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**INHIBITION OF ACID GENERATION
USING PHOSPHATE ROCK
PROJECT # 257140**

Final Report

Supported by

NRC/Tech

January 15th, 1996

Final report on project # 257140
Supported by NRC/Tech

Under this program in the summer of 1995 the following task were to be achieved.

Base metal waste rock - inhibition of Acid generation

1. Take down of waste rock drums which had received phosphate rock treatment and were monitored for effluent quality for a total of 700 days. During dismantling, data was collected by the students on pyrite content, surface area of rocks, particle size and description were made on the presence or absence of surface coatings.

This data has been summarized and was submitted to NRC as part of the last progress report.

2. Rocks from the drums were preserved in 1 % glutaraldehyde for the examination of secondary precipitates on the surfaces of the rocks. Samples were prepared for SEM EDX analysis. Based on the examination of control samples, it was generally found that no phosphate could be detected in the spectra. Control samples from 3 types of rock, at the differing weathering stages have been investigated using SEM EDX. One of the types (low pyrite fresh waste rock) with two treatments (phosphate rock on top or throughout the drum) of phosphate rock have been investigated.

A good phosphate signal was observed A-3 (phosphate treatment in top part of drum) in the sample collected from the bottom of the drum. This signal was not as strong in the treatment A -2 (phosphate rock throughout the drum) and from the samples collected at the top of treatment A-3.

This does lead to the preliminary suggestion, that dissolution products form more readily a coating on pyrite surfaces where AMD is generated. The coat formation is dependant on the contact and distribution of the phosphate rock throughout the drum. (Attachment 1, spectra and photographs of rocks investigated.)

3. Dissolution experiments were carried out using phosphate rock and acidified water by Martina Kasumovich, who was supported on the project for the takedown of the drums. Her fourth year thesis addressed, under Prof. Ferris, U of Toronto, some aspects of dissolution of phosphate rock. This work lent to the evaluation of the application quantities and the potential for secondary precipitation. (Attachment 2)

4. The last water samples collected prior to the takedown of the experimental drums have been submitted for chemical analysis. The results suggest that the water quality in the presence of phosphate treatment is significantly improved compared to the control drums for all applications. (Attachment 3)

Coarse coal waste rock - Laboratory and field experiments

1. In the laboratory, columns containing coarse waste rock were set up to simulate the worst case scenario (high temperature and high moisture regime) in application of phosphate rock to coarse coal waste. These columns were dismantled and the encrustment layers in the columns, which were expected to form, were mapped and sampled. A summary of these results has been submitted with the previous progress report.
2. Some of the encrustment layers were subjected to SEM EDX analysis determining the presence of a binding layer of phosphate rich material around coal waste rock. (Attachment 4)
3. The research results have been presented to the German Ruhrkohle Monatalith through Prof. Wiggering from the : Der Rat Sachverständigen für Umweltfragen (Government Organization advising Ministers on Environmental Matters). Their interest in the technology is expressed in proposing to start a joint project in 1996. (Attachment 5)

Conclusion

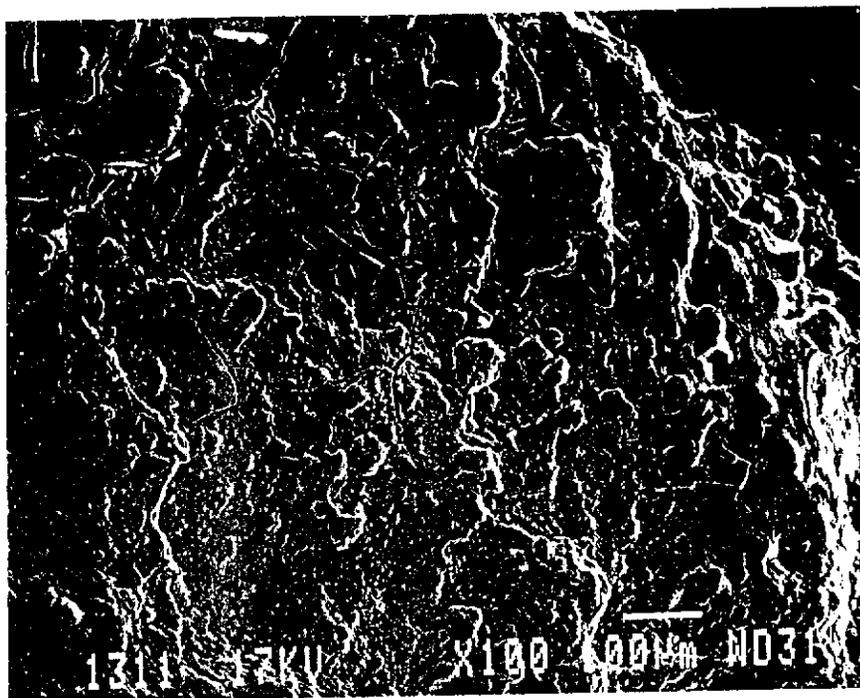
This data generated will form the basis of further technology applications both for coal and base metal waste rock.

ATTACHMENT 1

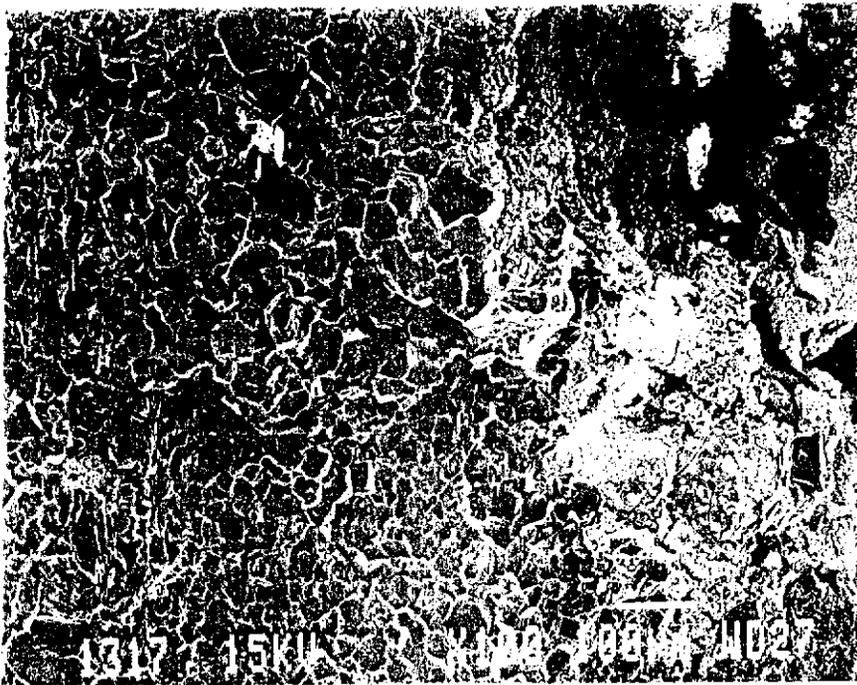
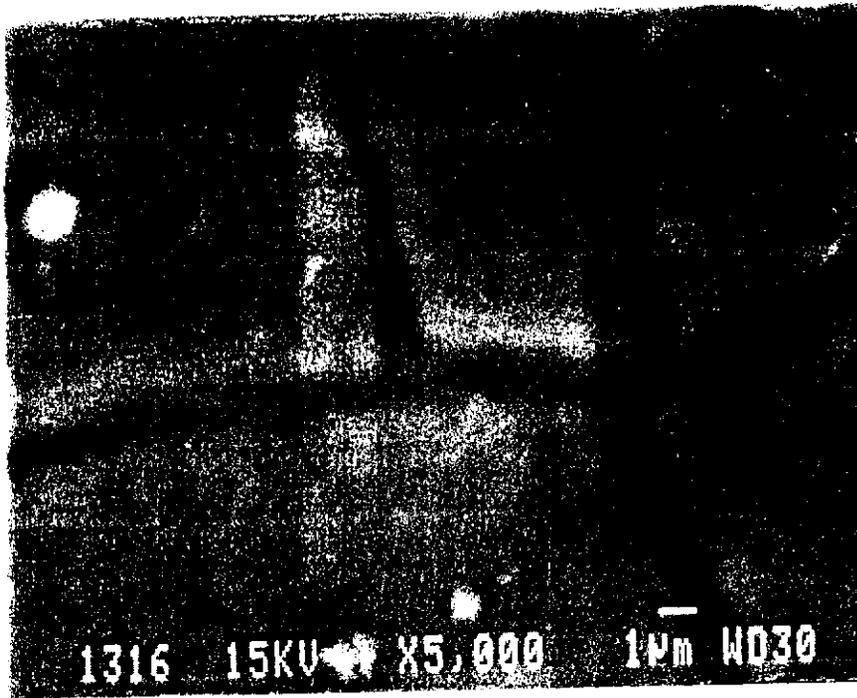
**SPECTRA AND PHOTOGRAPHS OF
ROCKS INVESTIGATED**

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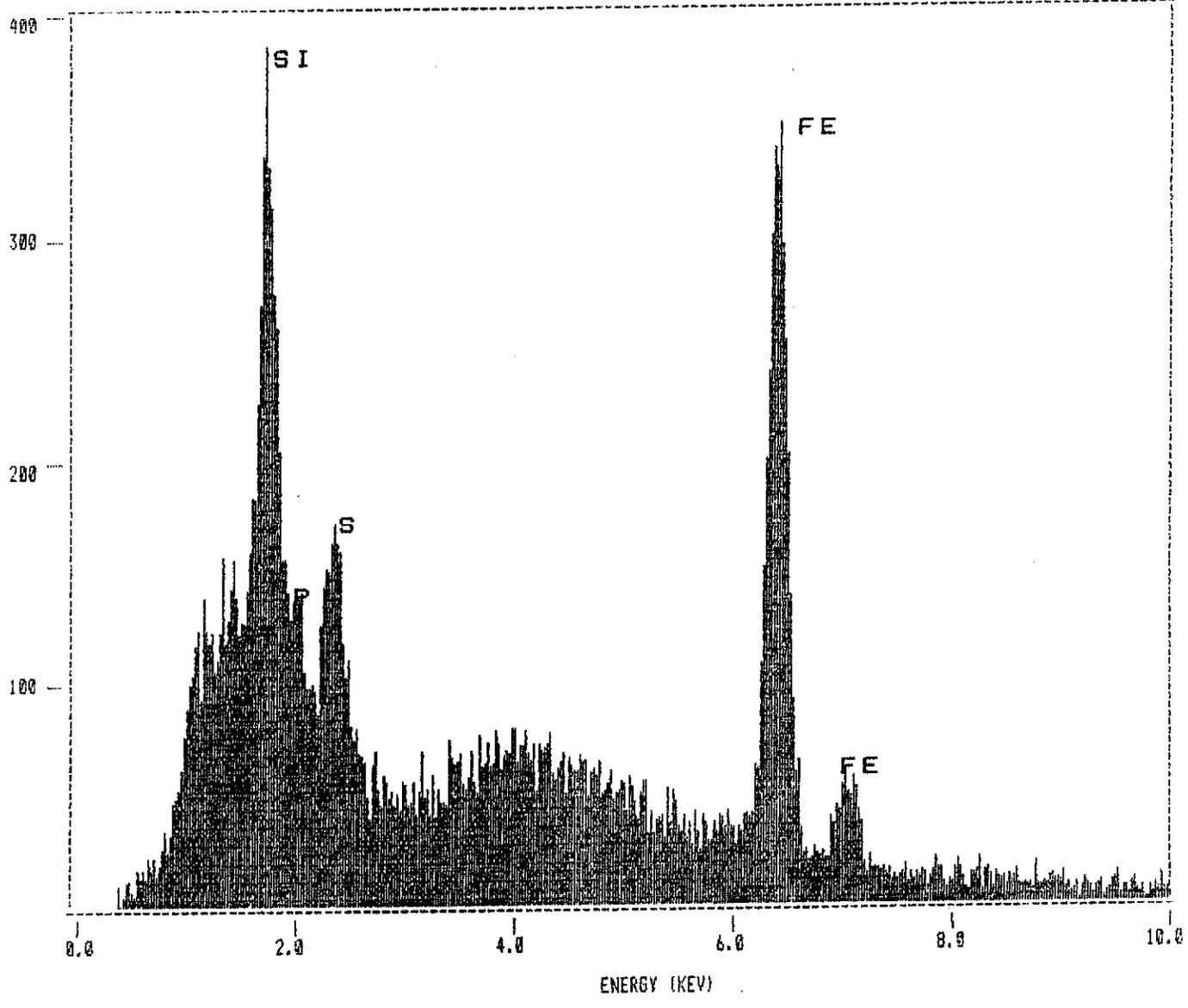


