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**BRANDSTOFNAVORSINGSINSTITUUT
VAN SUID-AFRIKA**

**FUEL RESEARCH INSTITUTE
OF SOUTH AFRICA**

ONDERWERP: INTERIM REPORT ON MINERAL MATTER IN COAL - THE
SUBJECT: _____

REACTIVITY OF THE MINERAL MATTER AT ROOM TEMPERATURE

CHEMISTRY

AFDELING: _____
DIVISION: _____

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TITLE : INTERIM REPORT ON MINERAL MATTER IN
COAL - THE REACTIVITY OF THE MINERAL
MATTER AT ROOM TEMPERATURE

ENQUIRIES TO : J L GAIGHER

SECTION : CHEMISTRY

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

REPORT NO. 36 OF 1977

INTERIM REPORT ON MINERAL MATTER IN COAL - THE REACTIVITY
OF THE MINERAL MATTER AT ROOM TEMPERATURE

SYNOPSIS:

The tendency to gypsum formation in the mineral matter obtained from coal by the radio-frequency oxidation method varies between different coals and may be a grain-size effect.

The inadequacy of the Institute's X-ray apparatus precluded convincing proof that reaction had occurred between the minerals as such, but indirect evidence indicates that calcium sulphate hydrates are not directly formed in the radio-frequency asher.

The enhanced reactivity of the mineral matter and hence the coal, caused by radio-frequency oxidation, may have a bearing on oil-from-coal studies.

INTRODUCTION:

The ash-forming part of coal, i.e. the mineral matter, plays a role in many aspects of the mining and utilization of coal.

Purely physical characteristics of the mineral matter e.g. hardness and abrasiveness, explain the damage caused to coal-milling and -burning appliances by minerals such as quartz and pyrite ¹⁾. Differences in density between coal and mineral matter have made the beneficiation of coal in the washing plant feasible. It is possible to predict the washability of coal from a knowledge of the type and grain-size distribution of the mineral matter in the coal ²⁾.

The chemical properties of the mineral matter in coal, however, are not so well known and have only recently been investigated, particularly from the point of view of their catalytic effect in the hydrogenation of coal ³⁾.

This report deals with the reactivity of mineral matter prepared from coal by the radio-frequency oxidation method. By the use of X-ray diffraction to detect mineral phase changes, possible reaction mechanisms are explored.

METHOD AND RESULTS

Four mineral matter samples were prepared from minus 150 µm (100 mesh) coal by the method of radio-frequency oxidation under standard conditions⁴⁾.

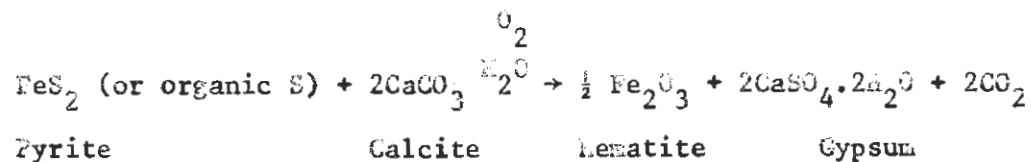
Without any further grinding, X-ray diffractometer traces were run on the mineral matter samples using Co-radiation (X-ray instrument settings are given in the appendix). From Figure 1, (appended to the report) the samples can be seen to have similar mineralogy with kaolinite (Al₂O₃·2SiO₂·2H₂O) the main constituent, followed by quartz (SiO₂), calcite (CaCO₃), pyrite (FeS₂) and subordinate dolomite-ankerite ((Ca, Mg, Fe).CO₃) and siderite (FeCO₃).

Five ml of distilled water were added to each of the mineral matter samples and they were allowed to dry at room temperature in a desiccator containing silica gel. This required three days. X-ray diffractometer traces were run on these treated samples. The results are shown in Figure 2. Except for the TNC sample, clear gypsum (CaSO₄·2H₂O) peaks occur at 13,55°2θ, and a smaller peak, partially overlapping with the calcite peak, occurs at about 34,2°θ.

The samples were then milled for two hours in methanol to reduce the grain size and the water treatment was repeated. Results of X-ray diffractometer traces on these samples are given in Figure 3. The milling has reduced the heights of the diffraction peaks indicating better statistics for particle orientations, and the major gypsum peak is now present on the diffractometer trace of the TNC sample as well.

DISCUSSION AND FURTHER EXPERIMENTS:

Ignoring any iron sulphates etc., as well as the intermediate reactions, sulphate formation under moist conditions can be summarized as follows:



Since the reaction product, gypsum, is known in different hydrated forms, the following tests were carried out to determine their stability relations:-

Figure 4a gives a diffractometer trace of a moistened gypsum reagent. No phase change or dehydration occurred when it was held in a desiccator for ten days (Figure 4b), but overnight drying in an air circulating oven at 100°C and radio-frequency ashing (gypsum mixed with graphite to simulate coal) resulted in the formation of bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), Figures 4c and 4d. The rehydration of bassanite to gypsum is easily accomplished by exposing the sample to 100 per cent relative humidity atmosphere (Figure 4e). By heating gypsum at 550°C for 1 hour it is converted to anhydrite (CaSO_4) (Figure 4f), which is stable to overnight moist atmosphere (Figure 4g), but rehydrates back to gypsum when water is added (Figure 4h).

It is also noteworthy that the main gypsum peak (at $13,6^\circ 2\theta$) is stronger by a factor of more than four, than the first bassanite peak (at $17,2^\circ 2\theta$) i.e. the detection threshold for gypsum in a sample is much lower than for bassanite.

As a further test, the milled mineral matter samples of Figure 3 were subjected to high temperature sulphur fixation. Figure 5A shows the results of heating the mineral matter samples at 450°C for 1 hour. Pyrite is decomposed to hematite (poorly defined peak at $38,7^\circ 2\theta$), and strong anhydrite (CaSO_4) peaks at $29,7^\circ 2\theta$ are present. By adding water, anhydrite is hydrated to gypsum (Figure 5B) and overnight drying at 100°C partially dehydrates gypsum to bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) (Figure 5C).

Referring to the previous section (Figures 1 - 3), it is evident that gypsum formed in the coal samples by either one or more of the following mechanisms:-

1. Gypsum or bassanite was originally present in the coal samples, and the former was merely dehydrated by the radio-frequency ashing to form bassanite. The addition of water rehydrated the bassanite to gypsum.

2. The calcium sulphate hydrates formed directly in the radio-frequency asher in the same way that high temperature sulphur fixation occurs in a ruffle furnace.
3. Gypsum formed by the reaction of the radio-frequency prepared mineral matter when water was added.

Some experiments were devised to test which of these three mechanisms was responsible for the gypsum formation in the coal samples.

Mechanism No. 1 original gypsum:

Samples of 2 g each of coal were milled in paraffin for 8 hours to reduce grain size i.e. improve particle orientation statistics and probably also increase any possible reactivity. Original gypsum should show on the diffractograms of the coal samples (Figure 6) which were made using a $\frac{1}{4}^{\circ}$ /minute scanning rate and a high recorder sensitivity.

The evidence is rather inconclusive. However, it can be stated that not enough gypsum was present in any of the coal samples to be positively detected by the Institute's diffractometer, although its presence is not excluded.

Mechanism No. 2 sulphate formation in the radio-frequency asher:

Figure 7 shows diffractometer traces of the coal samples after overnight radio-frequency oxidation under the standard conditions i.e. 200 watt power and 50 ml oxygen per minute. The positions where bassanite and anhydrite should appear on the diffractograms - indicating that sulphate formation had occurred during the radio-frequency ashing - is shown. Bearing in mind the poor detection threshold for these minerals compared with gypsum, the evidence is again not conclusive, although the presence of bassanite or anhydrite cannot be definitely ruled out.

In Figure 8, diffractometer traces are given of the radio-frequency ashed samples of Figure 7, left overnight in 100 per cent relative humidity atmosphere. The gypsum peak is clear in all of the samples, which is not necessarily explained by rehydration of undetected anhydrite or bassanite

in Figure 7, since reaction between the mineral phases could have occurred in the moist conditions.

