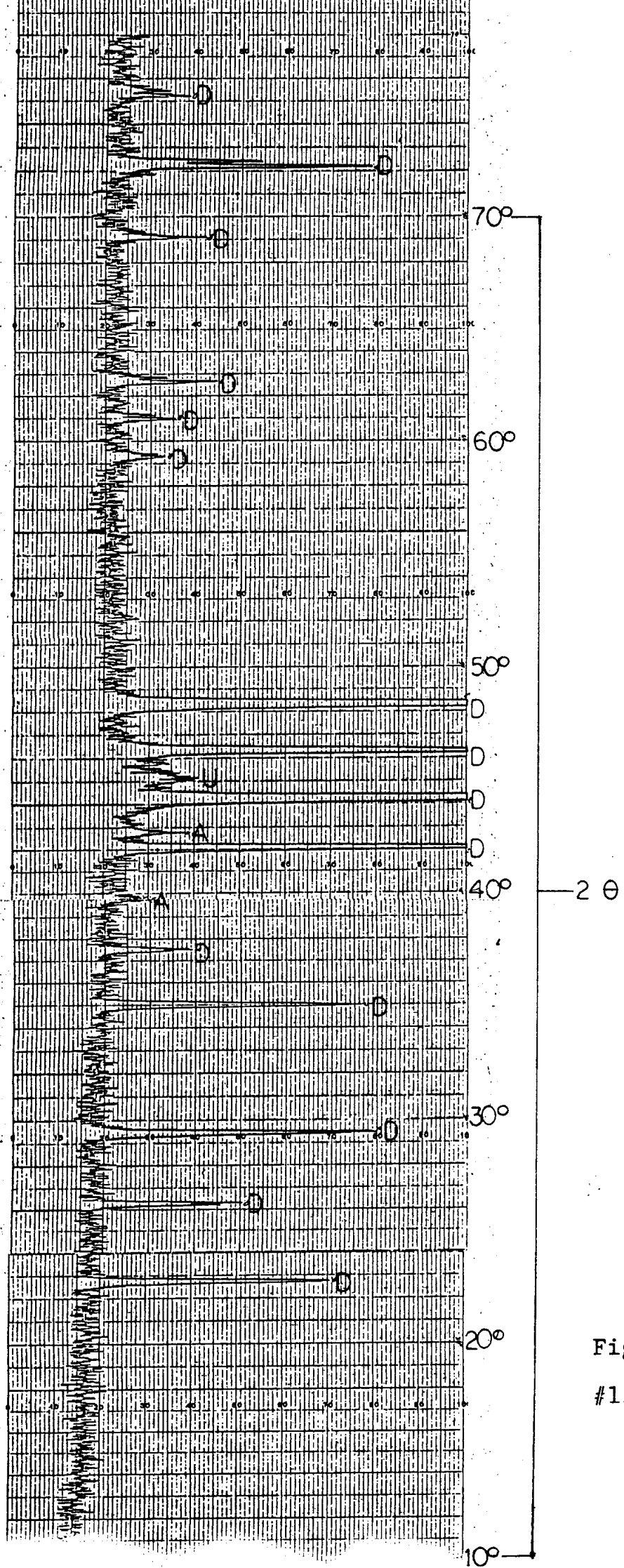


Figure 5.