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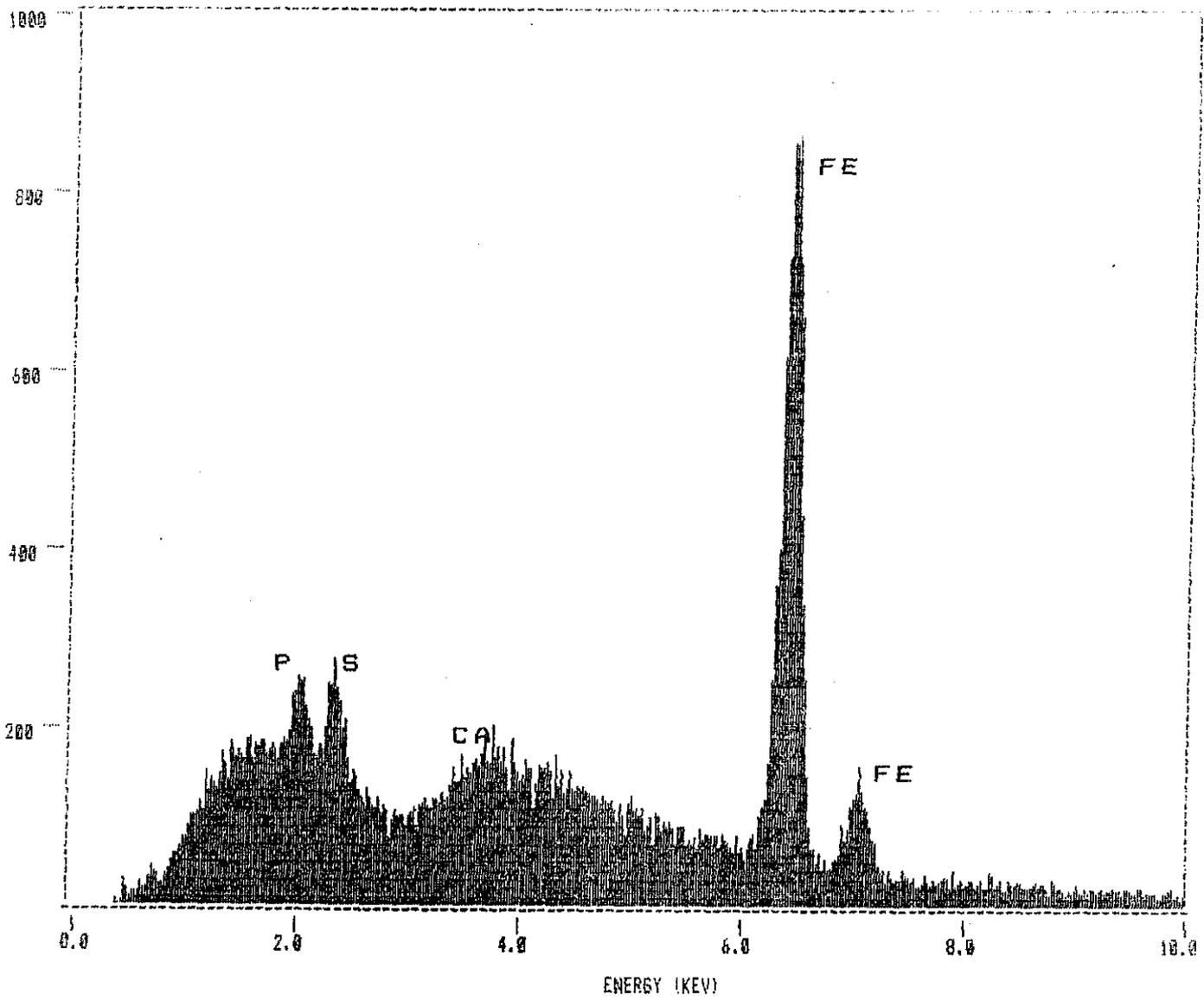
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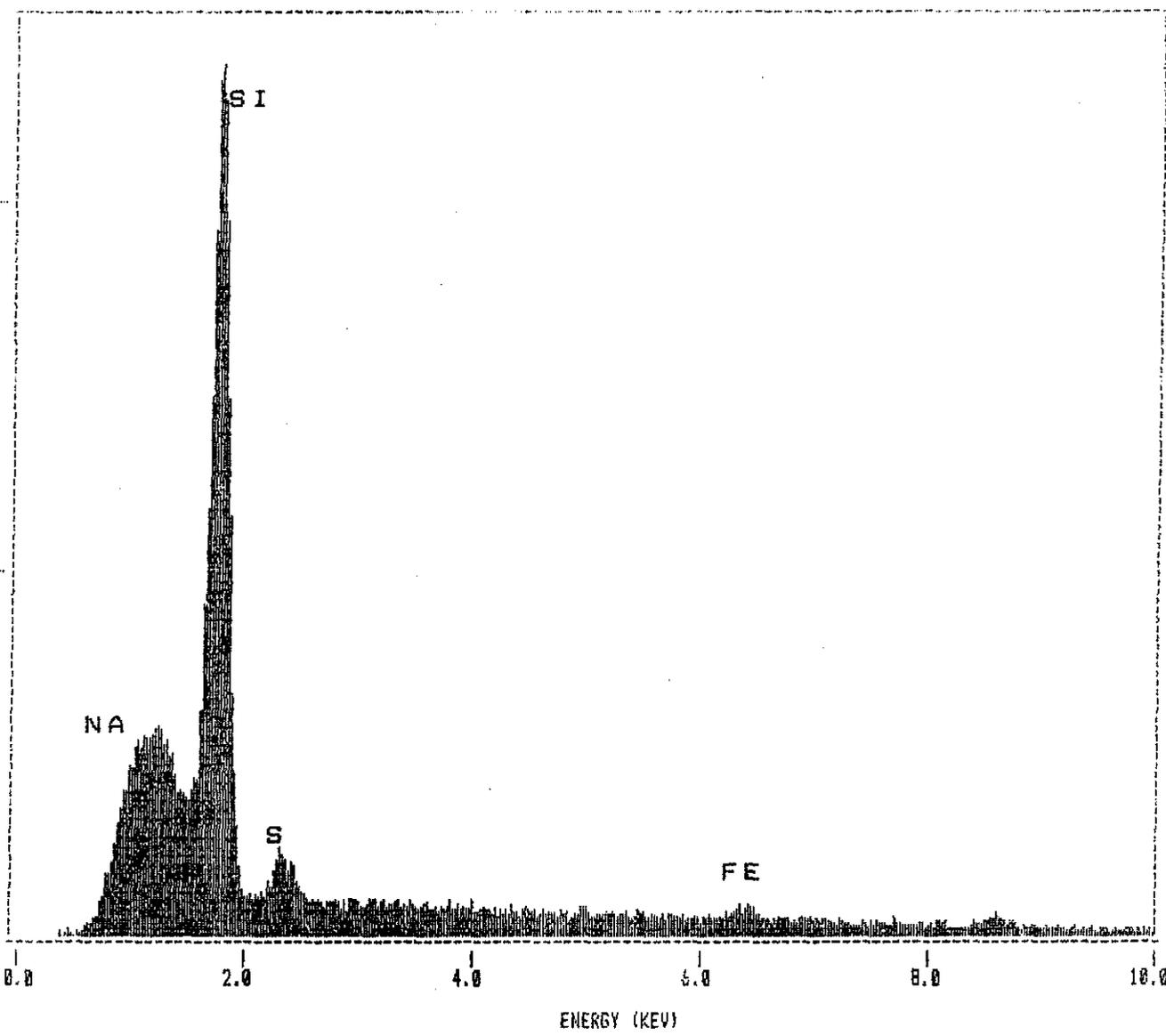
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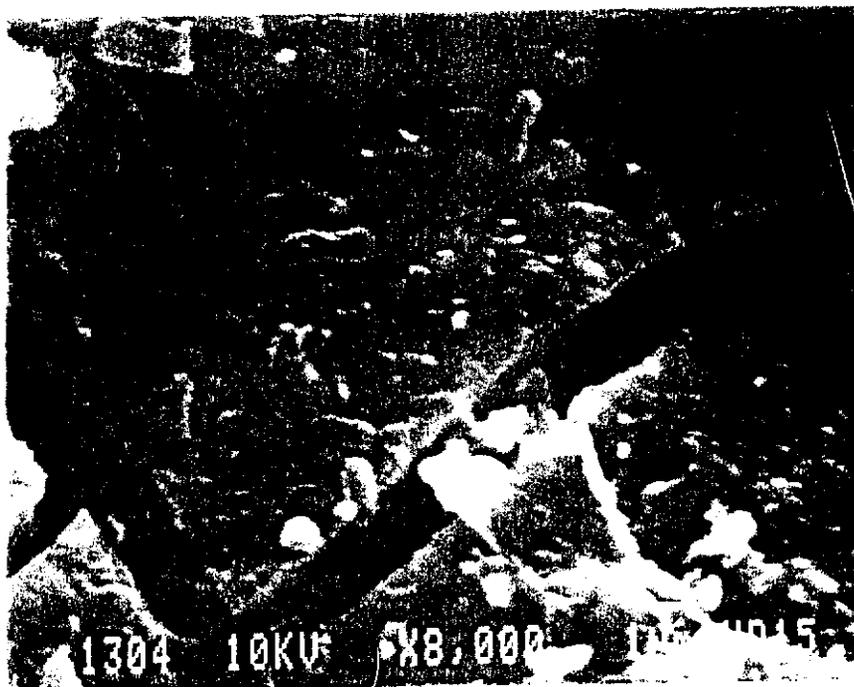