Mechanism No. 3 reaction between the mineral phases:

Should sulphate formation at room temperature occur, one would expect the reaction to continue until the source of the sulphur, e.g. pyrite or the source of the calcium, e.g. calcite is exhausted. That is, it should be possible to follow the reaction by noting changes in the relative amounts of the mineral phases as the reaction proceeds.

Table I gives quantitative data for the various mineral phases. Relative diffraction peak intensities expressed as a percentage of the kaolinite peak intensity are shown for the milled mineral matter samples of Figure 3, after successive water treatments.

TABLE I RELATIVE DIFFRACTION PEAK INTENSITIES

	K*	% of kaolinite peak intensity					
		Q	G	C	D-A	S	P
<u>2nd water treatment</u>							
Delmas	100	166	23,9	18,8	12,9	5,6	25,3
TNC	100	101	8,4	15,9	27,1	14,8	10,0
Coalbrook	100	59,5	52,2	28,8	8,6	15,2	16,7
Tavistock	100	6,2	17,3	24,8	12,2	2,1	12,3
<u>3rd water treatment</u>							
Delmas	100	188	30,4	22,5	14,2	10,8	27,1
TNC	100	94,6	6,7	18,0	29,3	10,6	10,5
Coalbrook	100	59,4	22,8	33,5	4,7	13,3	11,5
Tavistock	100	12,6	23,4	23,4	13,9	6,9	13,8

Note: * K = kaolinite, Q = quartz, G = gypsum, C = calcite,
 D-A = dolomite-ankerite, S = siderite and P = pyrite.

It is evident that the X-ray data are unreliable and that trends, if any, cannot be discerned. This is also shown by the mass proportions (method explained in the appendix) recalculated to 100 per cent given in Table II.

TABLE II MASS PROPORTIONS RECALCULATED TO 100 PER CENT

	K	Q	Mass %		D-A	S	P
			G	C			
<u>2nd water treatment</u>							
Delmas	63,9	14,9	10,4	3,1	1,8	0,6	5,3
TNC	73,5	10,4	4,2	3,1	4,4	2,0	2,4
Coalbrook	61,8	5,1	22,1	4,6	1,2	1,8	3,4
Tavistock	79,2	0,7	9,5	5,1	2,1	0,3	3,1
<u>3rd water treatment</u>							
Delmas	59,8	15,8	12,5	3,5	1,9	1,2	5,3
TNC	74,4	9,8	3,4	3,5	4,8	1,5	2,6
Coalbrook	71,5	6,0	11,1	6,3	0,7	1,8	2,6
Tavistock	75,3	1,3	12,1	4,7	2,3	0,9	3,4

In order to explain the poor X-ray data, a further experiment was carried out. Since X-ray quanta detected by the proportional counter obey the laws of statistics ⁵⁾, the standard deviation (σ) can be calculated when the number of quanta counted is known. This is not possible for the rate-meter deflections from which the data given in Tables I and II were calculated. However, a diffractometer trace was run under the same conditions as for the quantitative data, and the X-ray quanta counted at the same time. By means of a planimeter the unit area on the chart recording proportional to a certain number of counts could be calculated, and in Table III relative standard deviations for the Delmas sample, are given.

TABLE III COUNTING STATISTICS FOR THE DELMAS SAMPLE
(3rd water treatment)

	Total Counts (N_T)	Background Counts (N_{Br})	σ^* %	3 σ %
Kaolinite	13077	9472	4,2	12,5
Quartz	11698	5714	2,2	6,6
Gypsum	3414	2685	10,7	32,1
Calcite	2416	2148	25,2	75,6
Dolomite-Ankerite	5830	4449	7,3	22,0
Siderite	4142	3567	15,3	45,8
Pyrite	4104	3145	8,9	26,6

NOTE: * Relative standard deviation $\sigma\% = 100 \frac{(N_T + N_{Br})^{\frac{1}{2}}}{N_T - N_{Br}}$

It is obvious that the X-ray tube output is far too low by modern standards. To reduce σ , more X-ray quanta must be counted, which requires a period of time proportional to $\frac{1}{2}$ e.g. the data for the X-ray trace tabulated above required 48 minutes (excluding time needed for measurement and calculation) and to reduce σ of kaolinite to about 1 per cent it would be necessary to repeat the run about 16 times, a procedure which would require more than 12 hours; and even so, the counting statistics (σ) for the calcite peak would only be improved to about 6,3 per cent.

A final test - indirect evidence

Since the X-ray facilities were inadequate for direct proof of which mechanism was responsible for the sulphate formation in the coal samples, a final test was carried out.

In Figure 7 diffractometer traces of coal subjected to radio-frequency ashing were given (bassanite and anhydrite doubtful or absent) and in Figure 8, the same samples after exposure to moist atmosphere (clear gypsum

peaks present). If the samples of Figure 8, after drying at 100°C, are different from those of Figure 7, then an irreversible reaction must have taken place in the moist atmosphere, i.e. a reaction other than the re-hydration of bassanite must have occurred.

Results are shown in Figure 9. Clear bassanite peaks are present in all the diffractometer traces. Thus an irreversible reaction must have occurred due to the reaction of the moist atmosphere with the mineral matter samples.

Two irreversible reactions are possible. The rehydration of anhydrite below 200°C is one, and the reaction between the mineral phases is another. In both cases the end product is gypsum.

Granted that anhydrite is unlikely to form at the relatively low temperature of the radio-frequency ashing i.e. less than 200°C⁴, and it is reasonably stable to moist atmosphere - overnight exposure resulted in no detectable change (Figure 4g) - the gypsum formation could only have occurred by reaction between the mineral phases i.e. mechanism 3.

The position regarding the source of the sulphur requires some explanation. In high temperature sulphur fixation, pyrite is oxidized to hematite (Figures 5A-C) which is also shown by the reddish colour of ashed coal. However, tests have shown that pyrite remains unaffected when radio-frequency ashing is carried out at the low power of 200 watt. This radio-frequency ash readily forms gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) when it comes into contact with moisture, but no hematite was noted on any of the diffractograms (e.g. Figures 2, 3, 8 and 9), although it would be difficult to detect, being overlapped by pyrite as well as gypsum peaks.

Since sulphur is not supplied by the pyrite, some of the organic sulphur must have been mobilized by the radio-frequency ashing, and held in the ash until the addition of water allowed gypsum to form.

In order to determine whether Ca is supplied by the calcite, some further tests would have to be carried out viz. pH measurements to determine whether sulphuric acid had formed.

An "acid activity" index for radio-frequency ashed mineral matter, possibly determined in the same way that clays have been characterized ⁶⁾ could be a very useful parameter in defining the role the mineral matter plays in the reactions of coal, e.g. hydrogenation.

Since the radio-frequency ashing certainly makes the mineral matter more reactive, it would be interesting to determine whether partially radio-frequency ashed coal is also more reactive e.g. in oil-from-coal processes.

SUMMARY AND CONCLUSIONS:

Water added to the mineral matter prepared from coal by the radio-frequency oxidation method caused gypsum to be formed in three samples (Coalbrook, Delmas and Tavistock), but not in the fourth sample.

After a milling period, the further addition of water caused gypsum to be formed in the fourth sample (TNC) as well.

Due to the inadequacy of the Institute's X-ray apparatus no direct evidence could be furnished as to whether:-

- (i) CaSO_4 or its hydrates were originally present in the samples.
- (ii) Sulphate formation had occurred during the radio-frequency oxidation, the addition of water merely rehydrating anhydrite or bassanite to gypsum.
- (iii) Sulphate formation is due to the reactivity of the radio-frequency prepared mineral matter itself.

Milled coal samples which were partially radio-frequency ashed and then hydrated and subsequently dehydrated provided indirect proof that an irreversible reaction had occurred due to the moist atmosphere, which is favoured by explanation (iii).

The designation of an "acid activity" index to radio-frequency prepared mineral matter, or even the effect of partial radio-frequency ashing on coal, may be a fruitful field for study in increasing the yield in oil-from-coal processes.