#1218

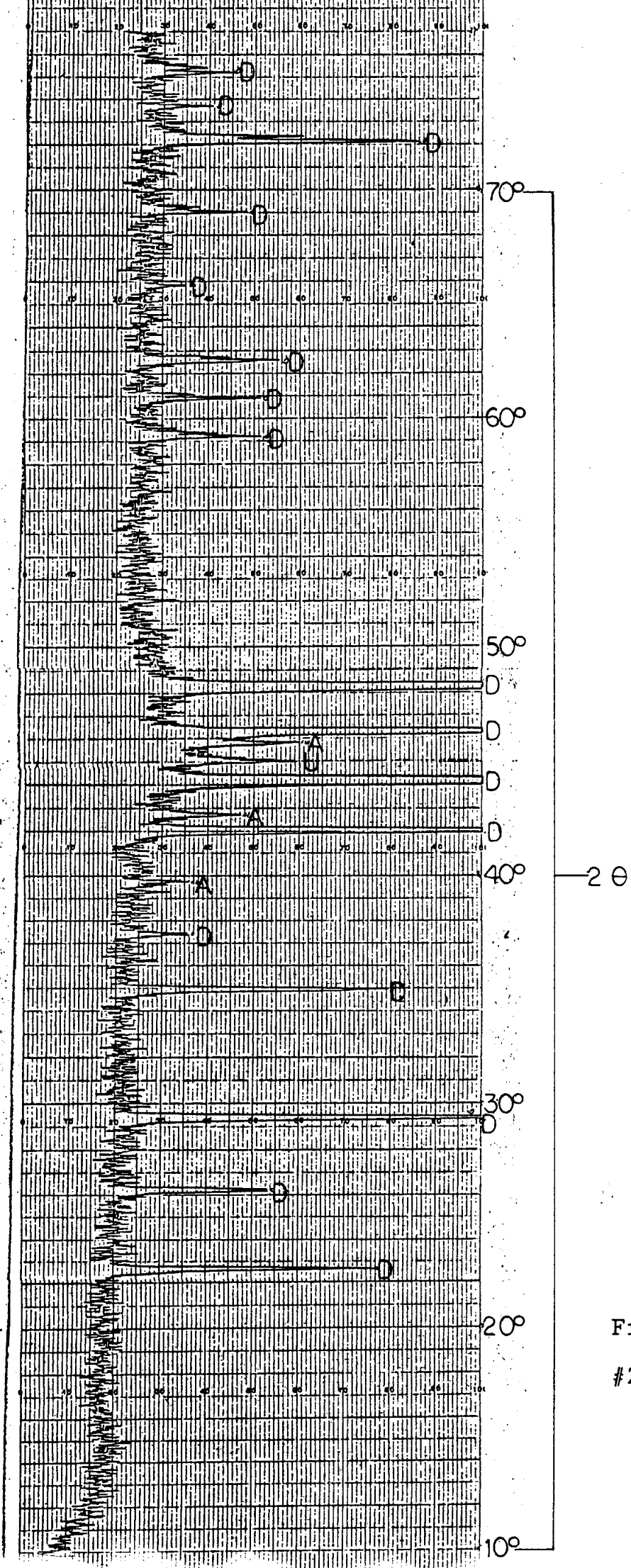


Figure 6.  
#2053

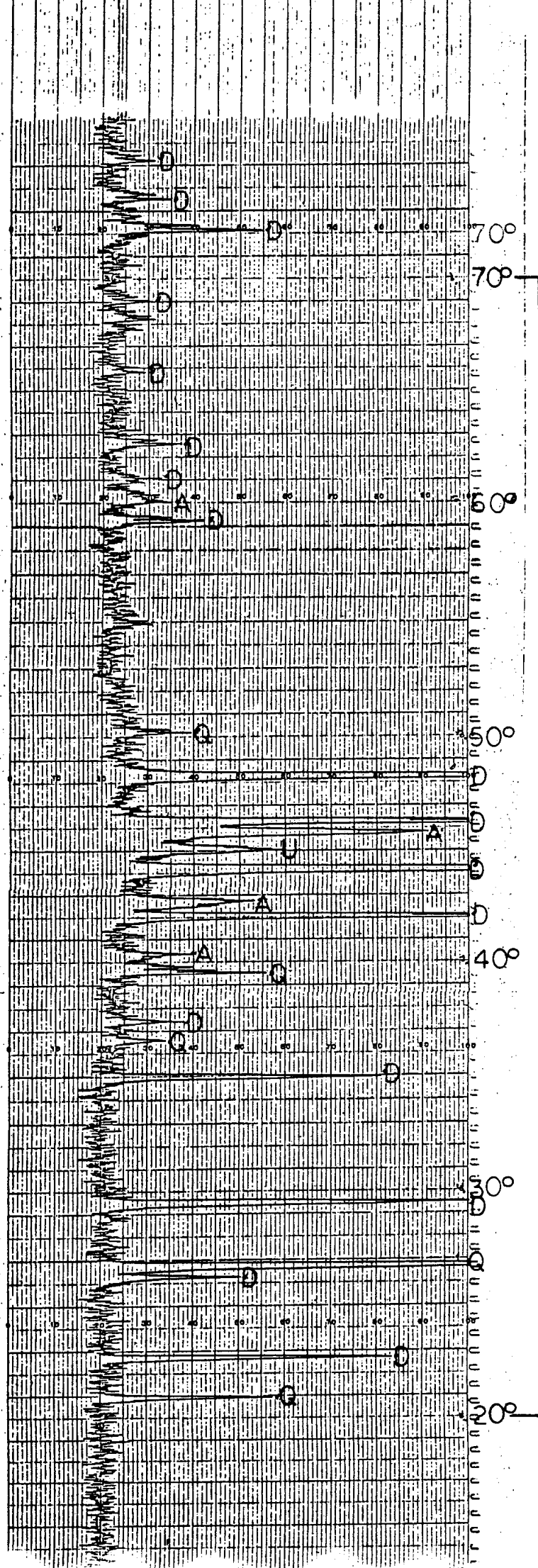


Figure 7.