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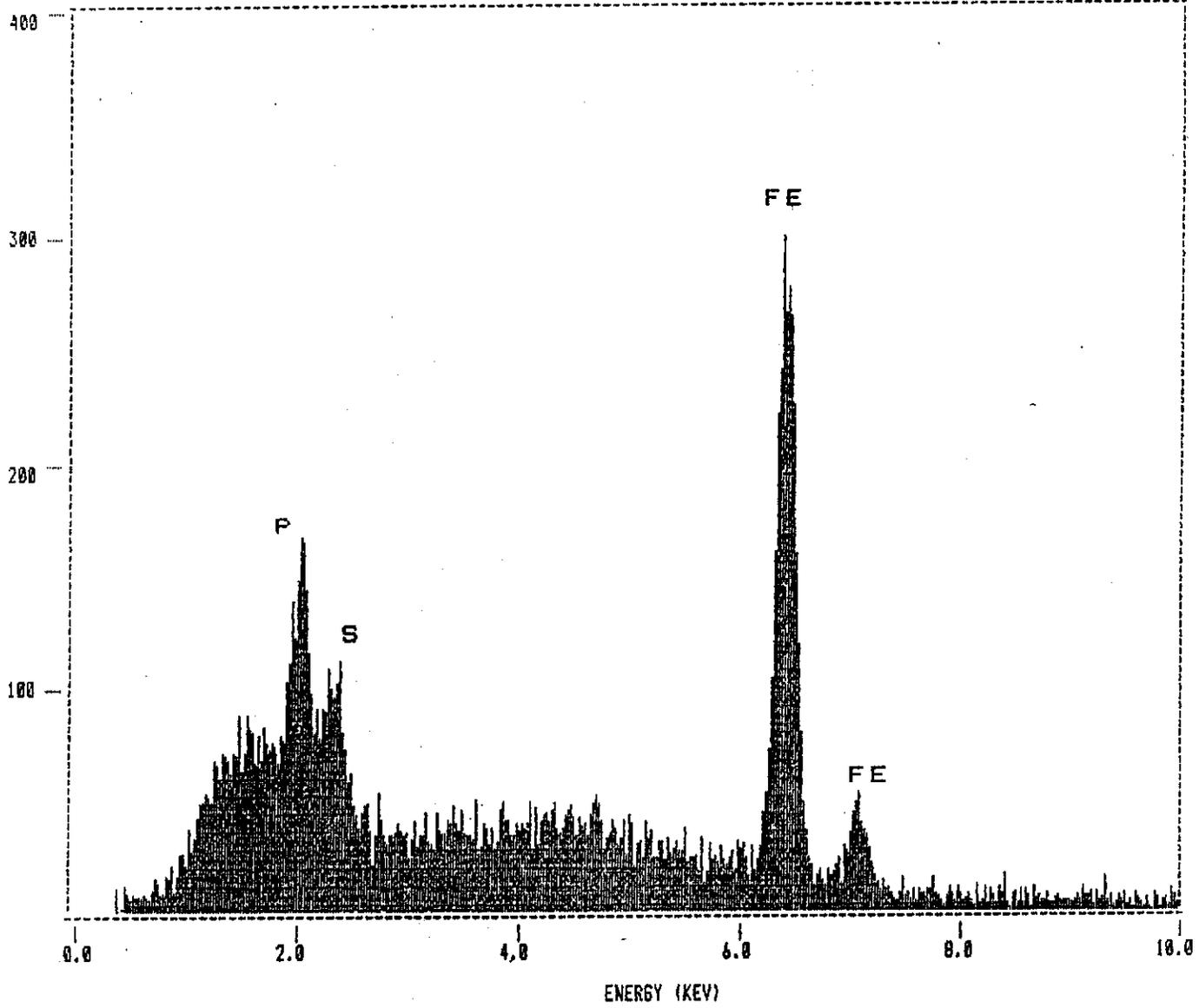
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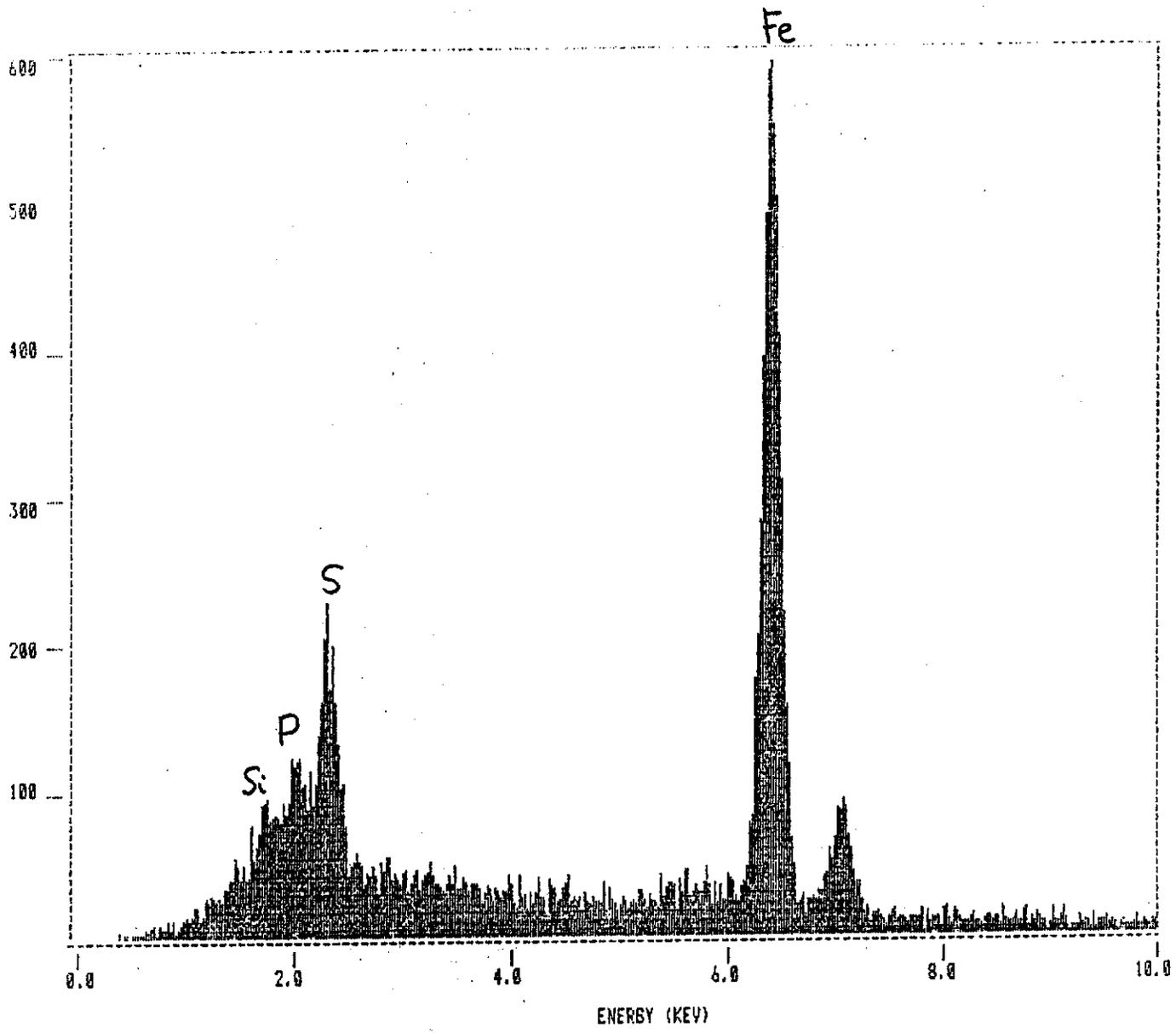
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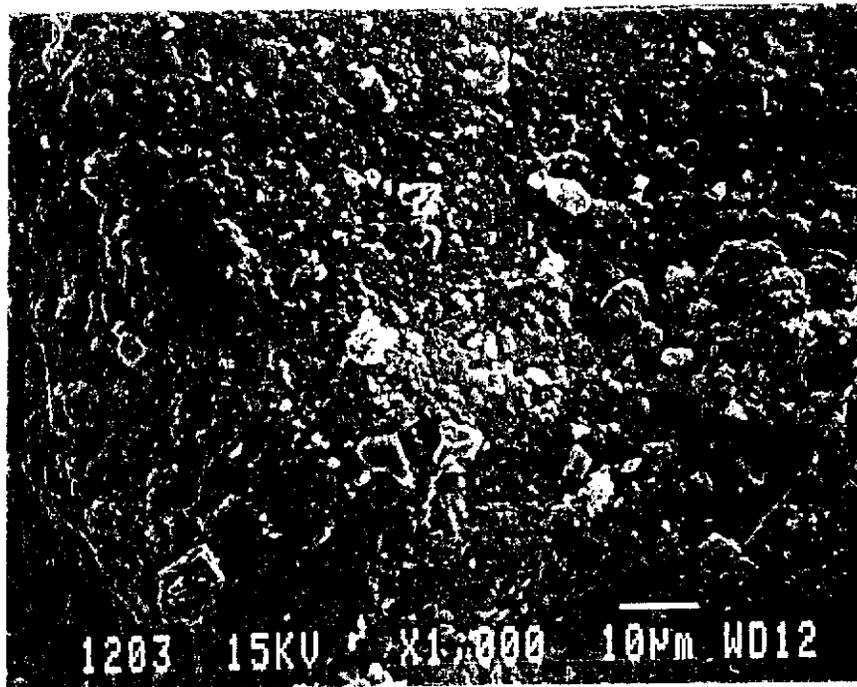
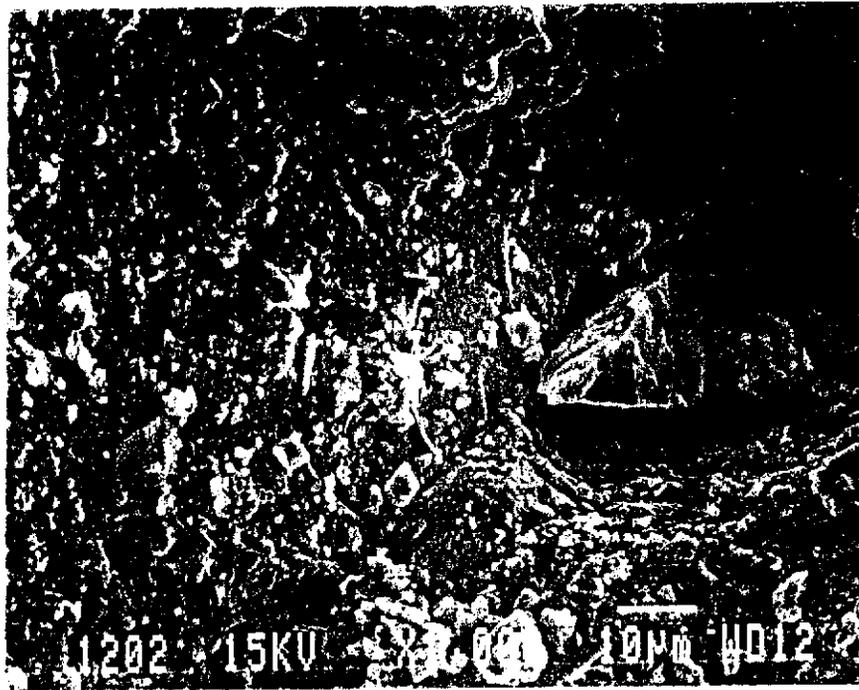
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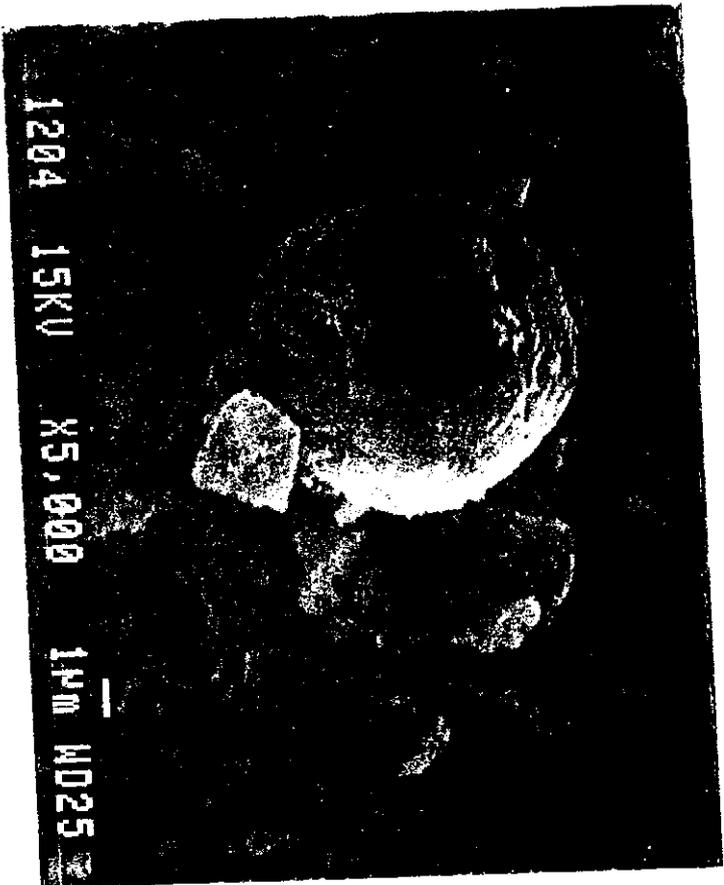
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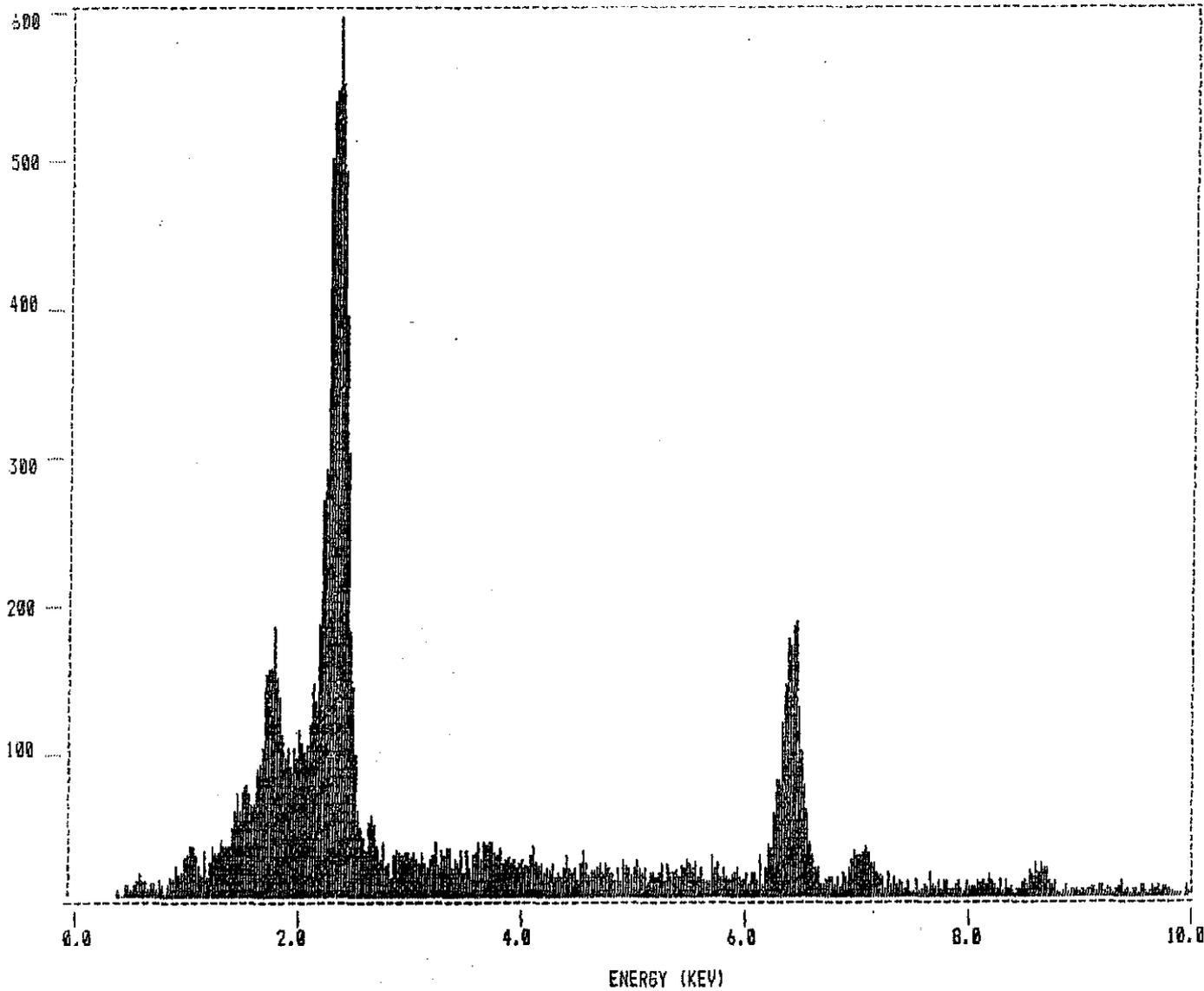