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SENIOR RESEARCH OFFICER

PRETORIA
1977 24th May
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Appendix - X-ray conditions

All the X-ray work was carried out using the Institute's 16 year old diffractometer and X-ray generator (Kristalloflex 4). Iron-filtered cobalt radiation was used near the maximum rating of the X-ray tube i.e. 30 kV x 14 mA. A sealed proportional counter water cooled to 20°C was used as detector and the valve type measuring electronics were stabilized as far as possible with a Wandel and Goltermann W5-6 alternating current stabilizer. Instrument settings for the various figures are as follows:-

Figure	Detector scanning gate /min	Ratemeter scale setting cpm	Damping error %	Time constant sec.	Chart speed mm/hr.
1-3	1	10^4	3	3,4	600
4	1	4×10^4	$1\frac{1}{2}$	3,4	300
5-9	$\frac{1}{2}$	4×10^3	2	19	150

* cpm: counts per minute.

The quantitative data for Tables I and II were measured from the chart recordings between 28 to 40 °2θ using the same X-ray conditions as for Figures 5 - 9, except that rate meter scale settings had to be increased to 10^4 cpm at $1\frac{1}{2}$ per cent error for a time constant of 13,4 seconds to accommodate the stronger peaks which left the chart at the more sensitive setting of 4×10^3 cpm..

For the data of Table III, the baseline was carefully adjusted and chart speed increased to 600 mm/hr. (40 mm = 1 °2θ) for 10^4 cpm at $1\frac{1}{2}$ per cent error, with a detector scanning speed of $\frac{1}{2}$ °/minute. The calculated unit area was $1 \text{ mm}^2 = 3,835$ counts.

A2

For the quantitative data of Table II, use was made of Chung's "matrix flushing" concept⁷⁾. Since no internal standard was added, only the mass proportions of the minerals relative to each other could be determined and recalculated to 100 per cent, using the following relationship:

$$X_i = \left(\frac{K_i}{I_i} \sum_{j=1}^n \frac{I_j}{K_j} \right)^{-1}$$

where X_i is the mass proportion

I_i is the diffraction peak intensity

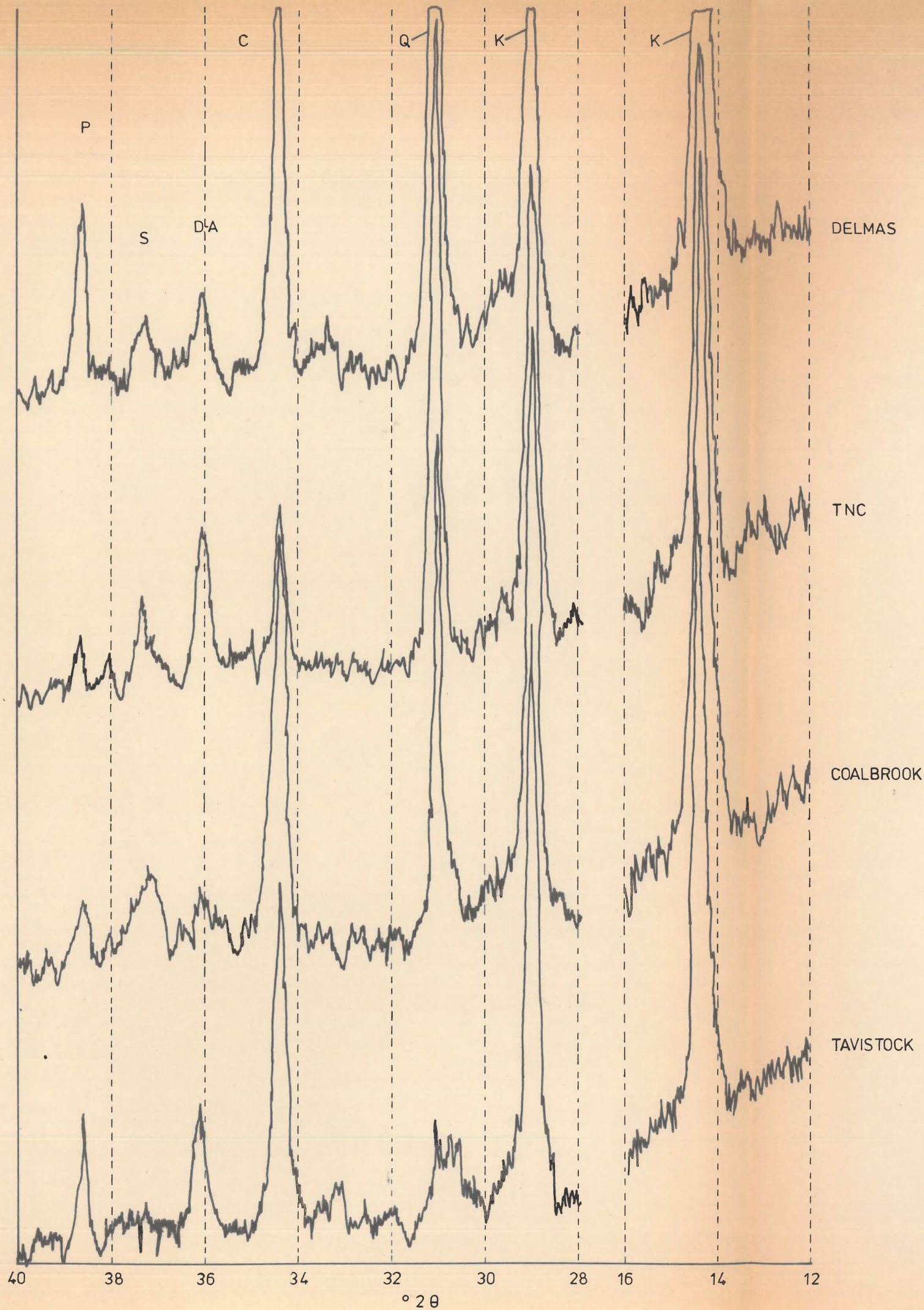
and K_i is the reference intensity.

The reference intensities were determined relative to the 3,5⁰ A d-spacing of corundum ($\alpha - Al_2O_3$) and were as follows:

Mineral	Reference Intensity - K_i
Kaolinite	1,28
Quartz	9,12
Gypsum	1,87
Calcite	4,89
Siderite	6,66
Pyrite	3,91

For dolomite-ankerite the average reference intensity between calcite and siderite was used i.e. 5,78.

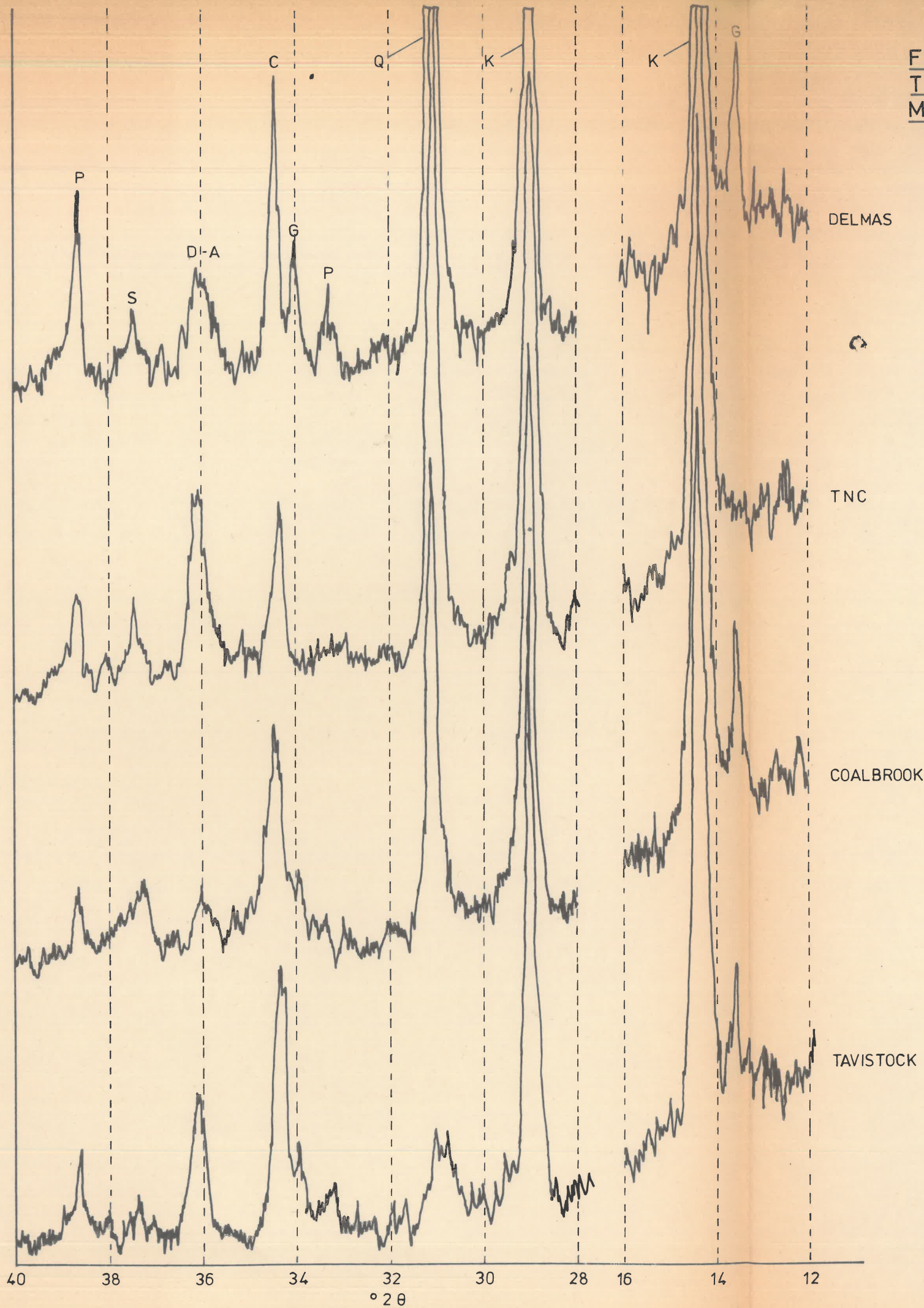
FIGURE 1 DIFFRACTOMETER TRACES OF MINERAL MATTER PREPARED FROM COAL.