#5095

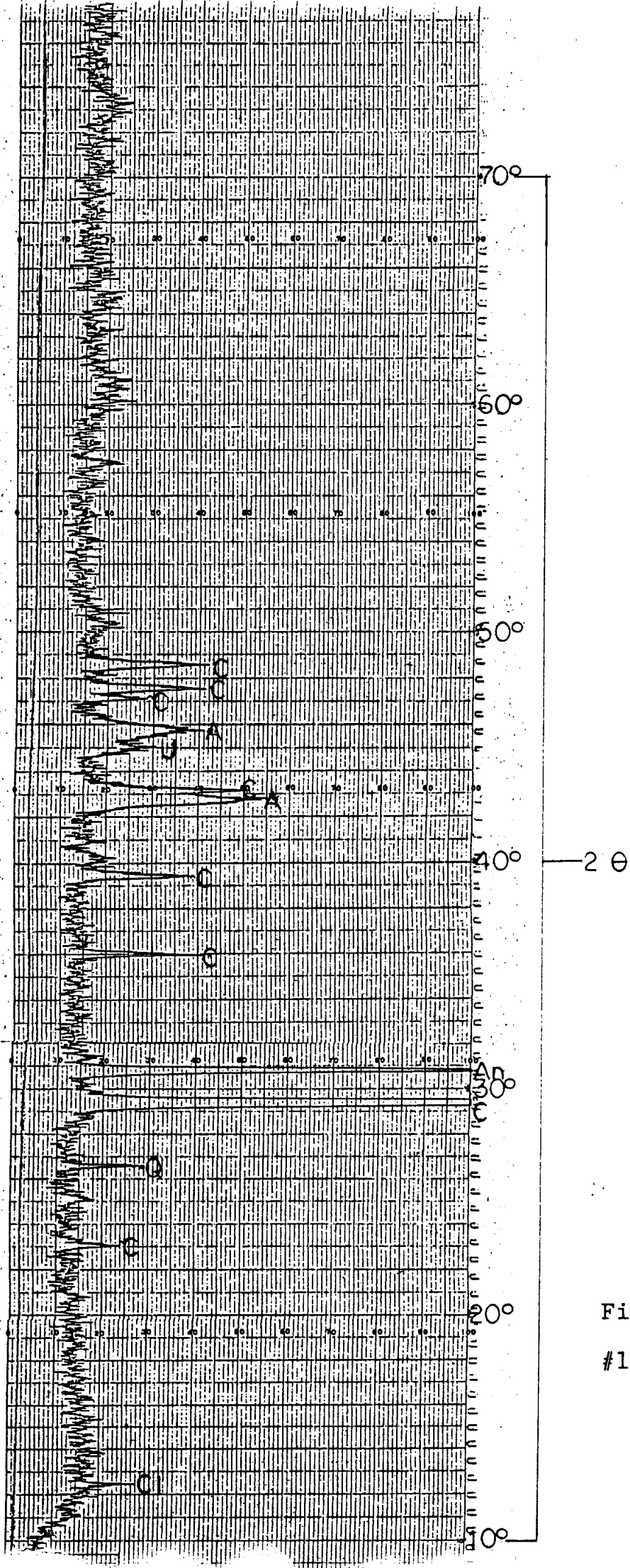


Figure 8.  
#10099