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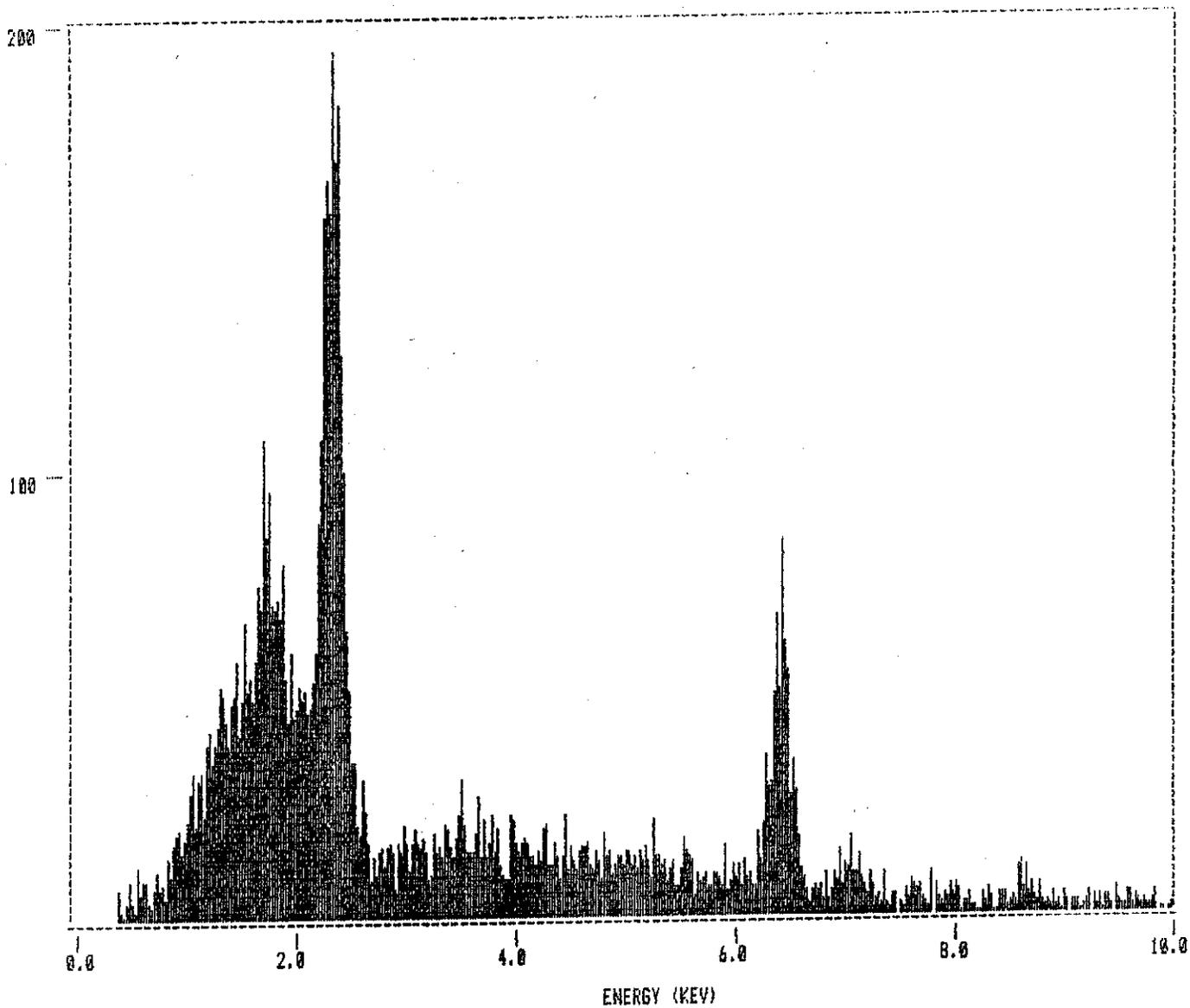
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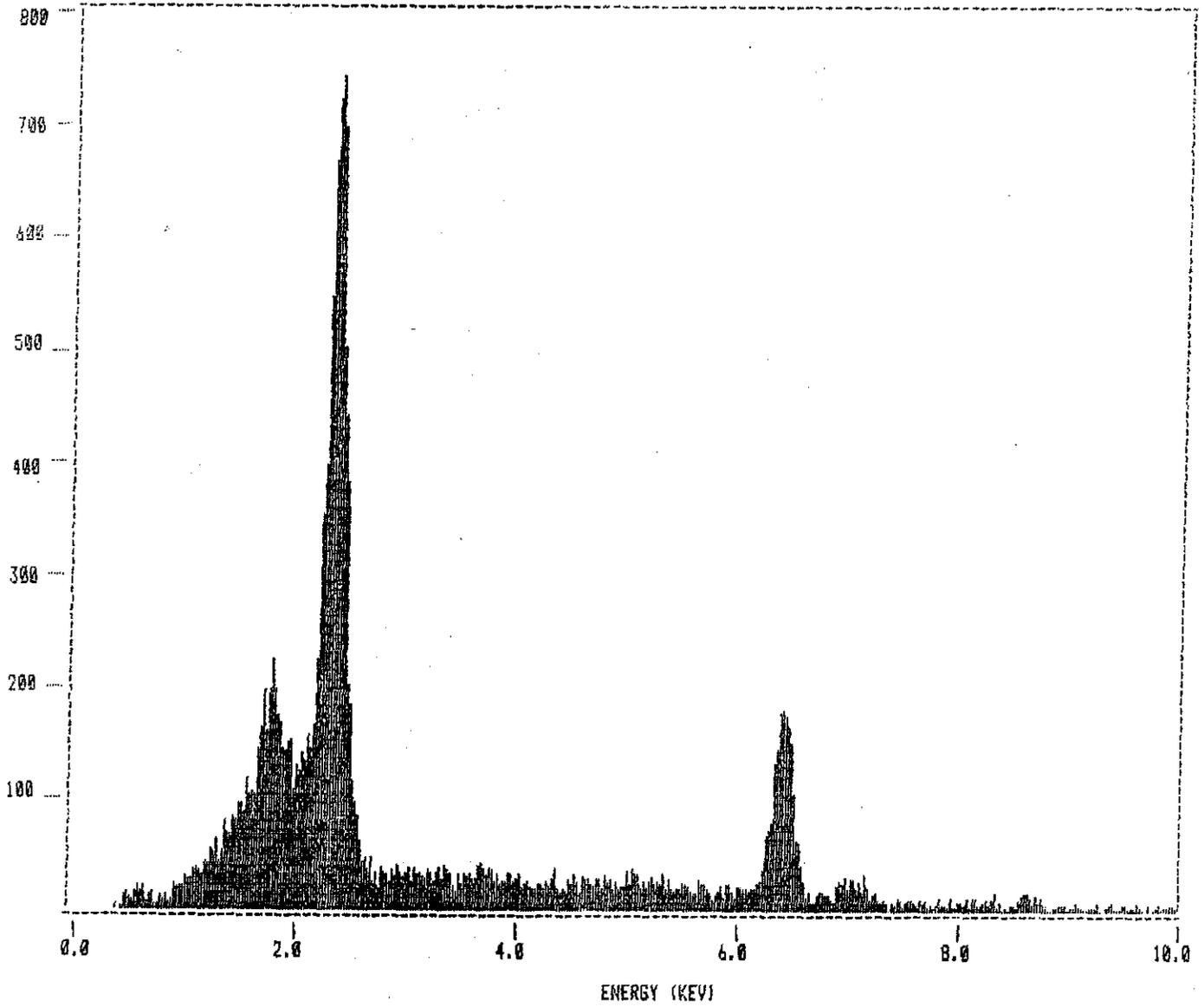
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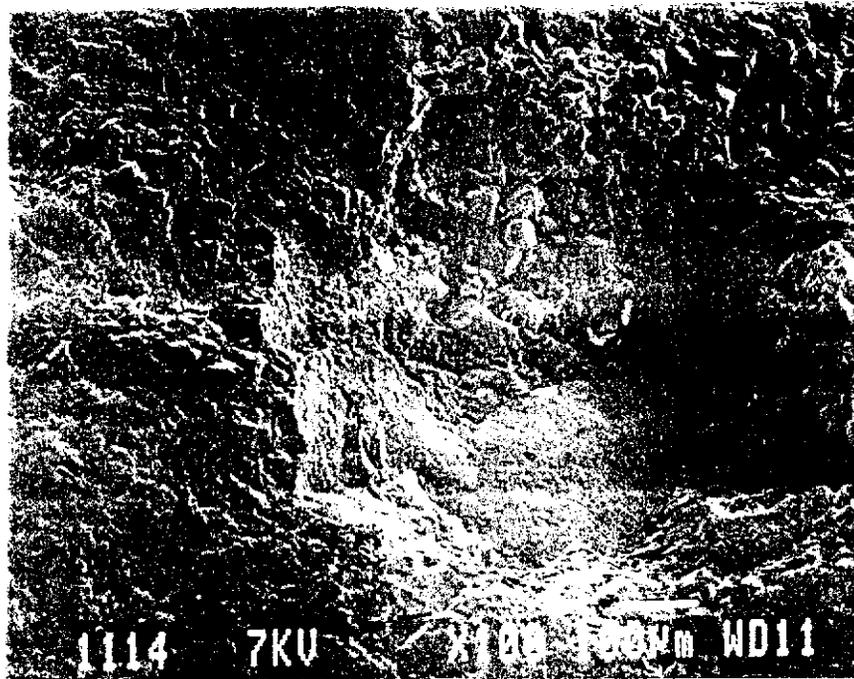
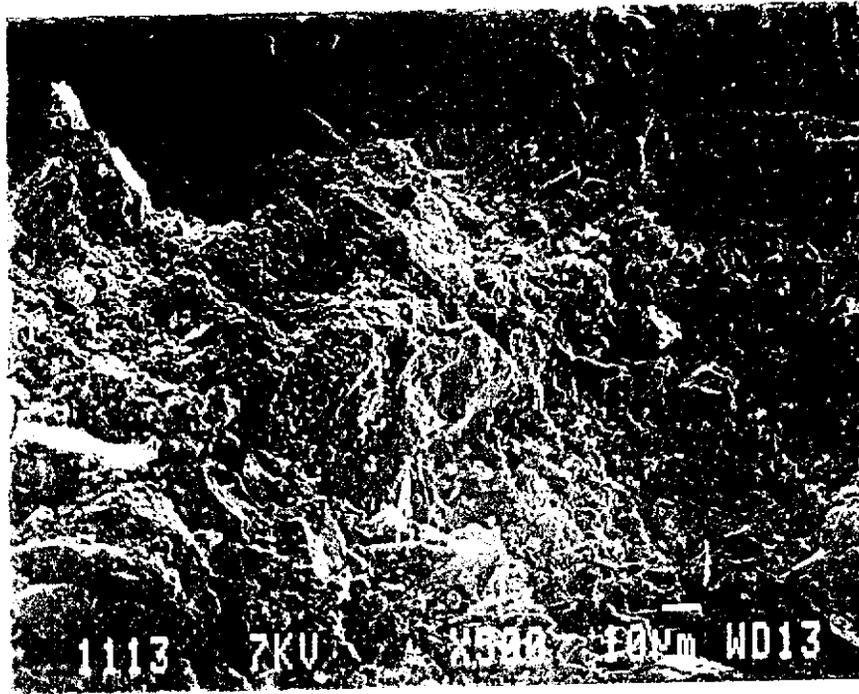




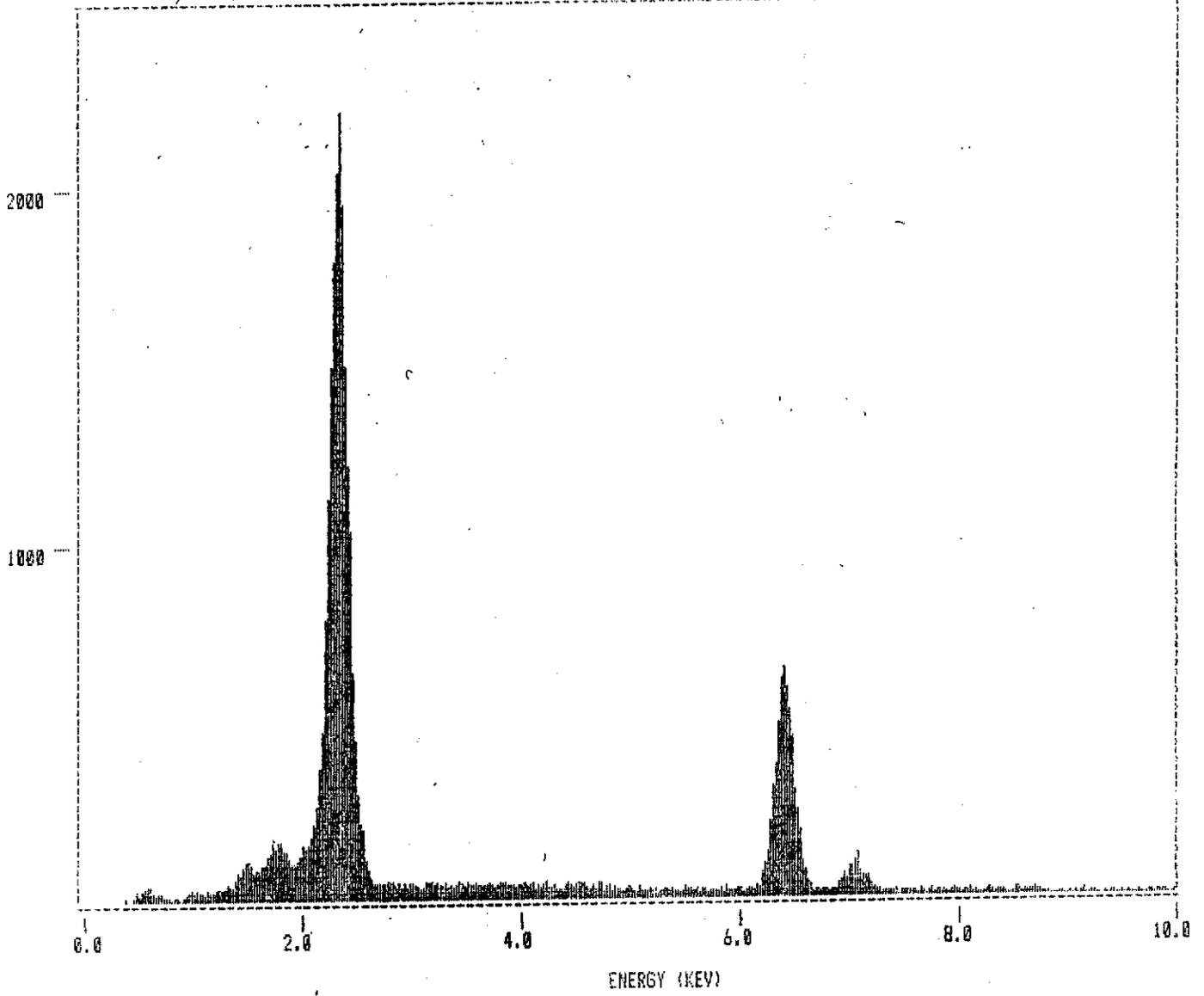
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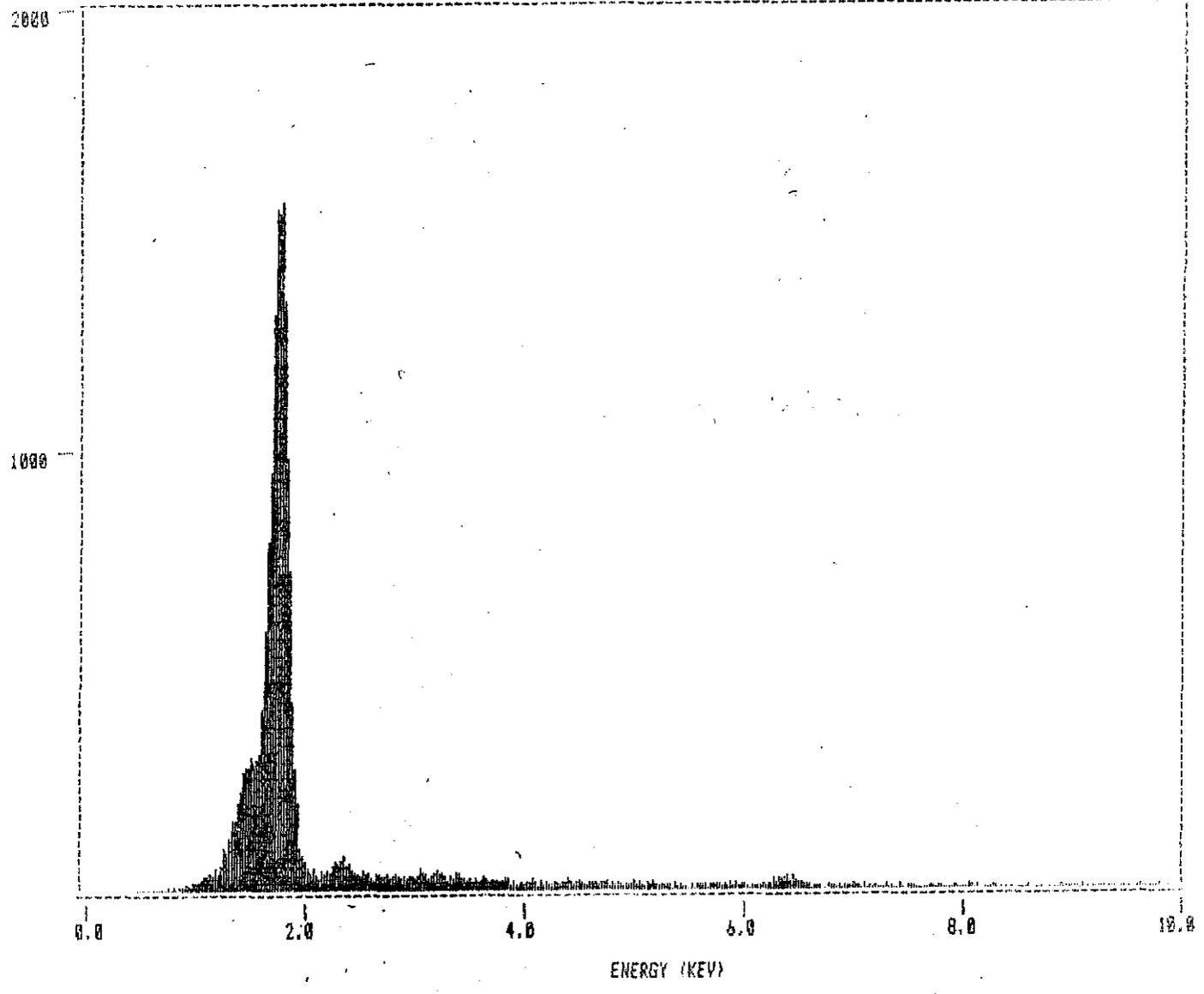