K=KAOLINITE
Q=QUARTZ
C=CALCITE
D-A = DOLOMITE -ANKERITE
S=SIDERITE
P=PYRITE

VERTICAL SCALE : 1mm=417 c.p.m.
HORIZONTAL SCALE : 10mm=1°2θ

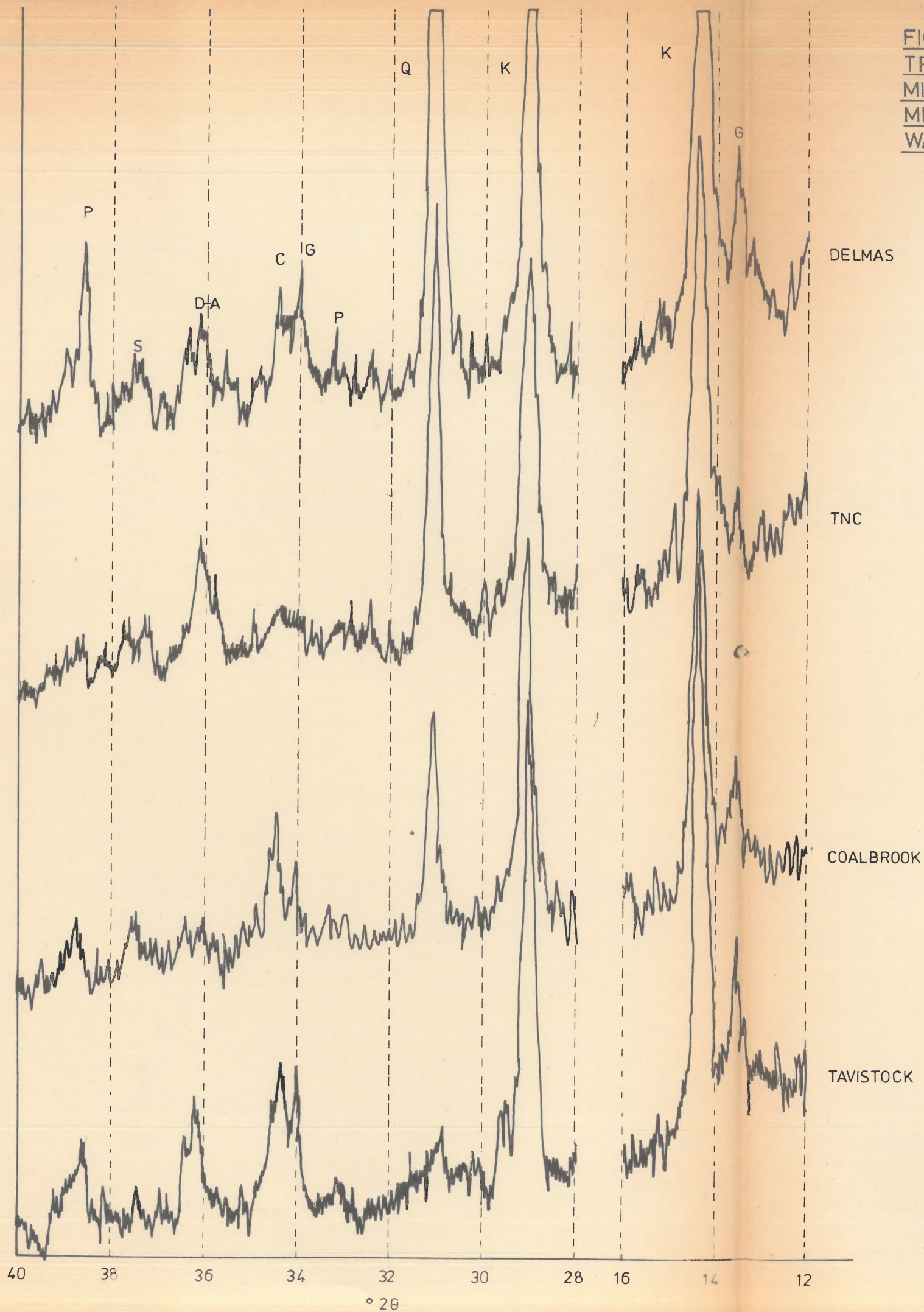
FIGURE 2. DIFFRACTOMETER TRACES OF WATER TREATED MINERAL MATTER SAMPLES.



K=KAOLINITE
 Q=QUARTZ
 C=CALCITE
 D-A=DOLOMITE -ANKERITE
 S=SIDERITE
 P=PYRITE
 G=GYPSUM

VERTICAL SCALE : 1 mm = 417 c.p.m.
 HORIZONTAL SCALE : 10 mm = 1° 2θ

FIGURE 3 DIFFRACTOMETER TRACES OF WATER TREATED MINERAL MATTER SAMPLES MILLED FOR 2 HOURS AND WATER ADDED.