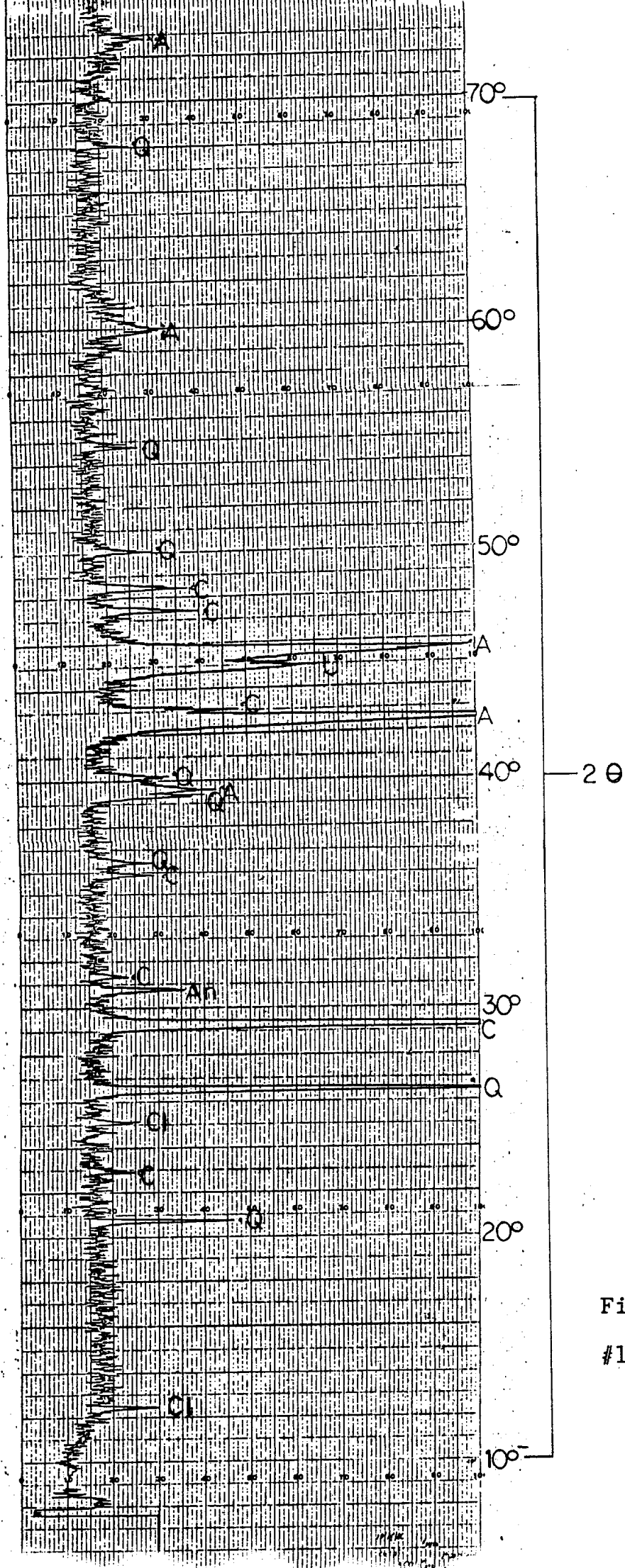


Figure 9.  
#10100