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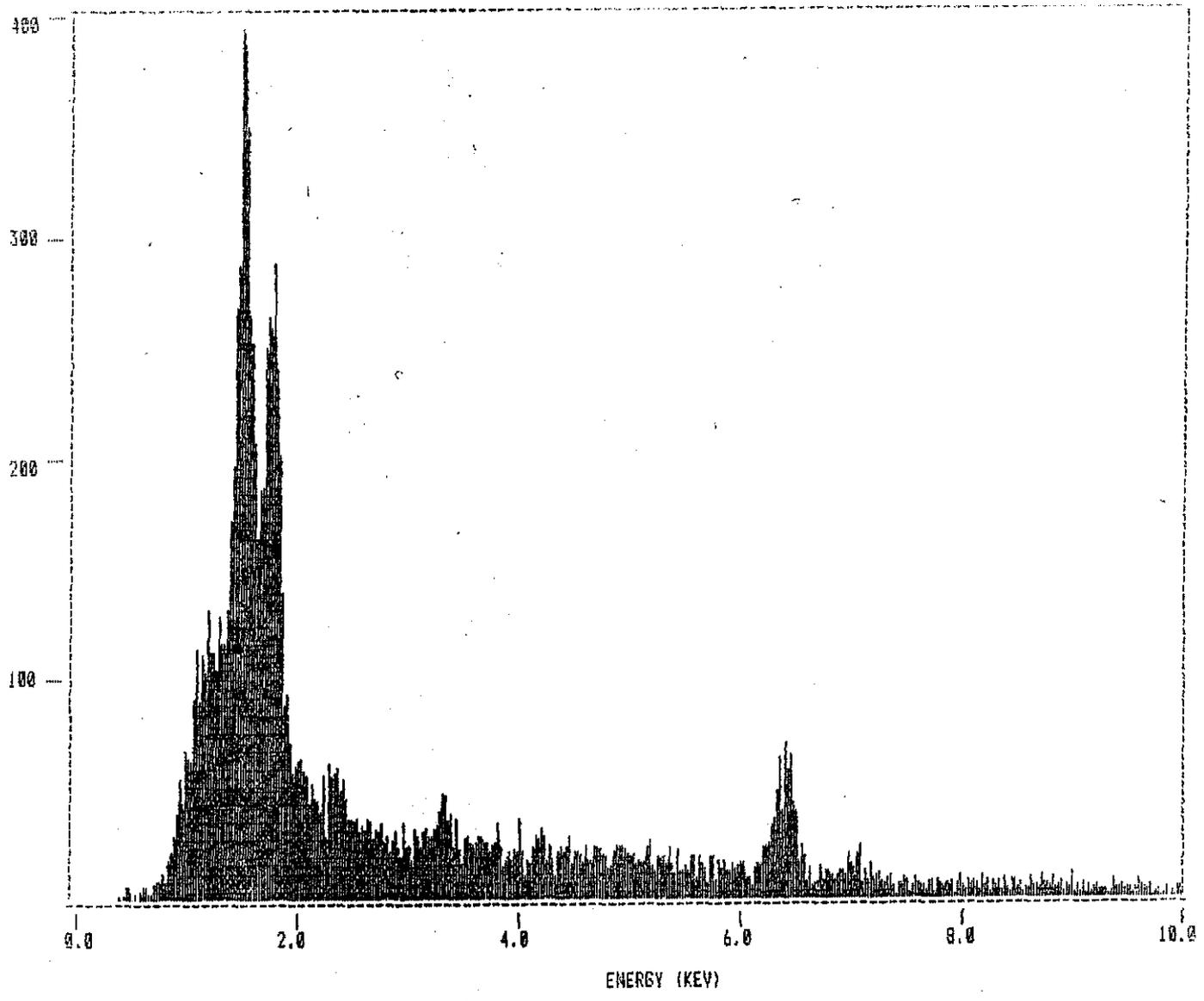
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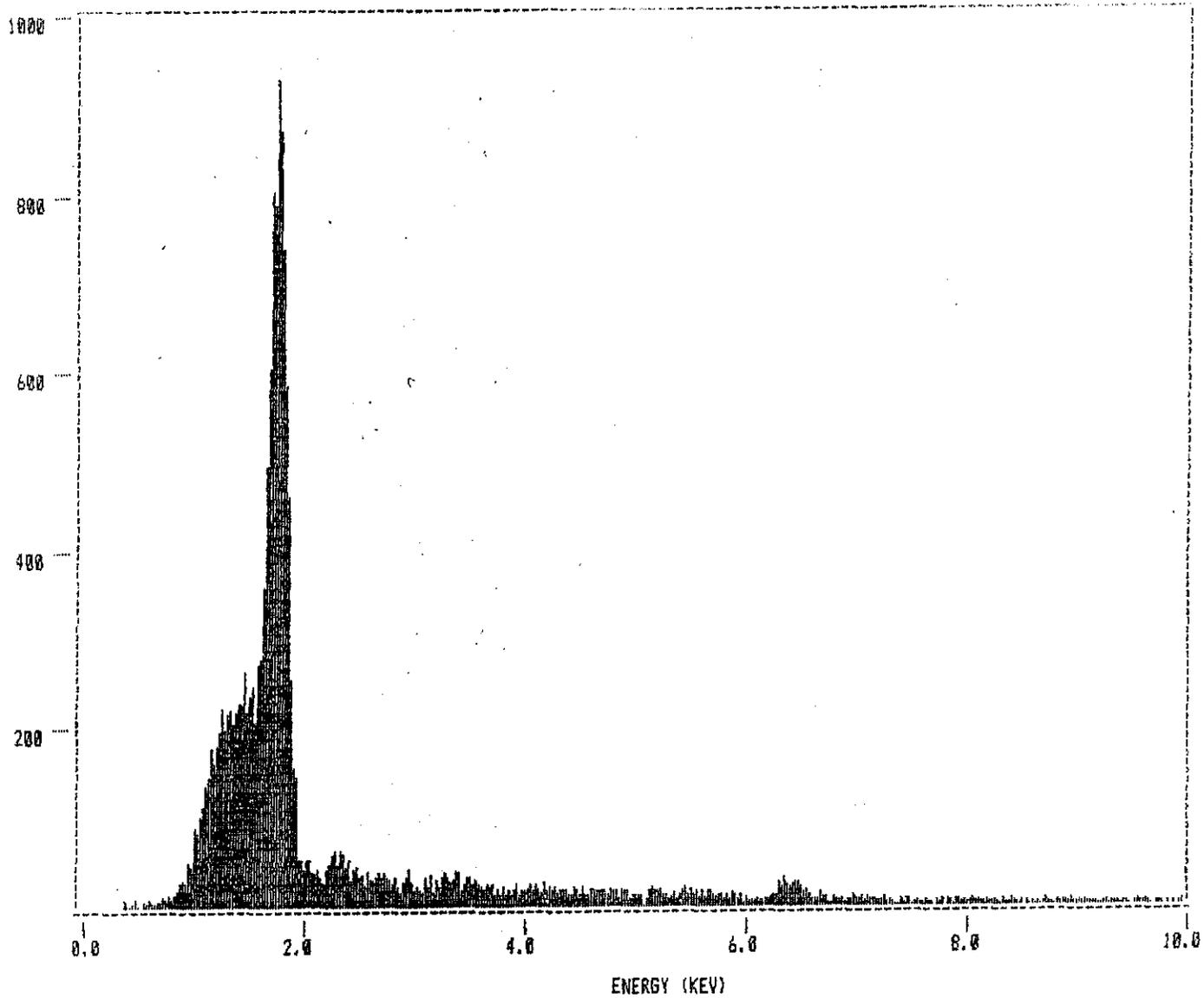
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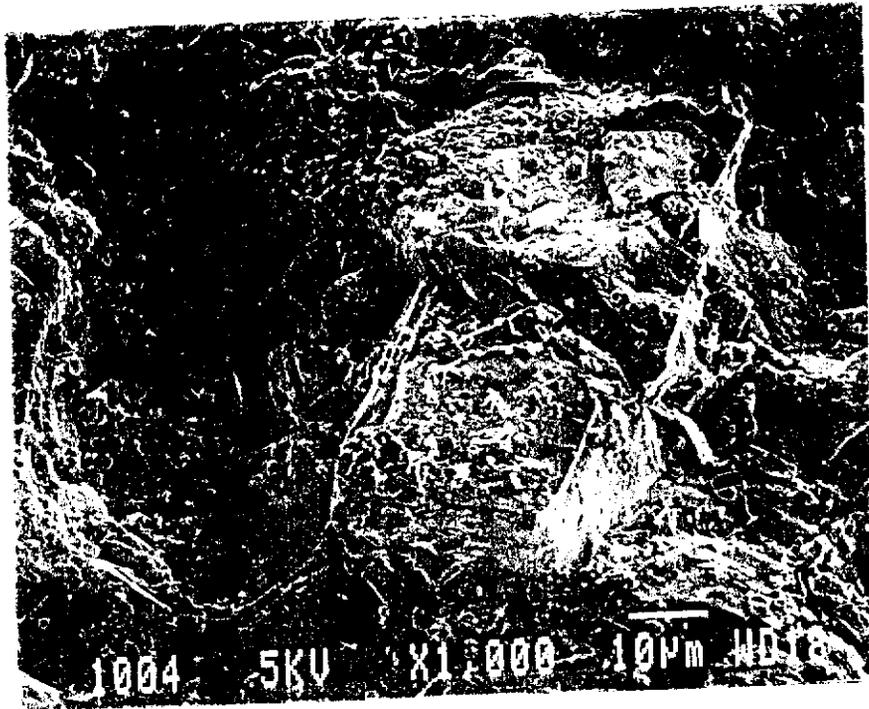


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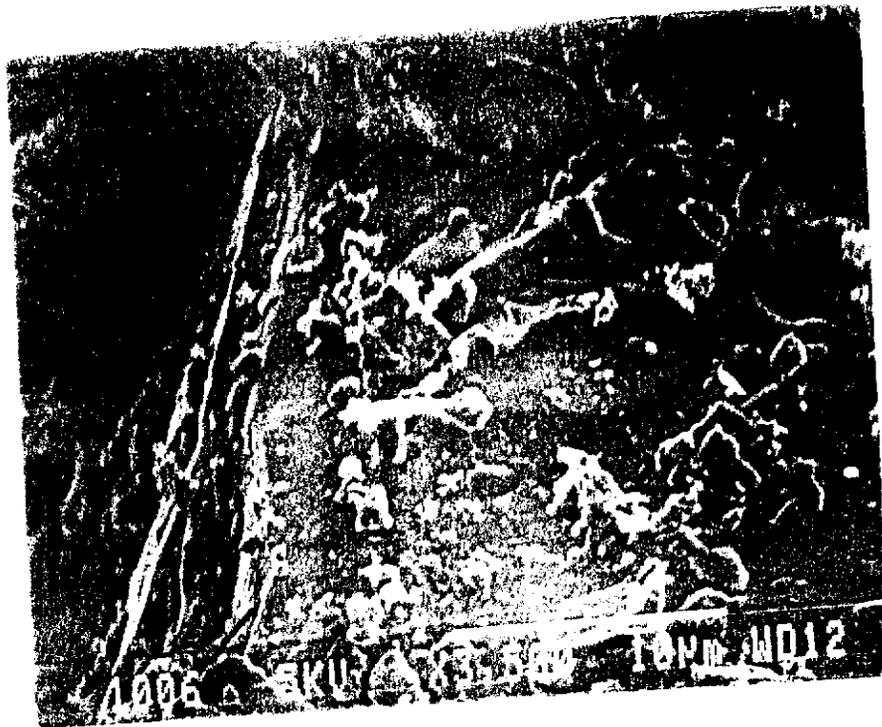
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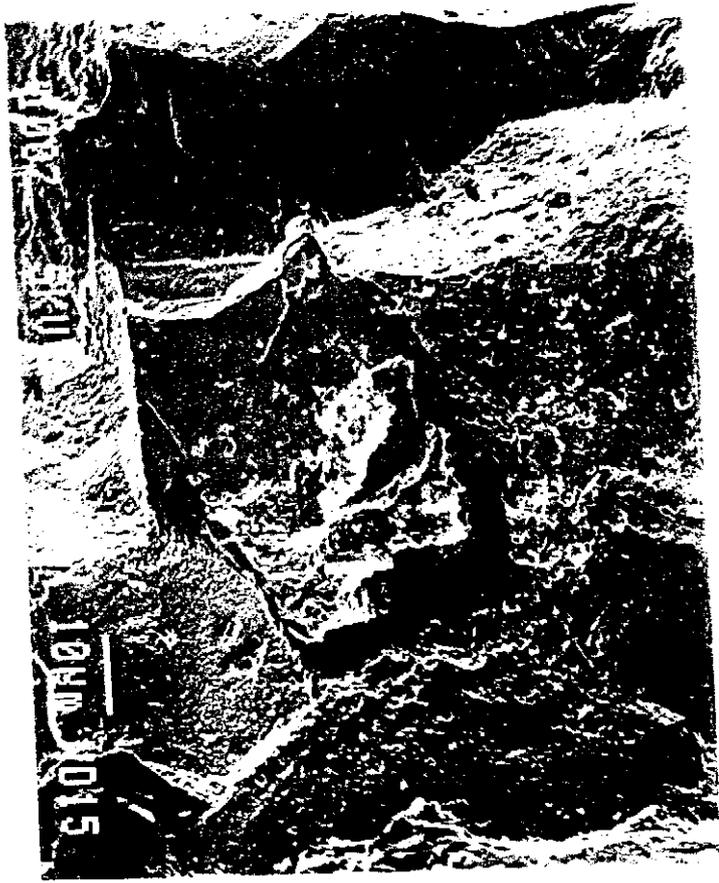