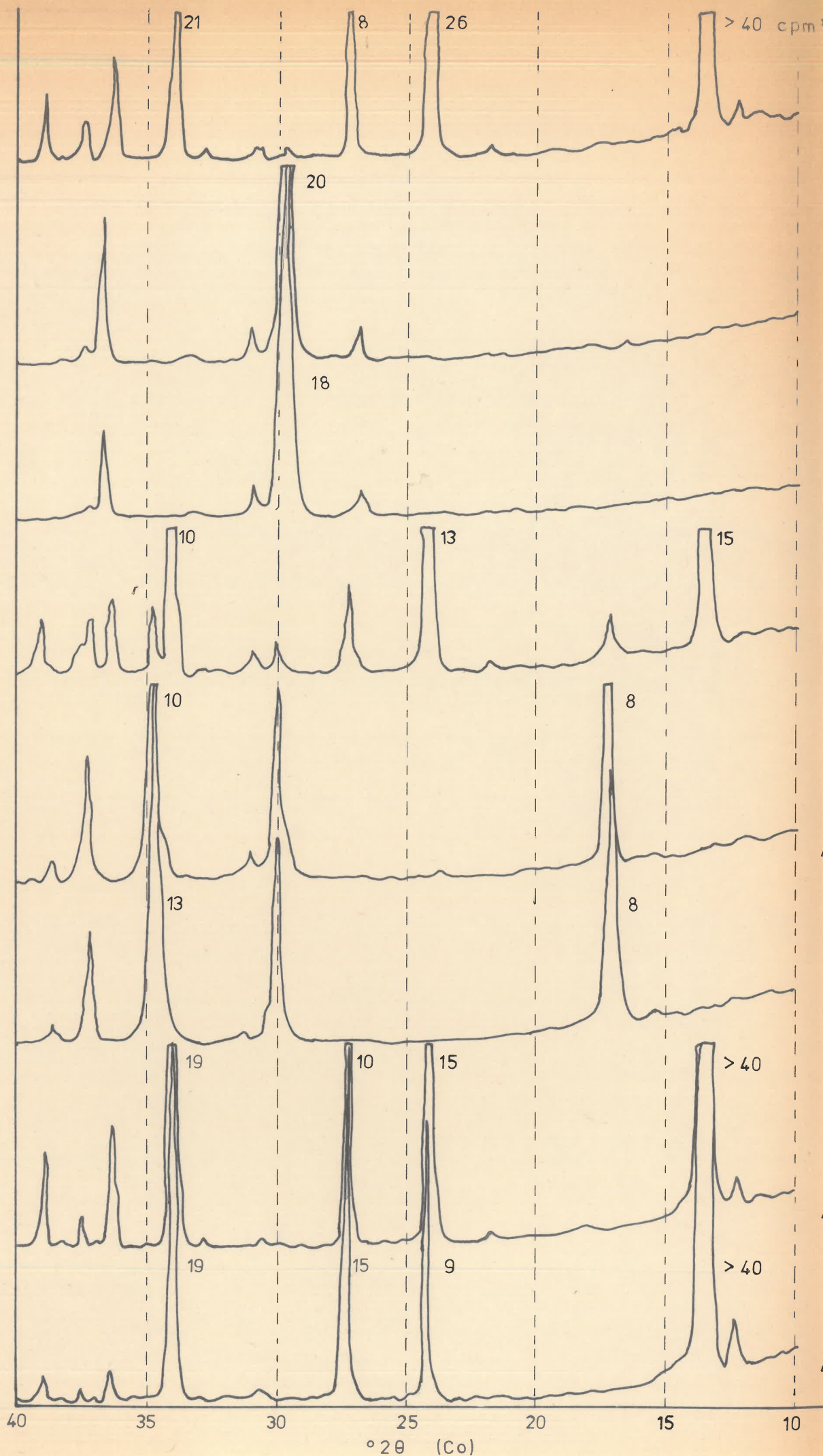


K=KAOLINITE
 Q=QUARTS
 C=CALCITE
 D-A=DOLOMITE-ANKERITE
 S=SIDERITE
 P=PYRITE
 G=GYPSUM

VERTICAL SCALE : 1mm=41,7 cpm.

HORIZONTAL SCALE 10mm= $1^{\circ} 2\theta$

FIGURE 4 DIFFRACTOMETER TRACES
STABILITY RELATIONS OF HYDRATED CaSO_4

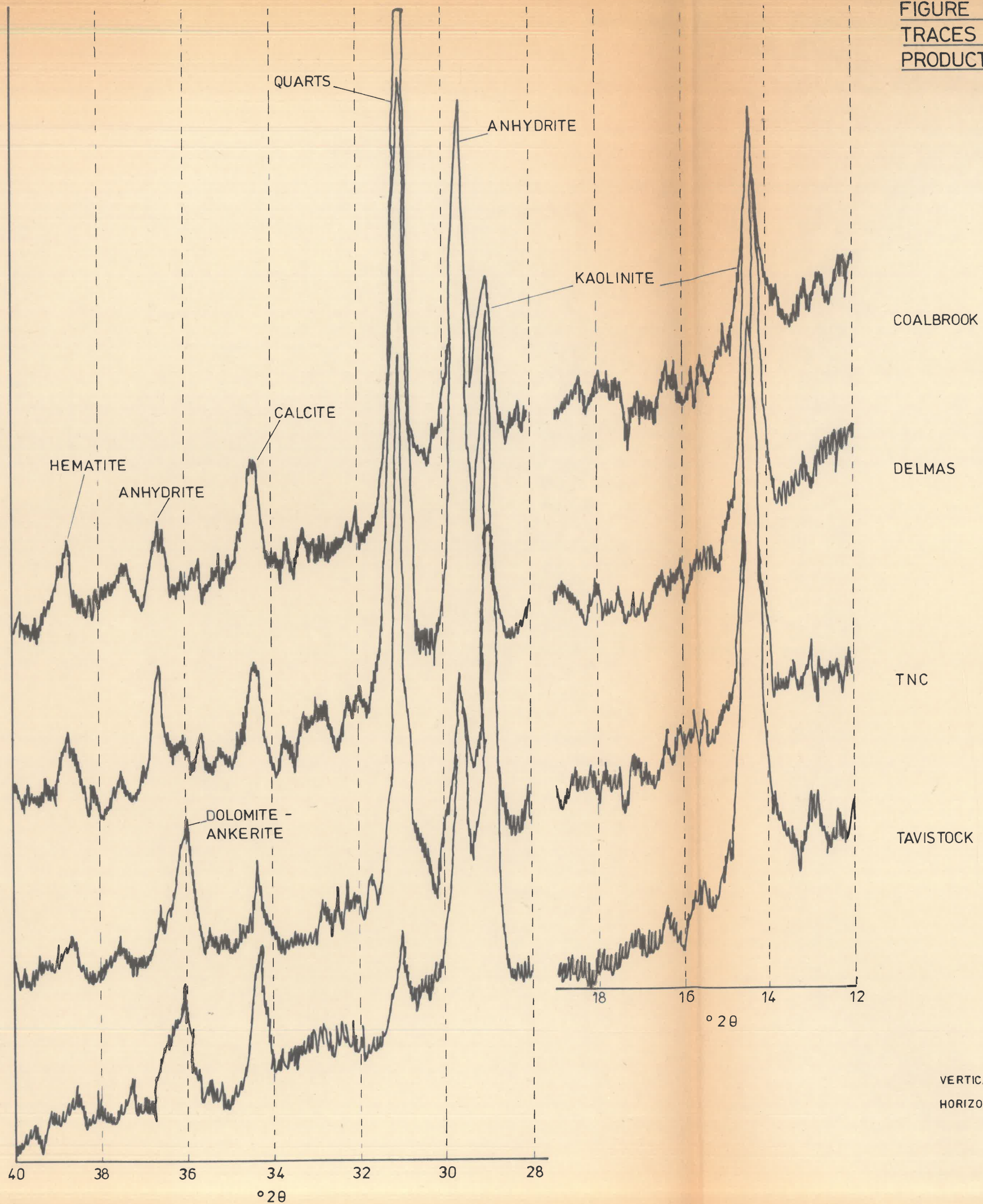


- 4h ANHYDRITE TREATED WITH WATER = GYPSUM
- 4g ANHYDRITE HELD IN MOIST ATMOSPHERE OVERNIGHT
- 4f GYPSUM HEATED 550°C FOR 1 hr = ANHYDRITE
- 4e BASSANITE HELD IN MOIST ATMOSPHERE OVERNIGHT = GYPSUM
- 4d GYPSUM RADIO-FREQUENCY ASHED WITH GRAPHITE = BASSANITE.
- 4c GYPSUM DRIED AT 100 °C OVERNIGHT = BASSANITE
- 4b GYPSUM HELD IN DISICCATOR FOR 10 DAYS
- 4a MOISTENED GYPSUM