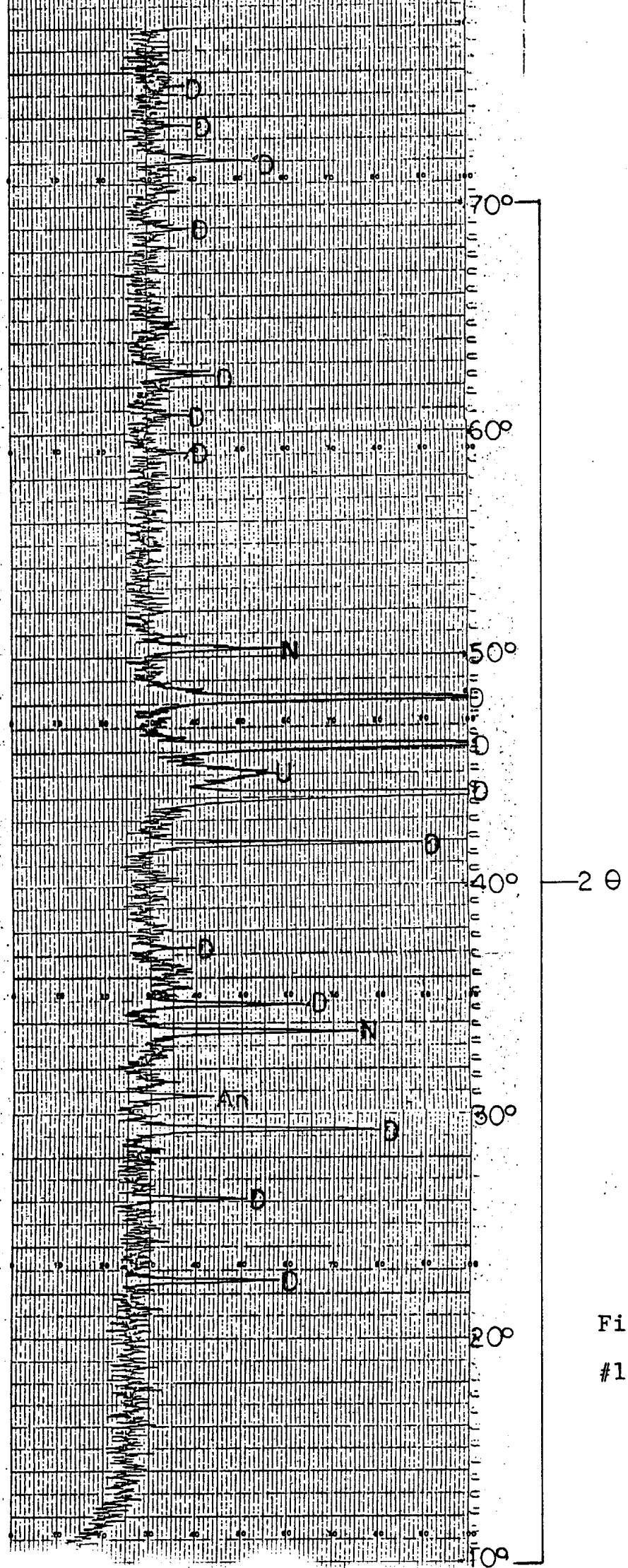


Figure 10.  
#10102

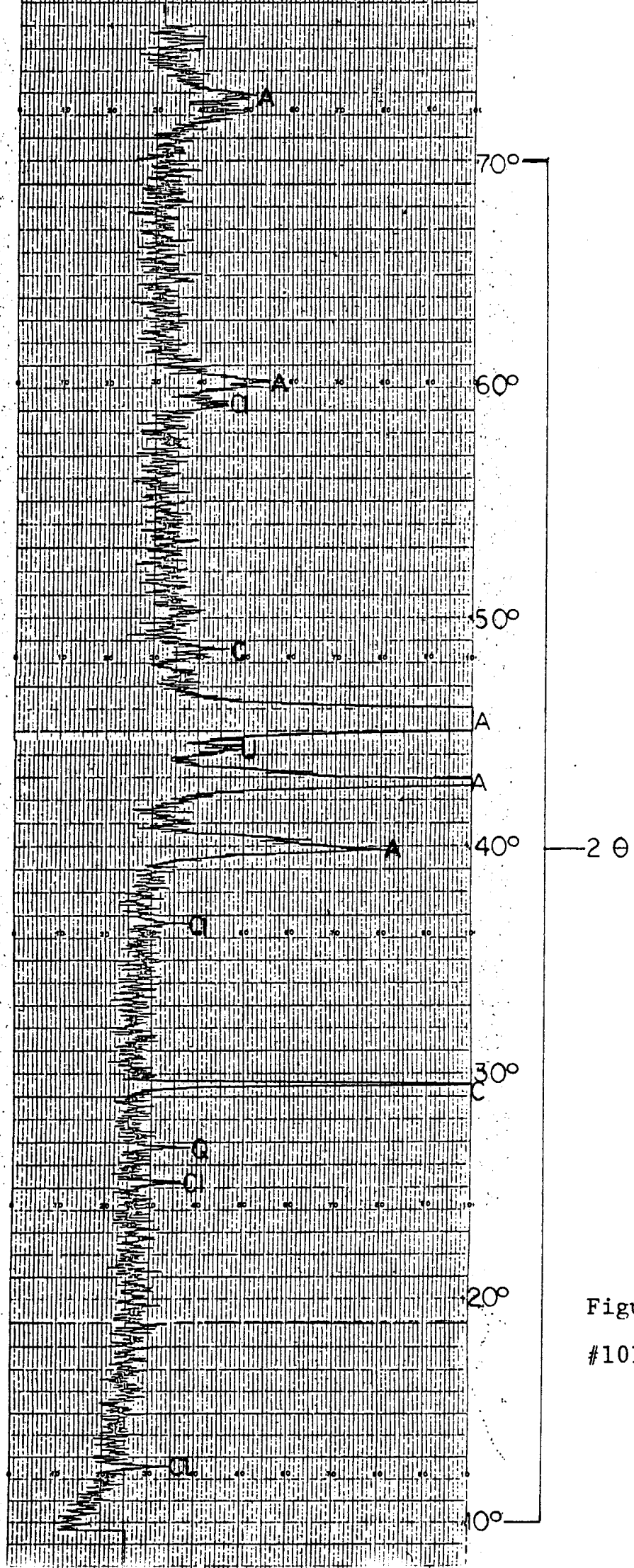