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1005 5KV X12000 10µm WD12

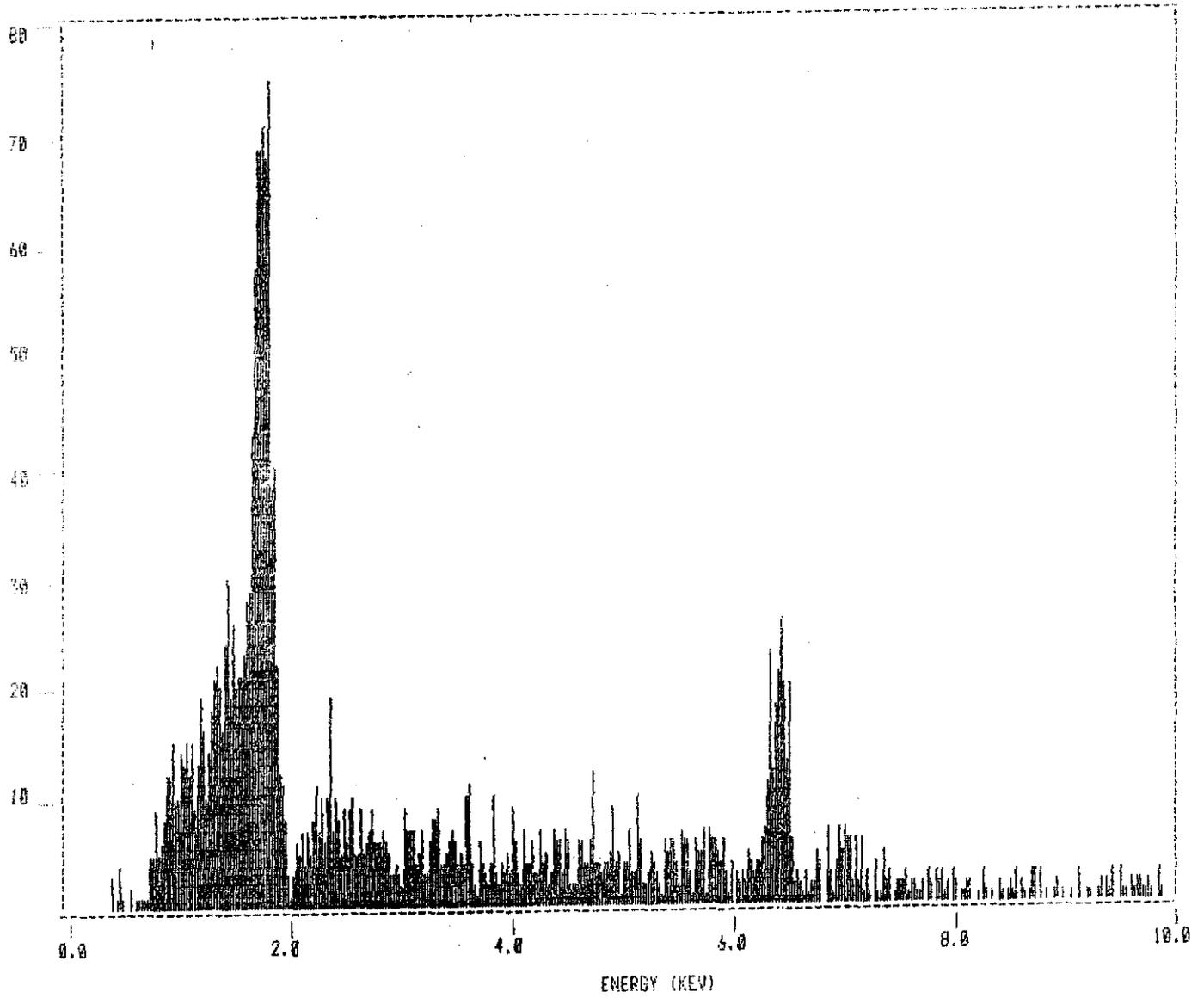


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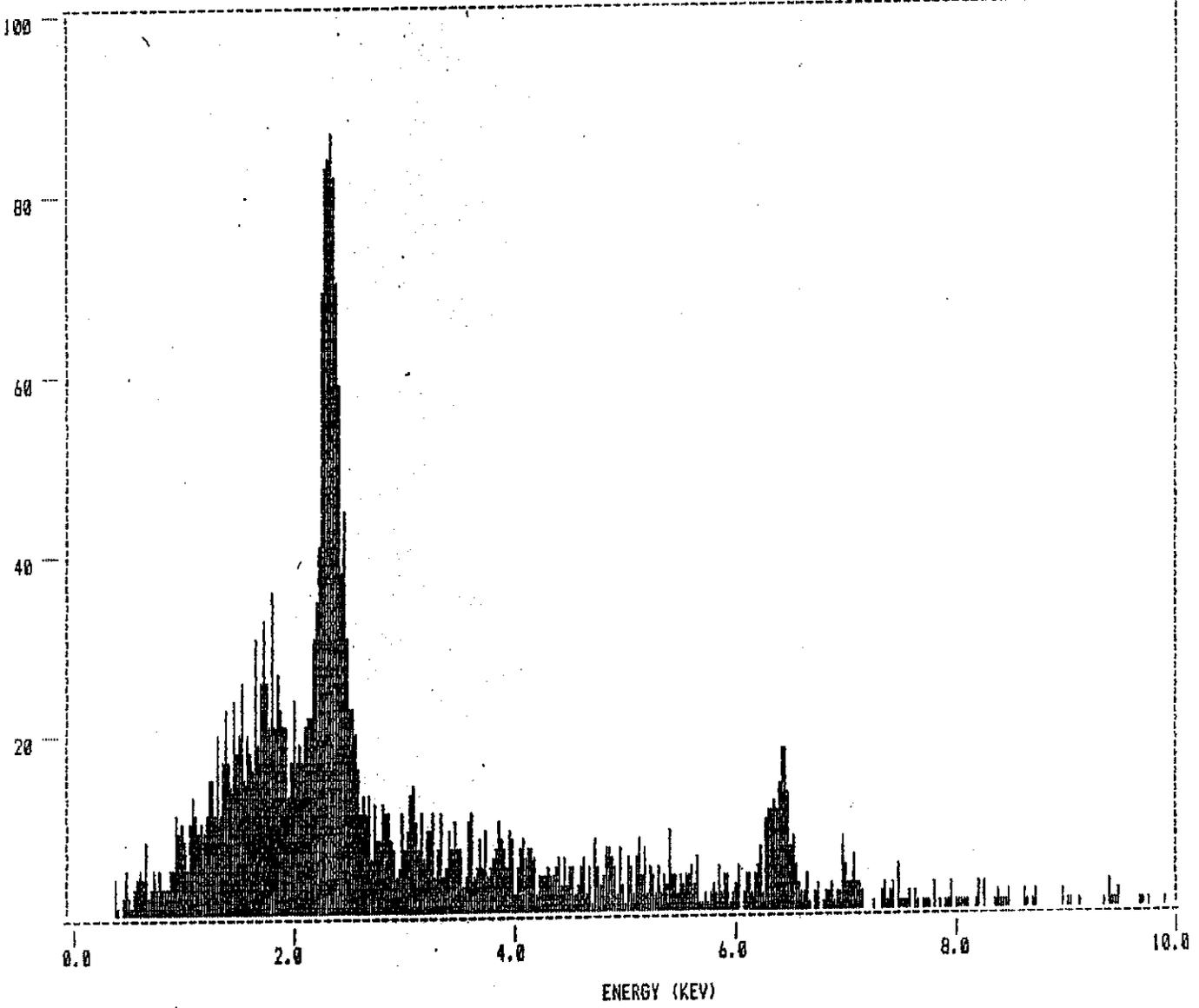
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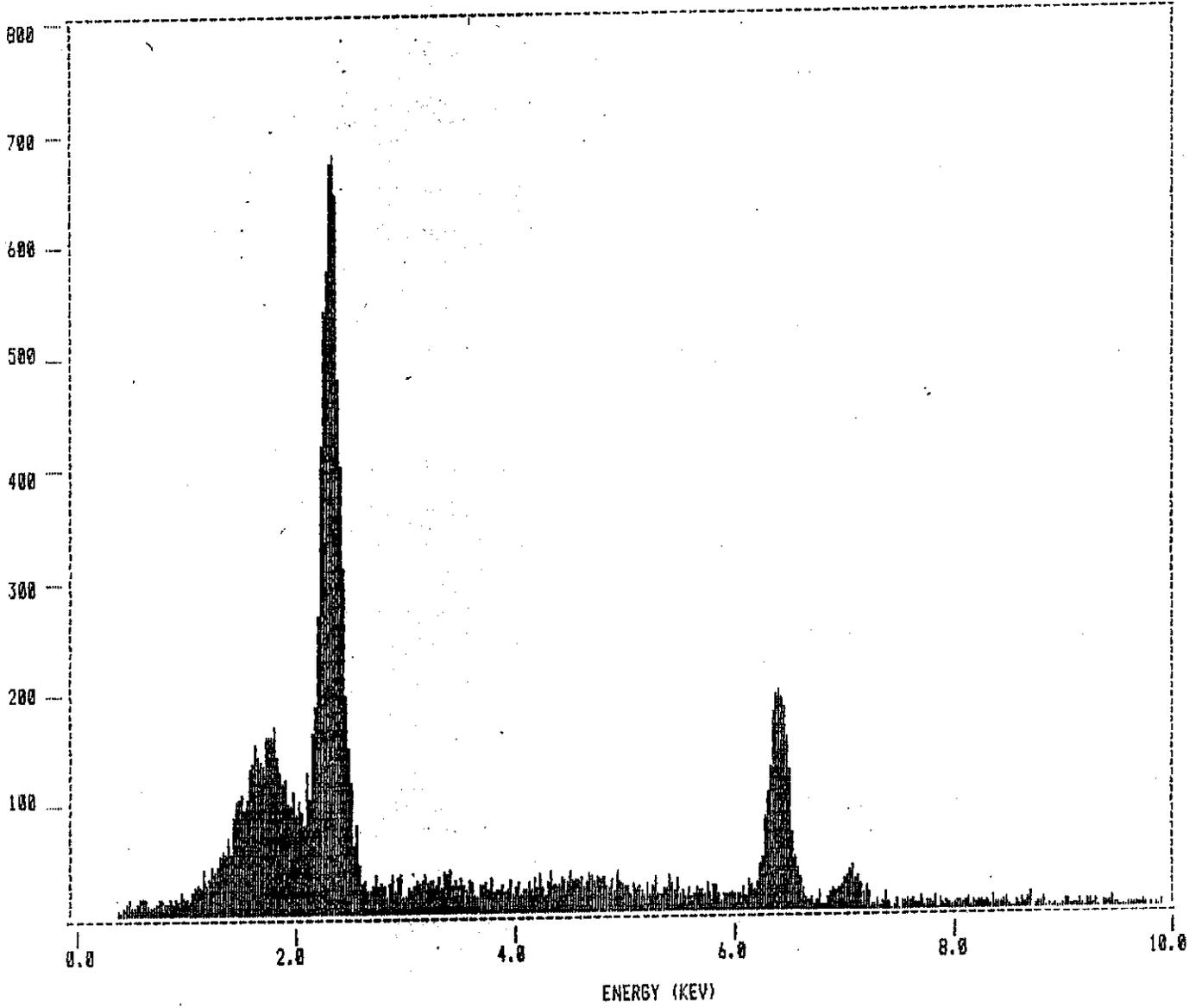
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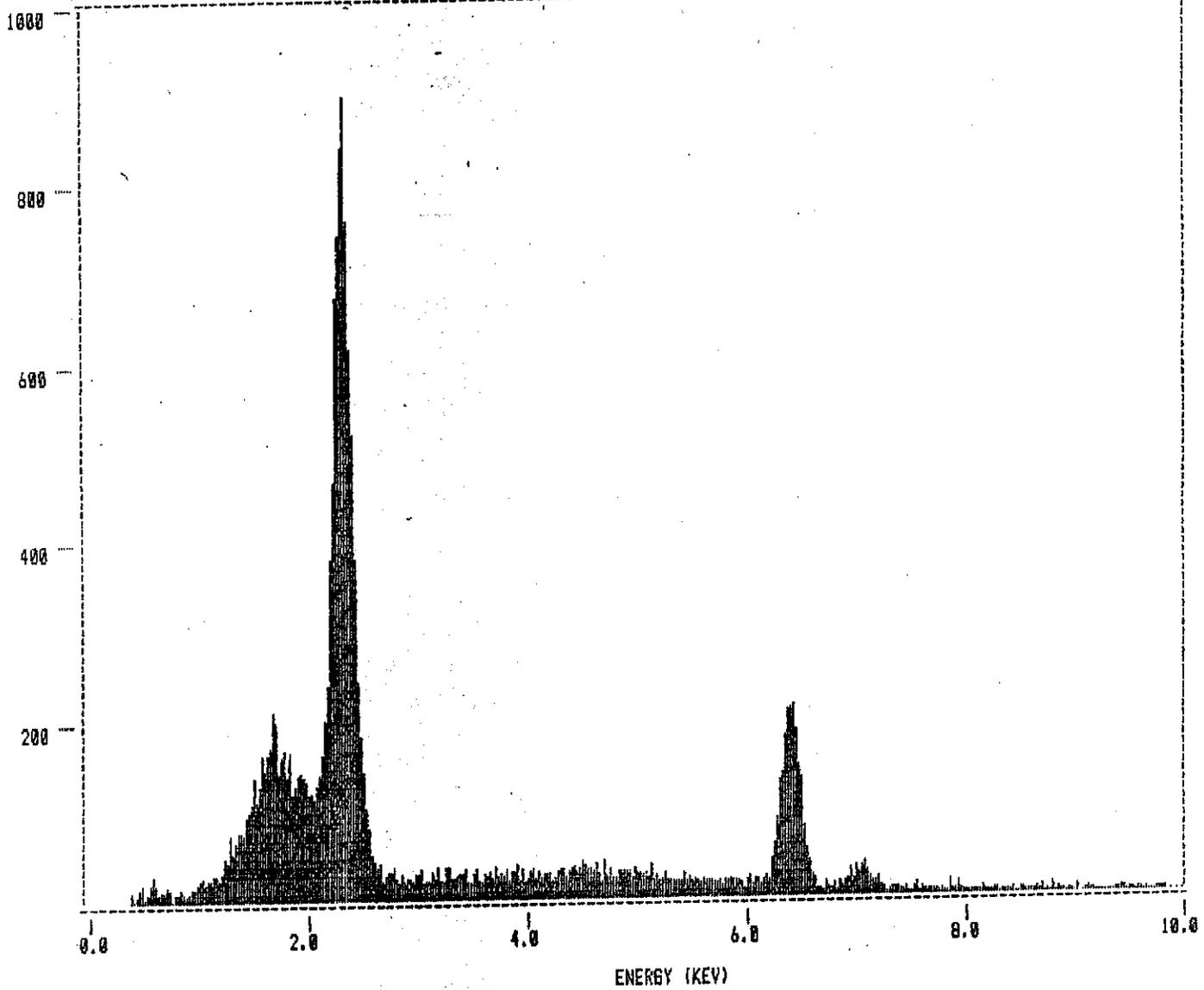