* cpm = COUNTS PER MINUTE $\times 10^3$

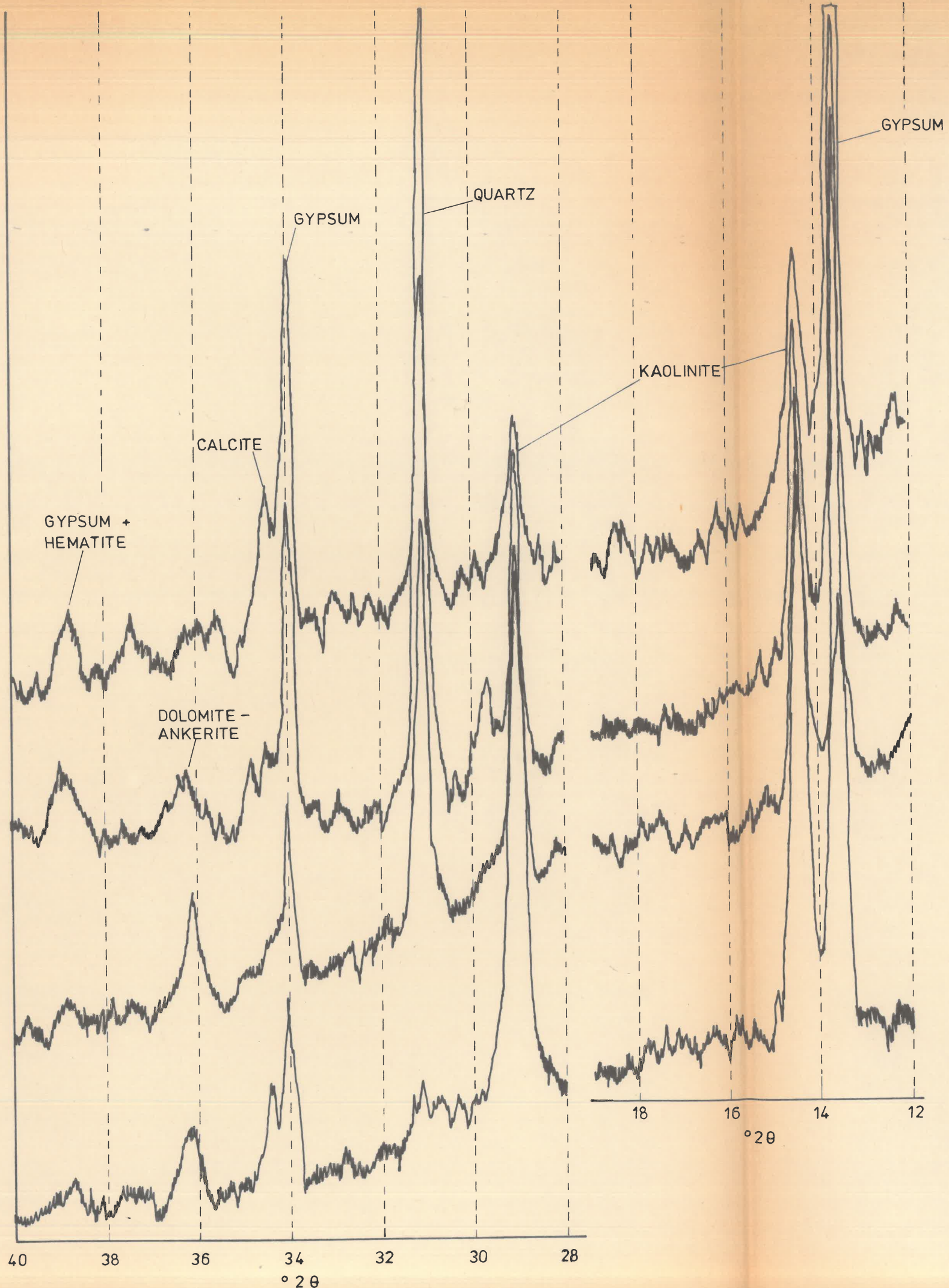
VERTICAL SCALE : 1mm = 167 c.p.m.
HORIZONTAL SCALE : 10 mm = 2° 2θ

FIGURE 5A DIFFRACTOMETER
TRACES SULPHUR FIXATION
PRODUCTS UNHYDRATED.



VERTICAL SCALE : 1 mm = 167 c.p.m.
HORIZONTAL SCALE : 10 mm = $1^\circ 2\theta$

FIGURE 5B. DIFFRACTOMETER TRACES SULPHUR FIXATION PRODUCTS - FULLY HYDRATED.



COALBROOK

DELMAS

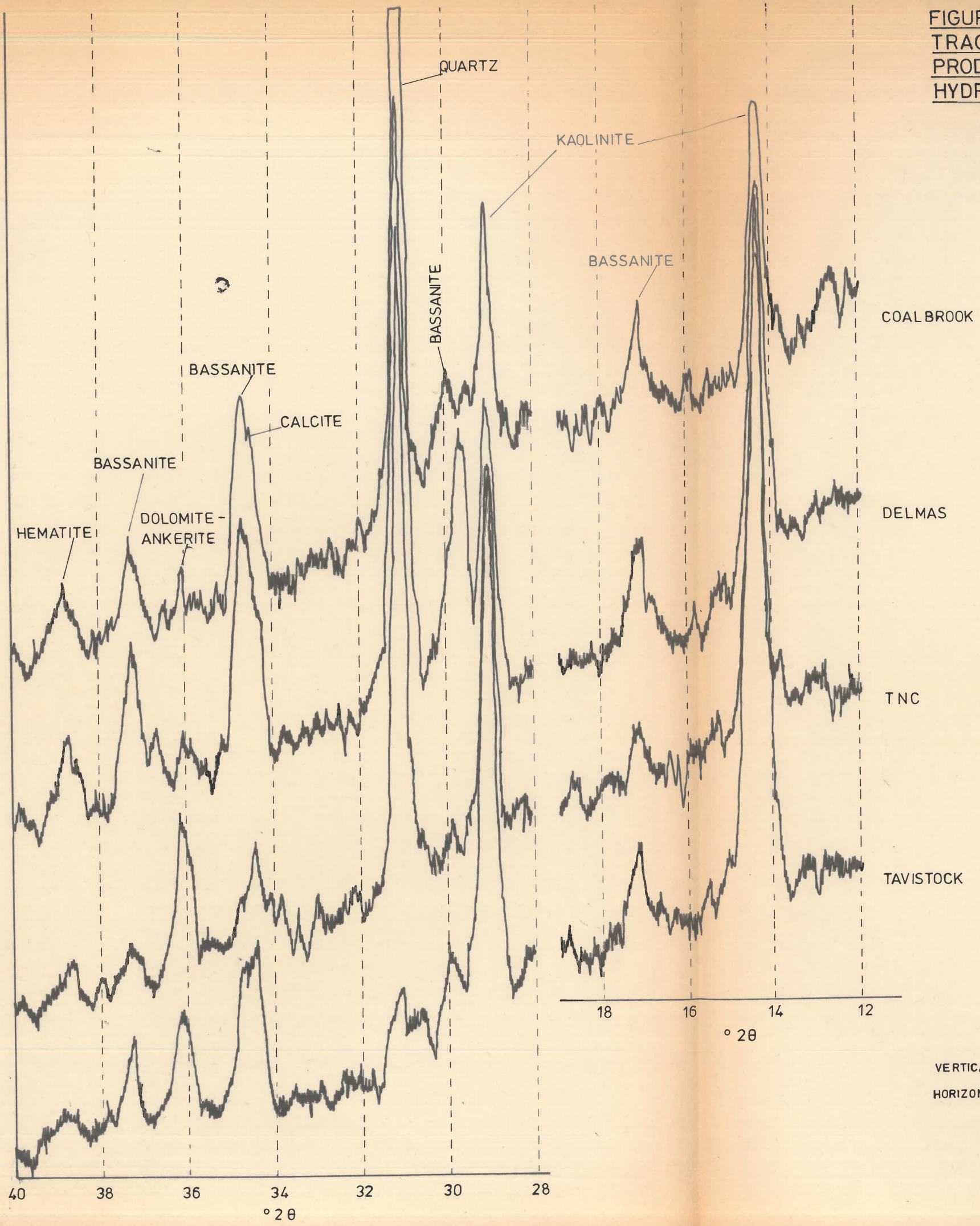
TNC

TAVISTOCK

VERTICAL SCALE : 1 mm = 16,7 c.p.m.

HORIZONTAL SCALE : 10 mm = 1° 2θ

FIGURE 5C. DIFFRACTOMETER TRACES SULPHUR FIXATION PRODUCTS - PARTIALLY HYDRATED.