Figure 11.  
#10103

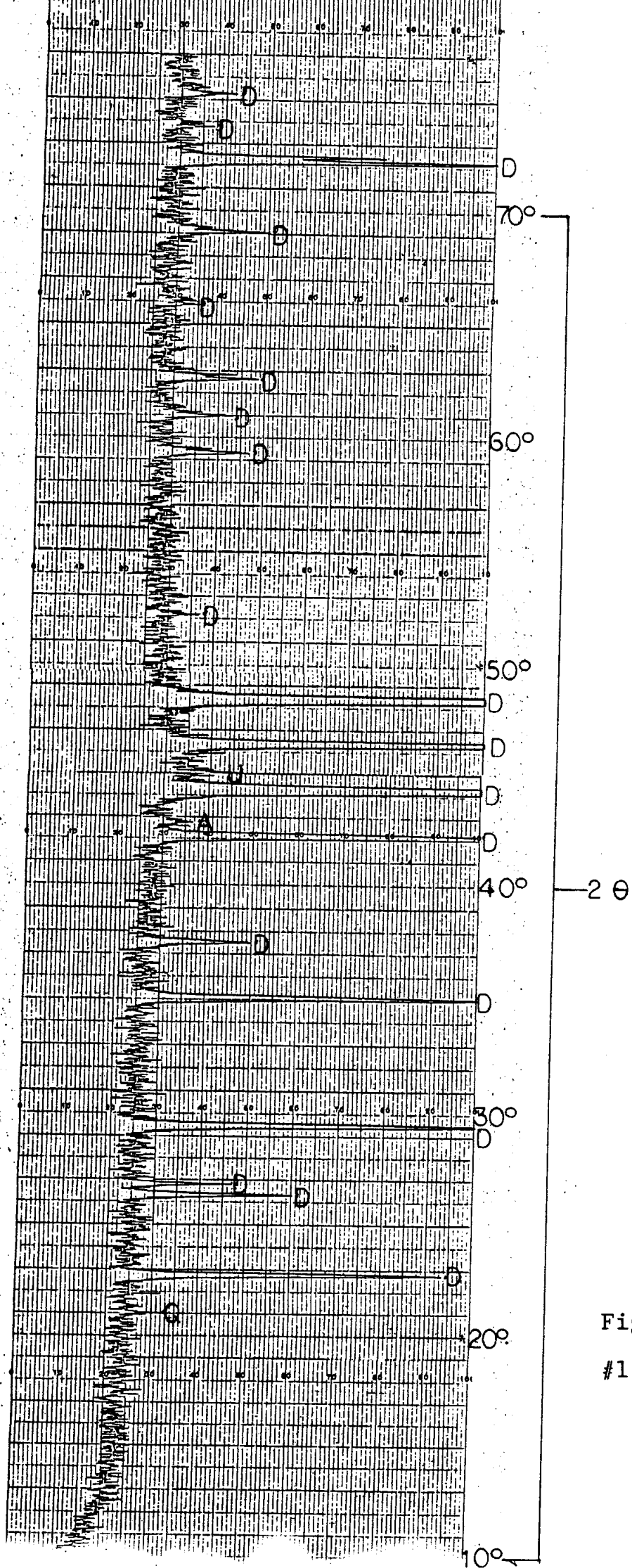