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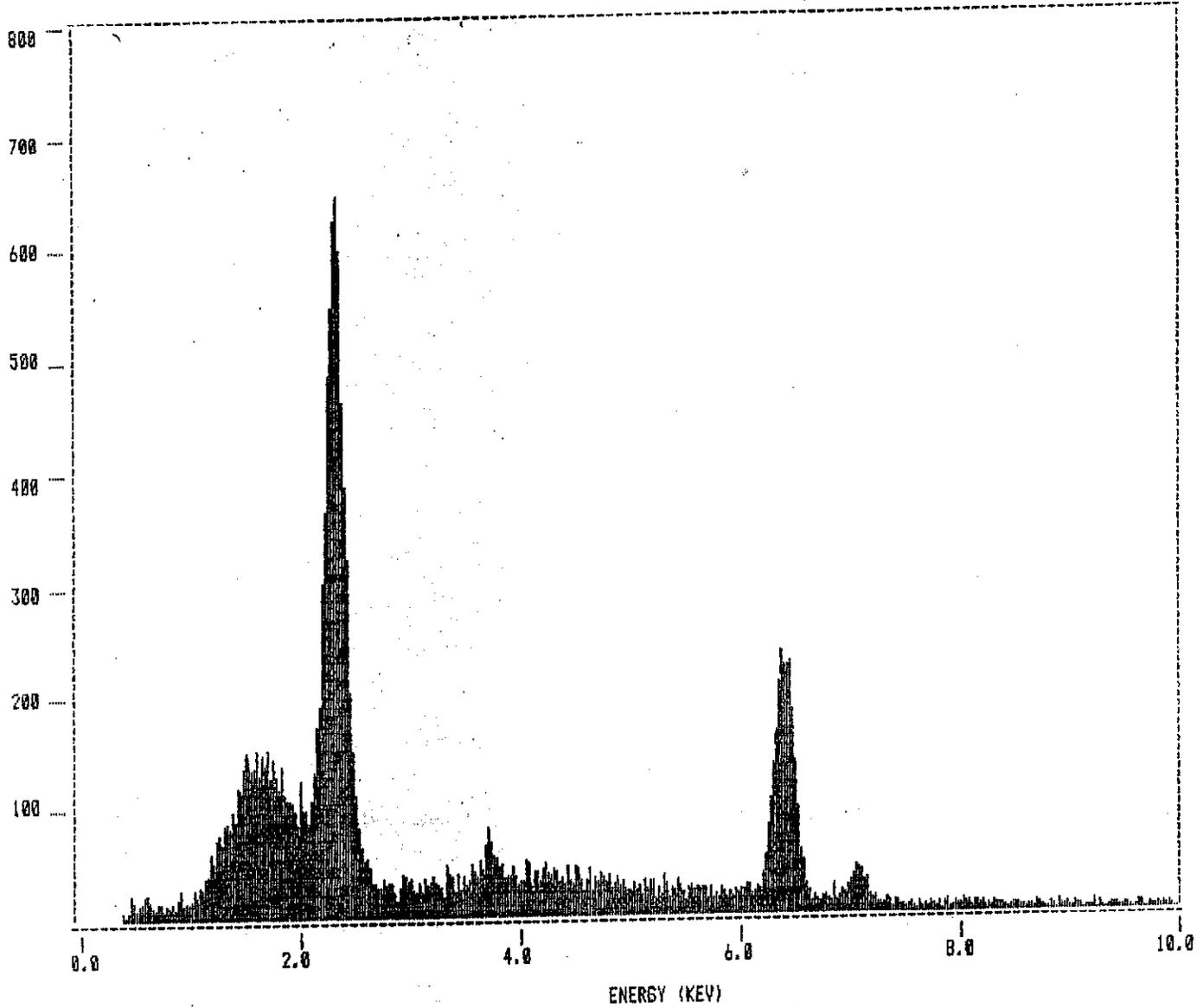
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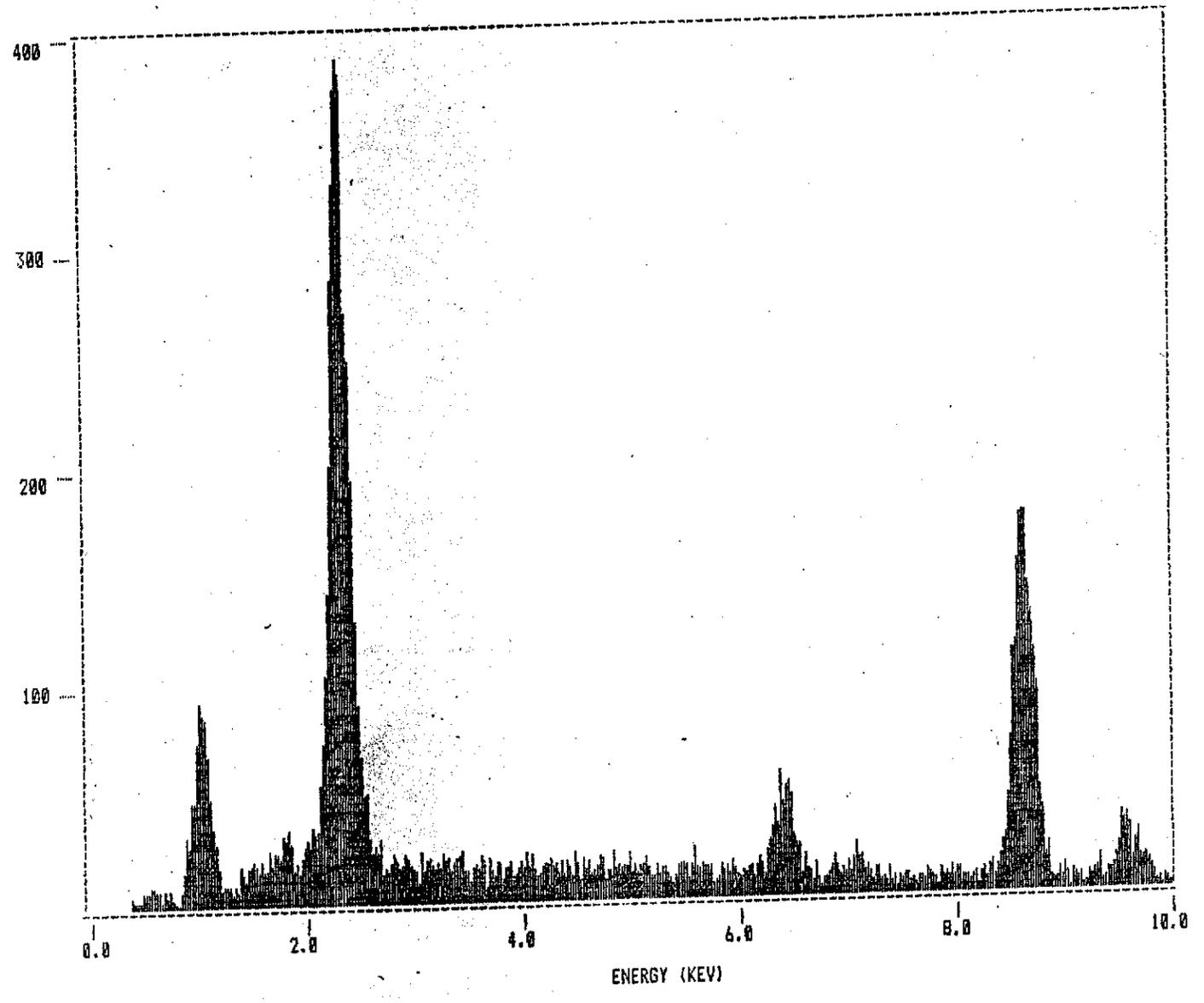
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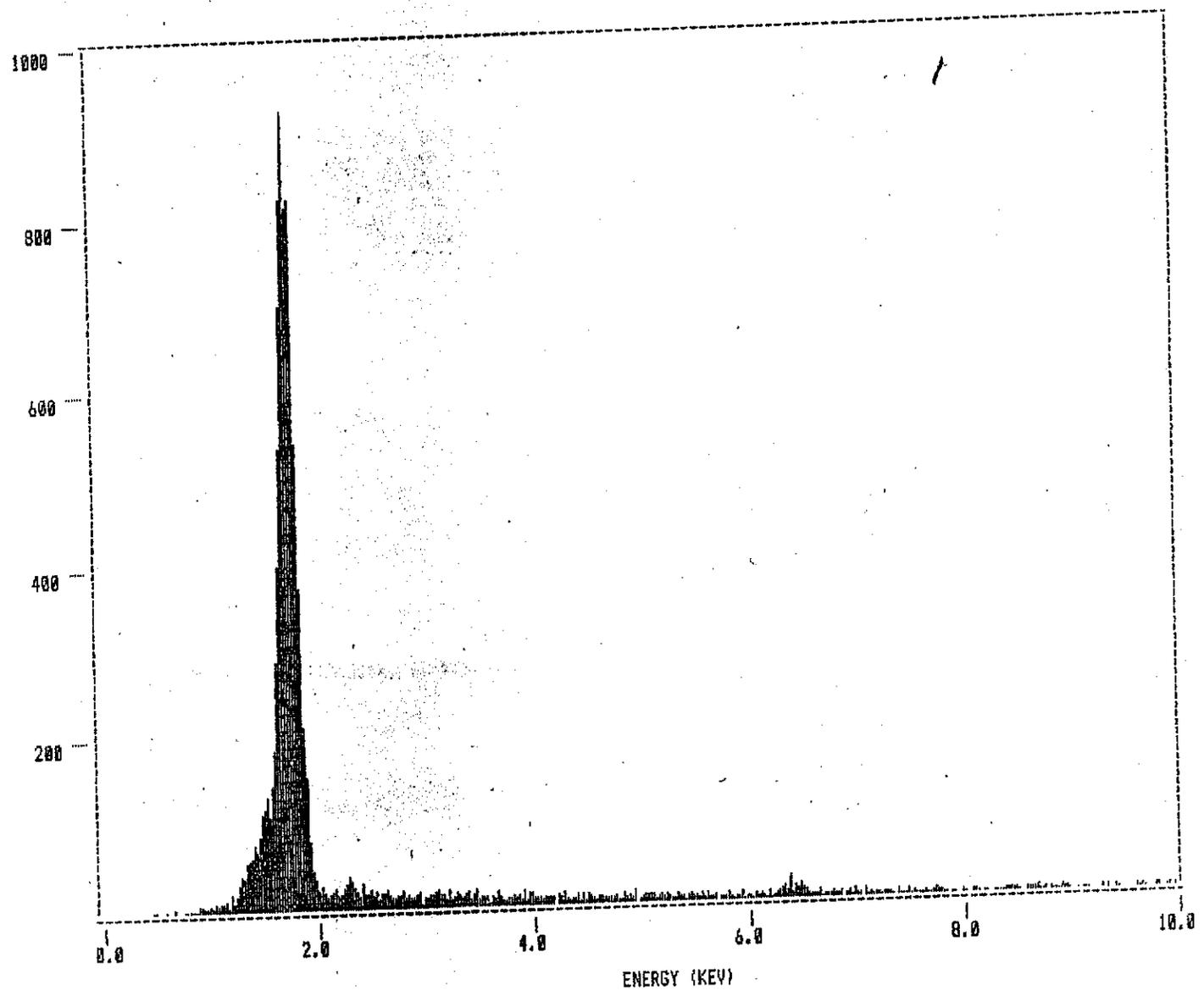
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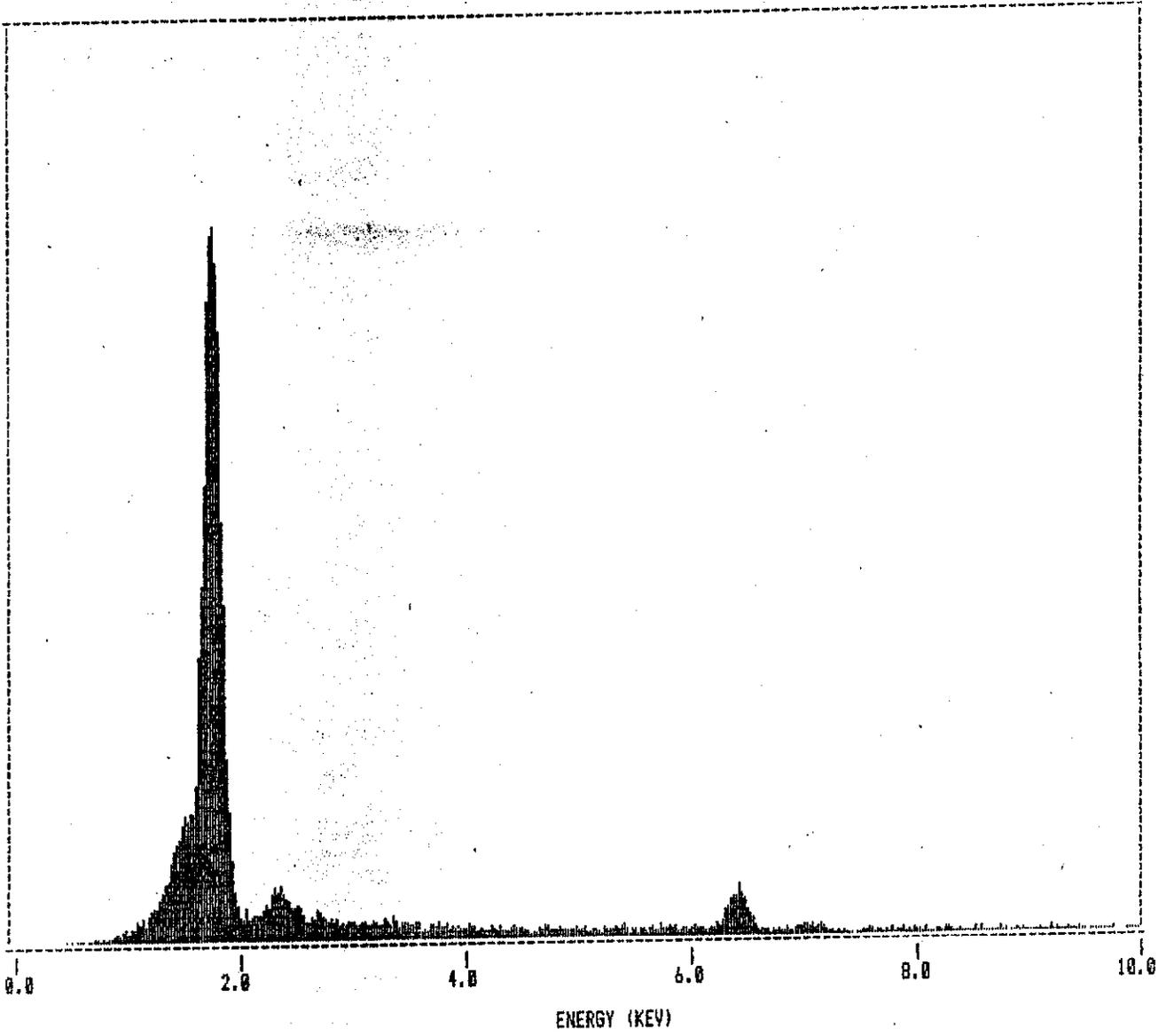
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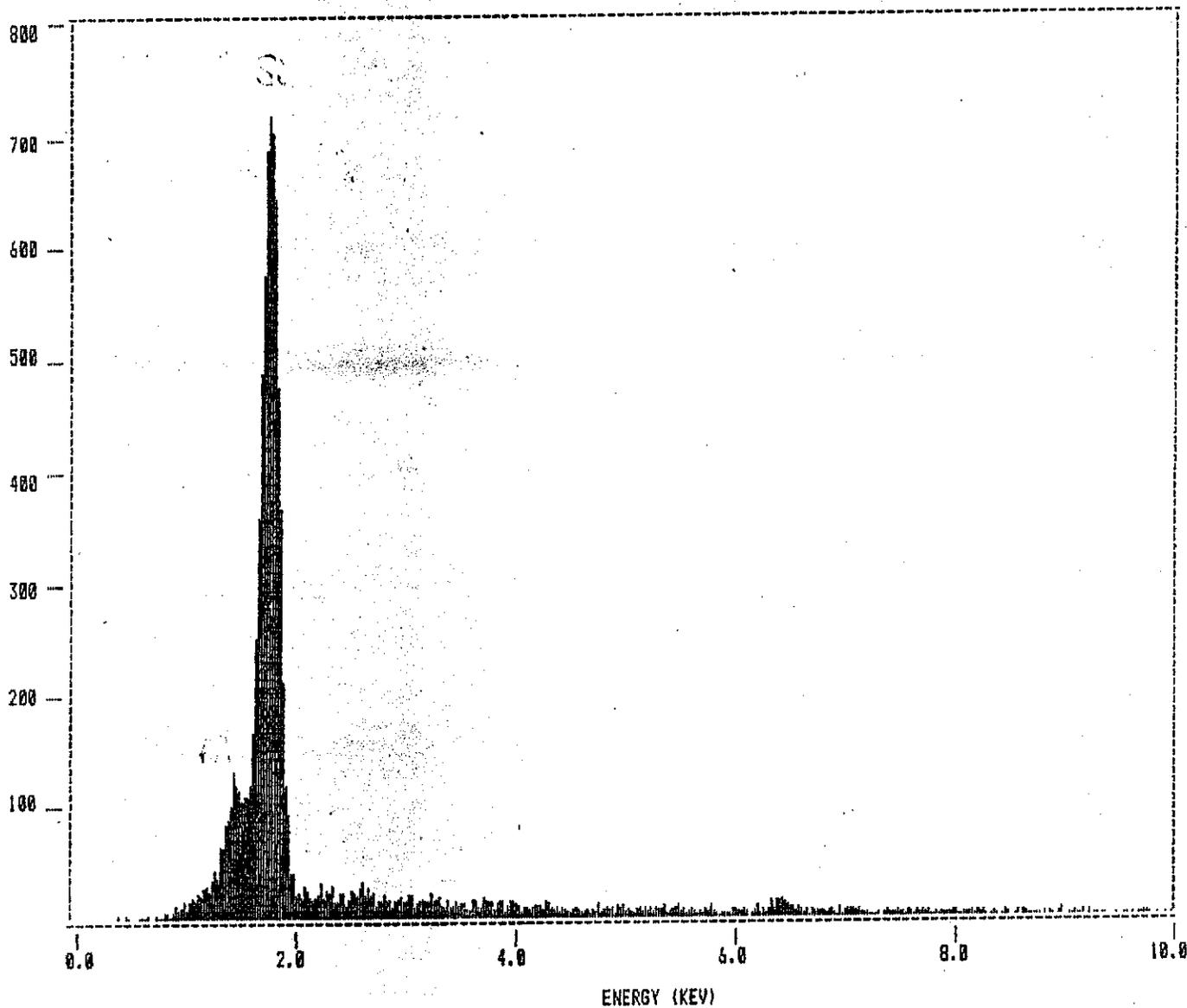