VERTICAL SCALE: 1mm = 167 c.p.m.
 HORIZONTAL SCALE: 10 mm = $1^\circ 2\theta$

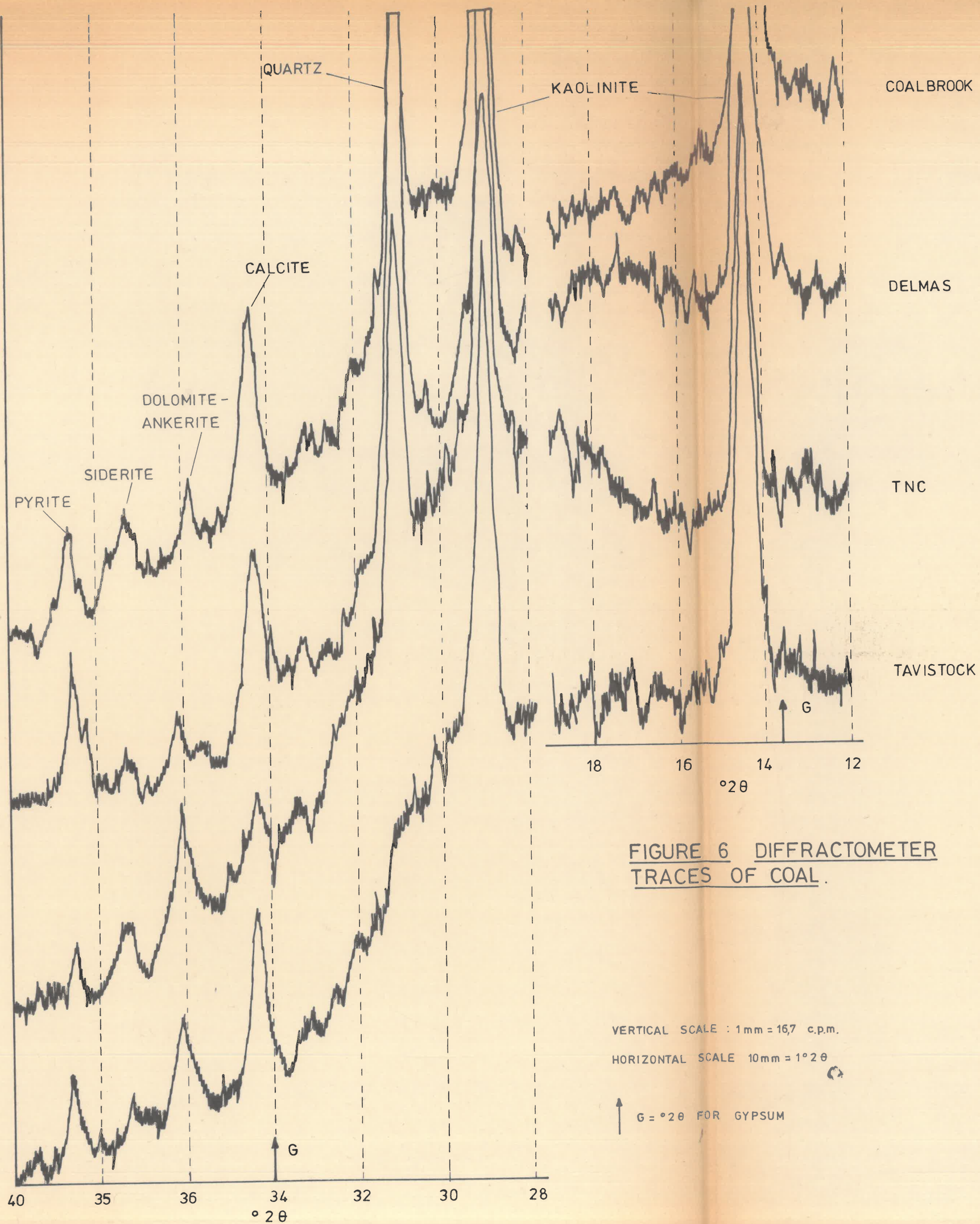
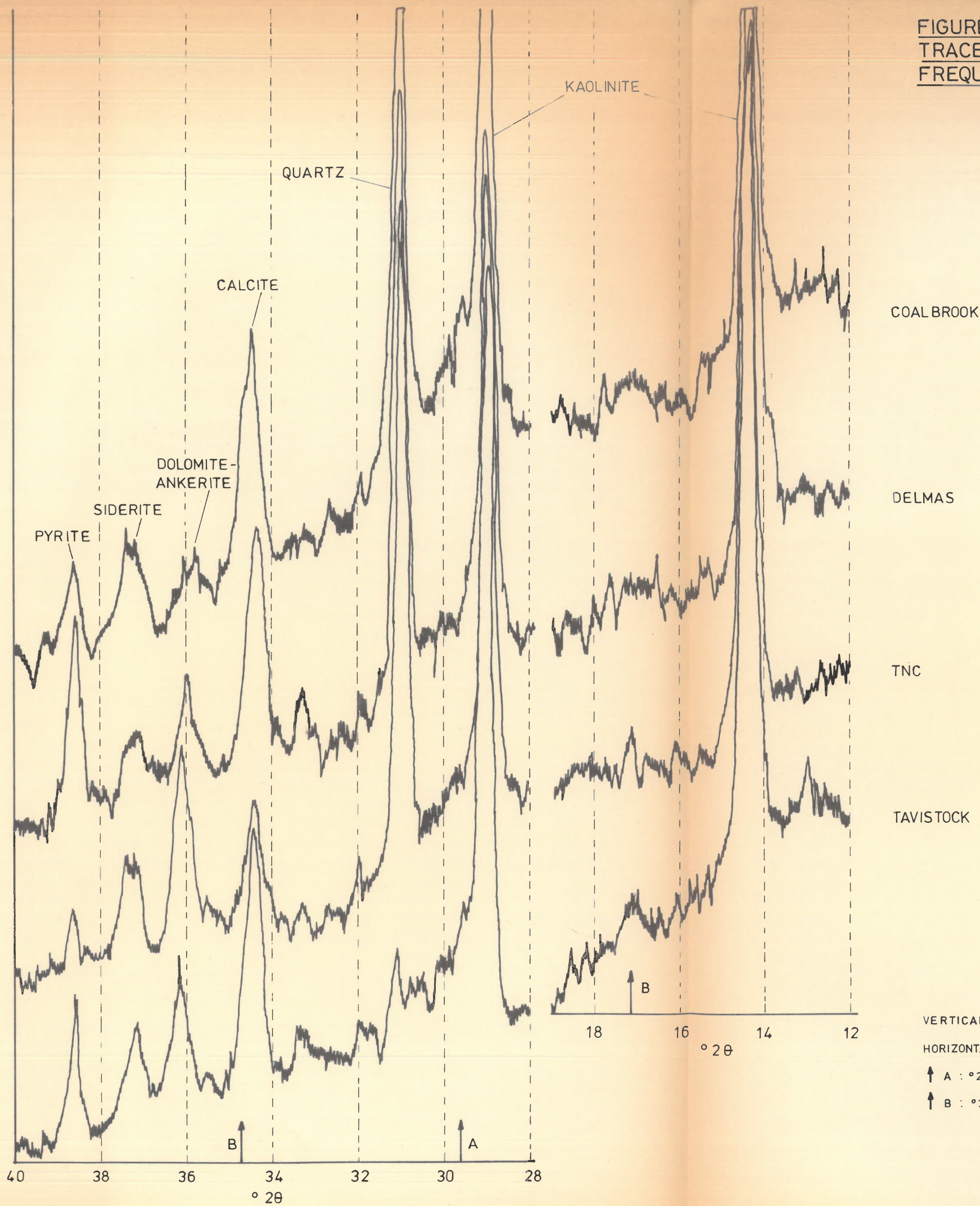


FIGURE 6 DIFFRACTOMETER TRACES OF COAL.