Figure 12.

#10105

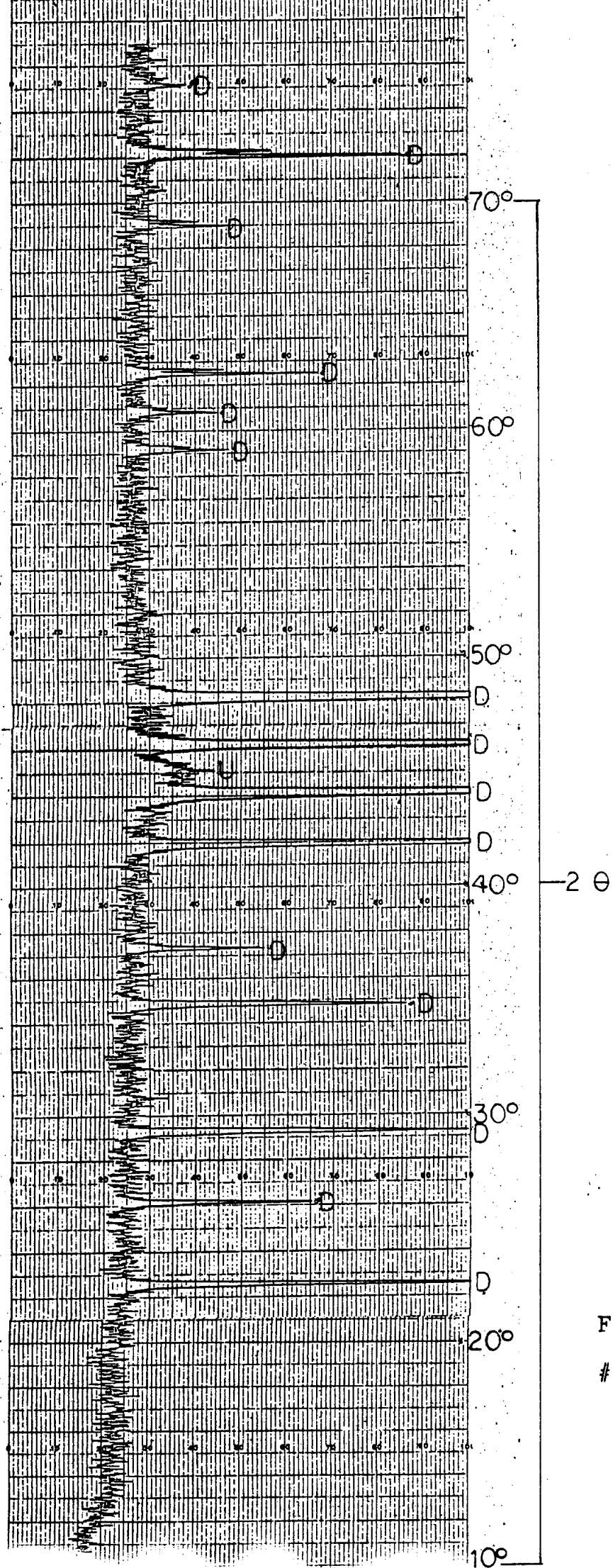


Figure 13.

#10106