FIGURE 7 DIFFRACTOMETER TRACES OF COAL RADIO - FREQUENCY ASHED 'OVERNIGHT



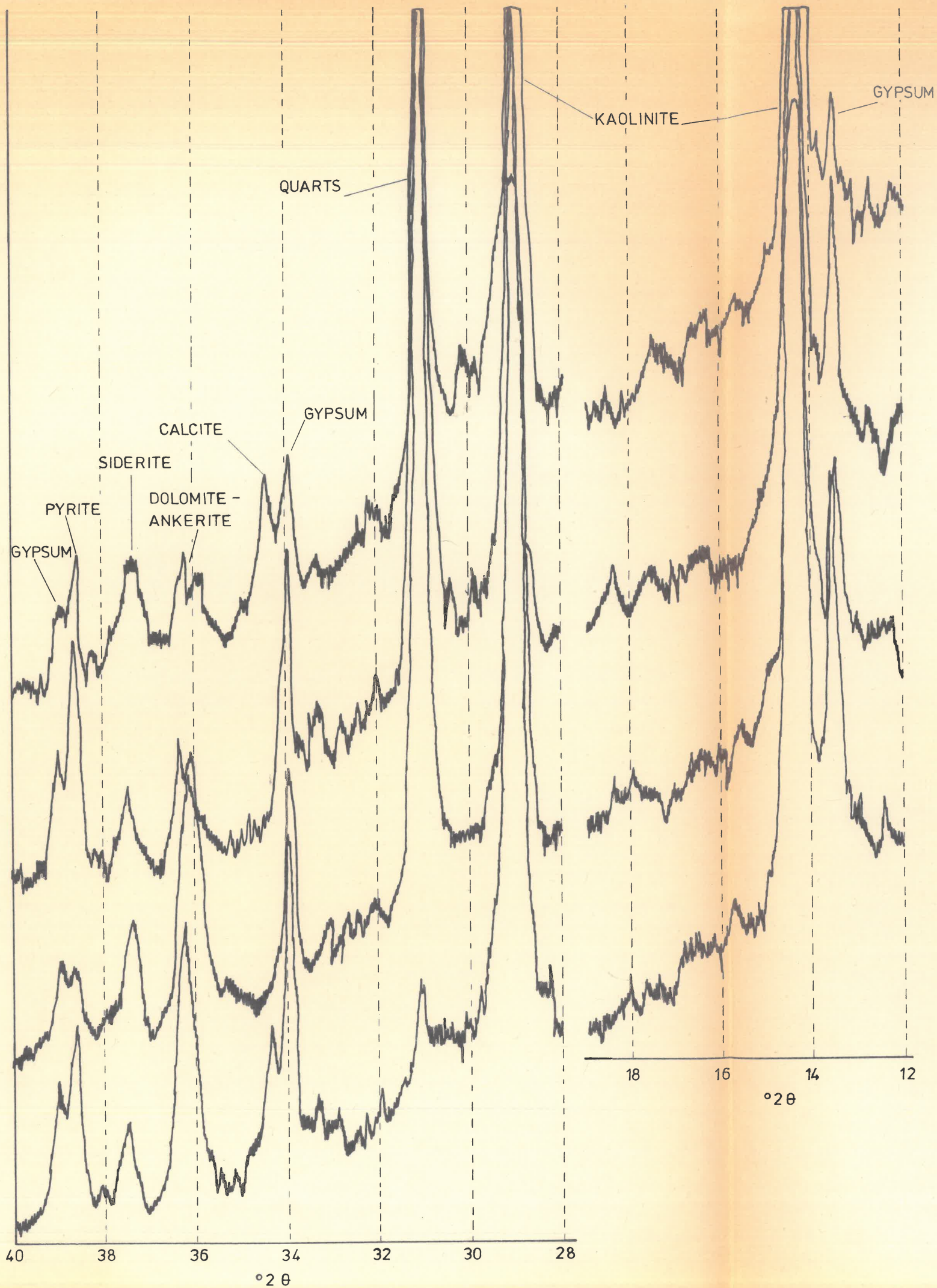
VERTICAL SCALE : 1mm = 167 c.p.m.

HORIZONTAL SCALE : 10 mm = $1^\circ 2\theta$

↑ A : 2θ FOR ANHYDRITE

↑ B : 2θ FOR BASSANITE

FIGURE 8. DIFFRACTOMETER TRACES RADIO-FREQUENCY ASHED COAL LEFT IN MOIST ATMOSPHERE OVERNIGHT.



COALBROOK

DELMAS

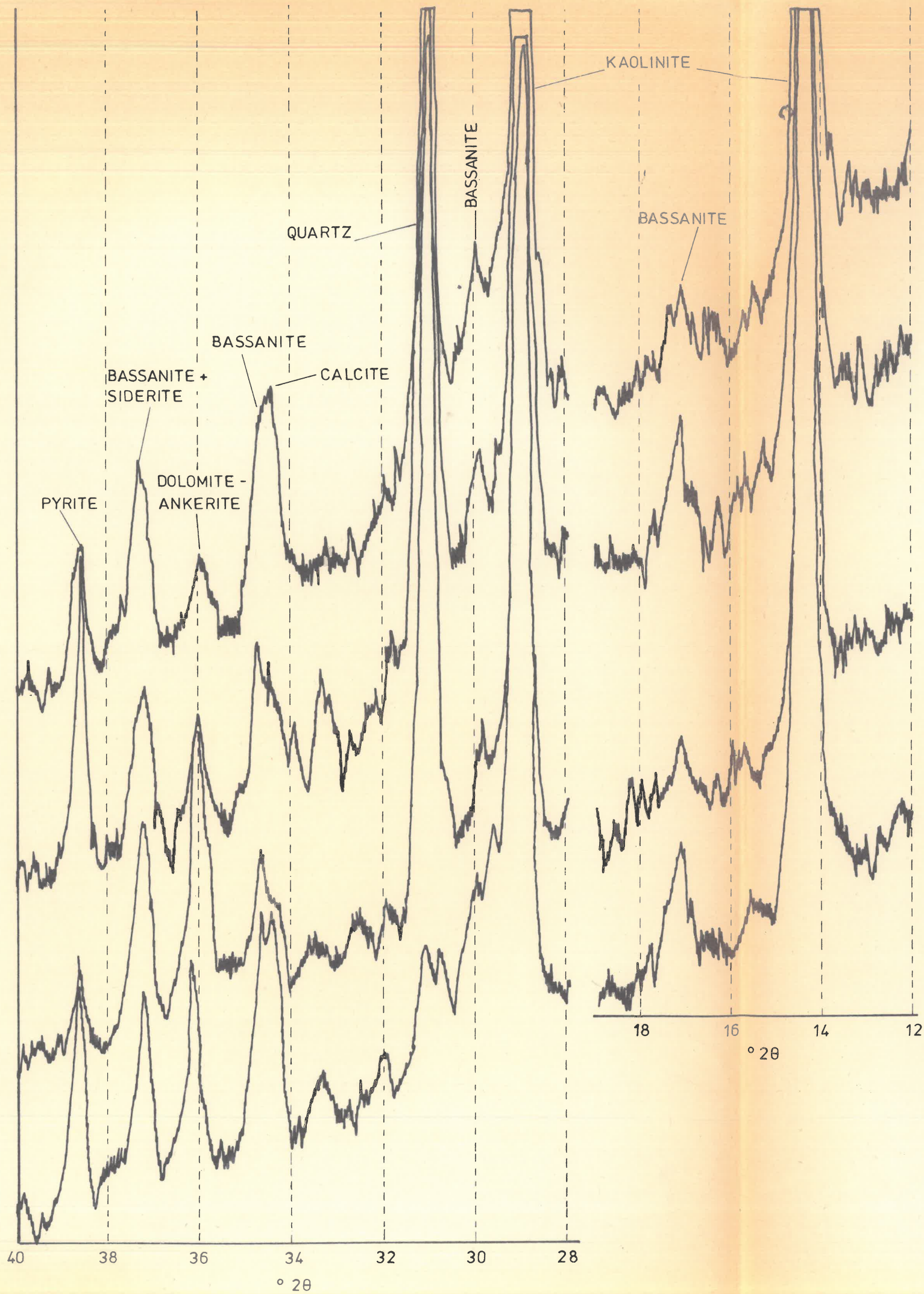
TNC

TAVISTOCK

18 16 14 12
°2θ

VERTICAL SCALE : 1mm = 167 c.p.m.
HORIZONTAL SCALE : 10 mm = 1° 2θ

FIGURE 9. DIFFRACTOMETER TRACES RADIO-FREQUENCY ASHED COAL, LEFT IN MOIST ATMOSPHERE, THEN DRIED AT 100°C.



COALBROOK

DELMAS

TNC

TAVISTOCK

VERTICAL SCALE: 1 mm = 167 c.p.m.

HORIZONTAL SCALE: 10 mm = $1^\circ 2\theta$