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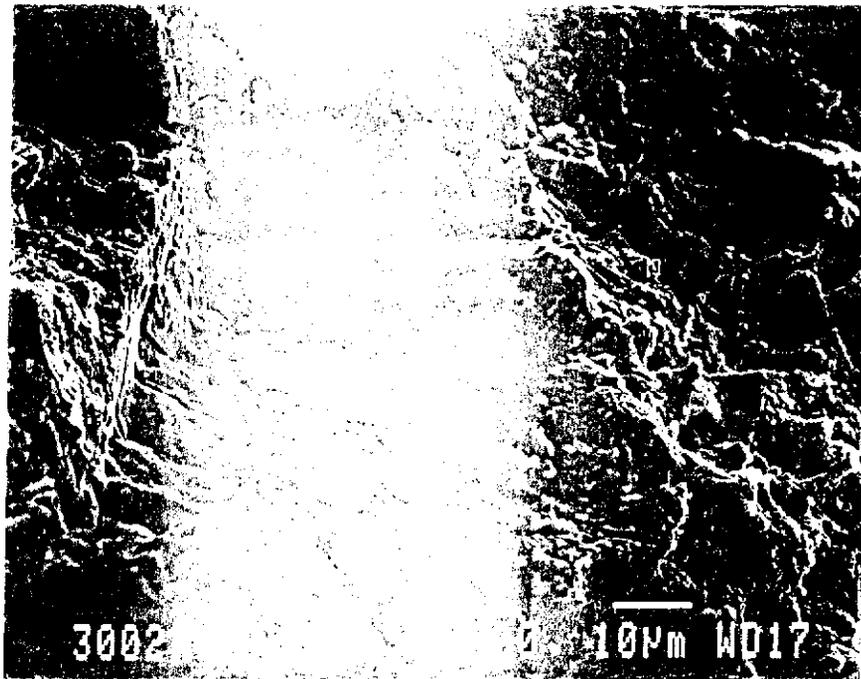
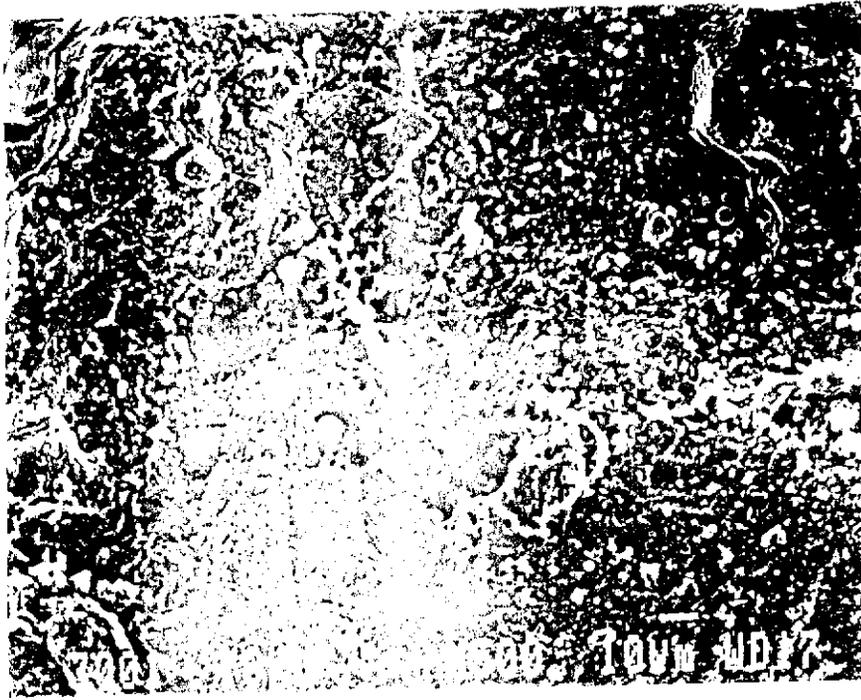
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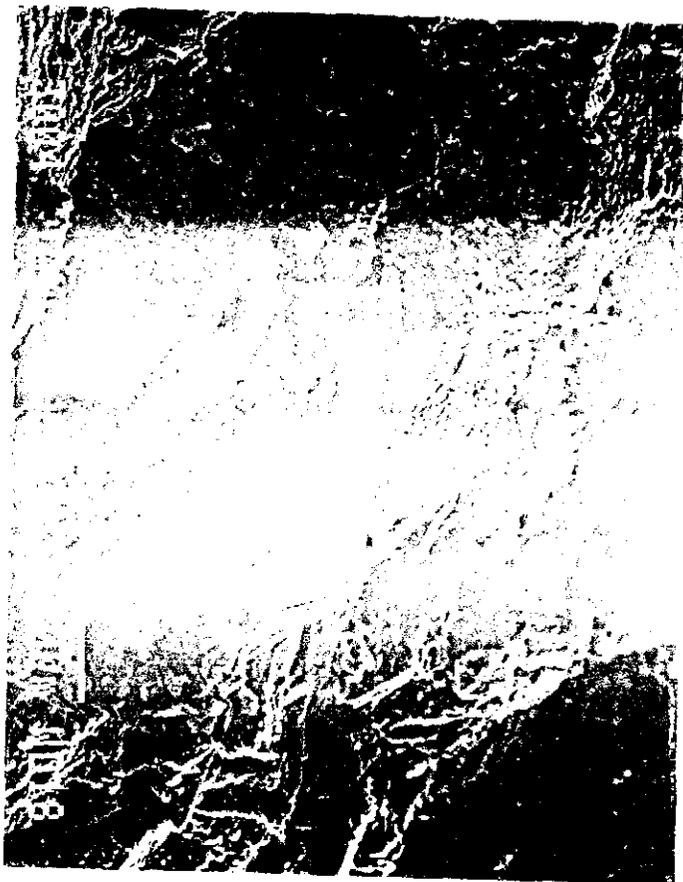


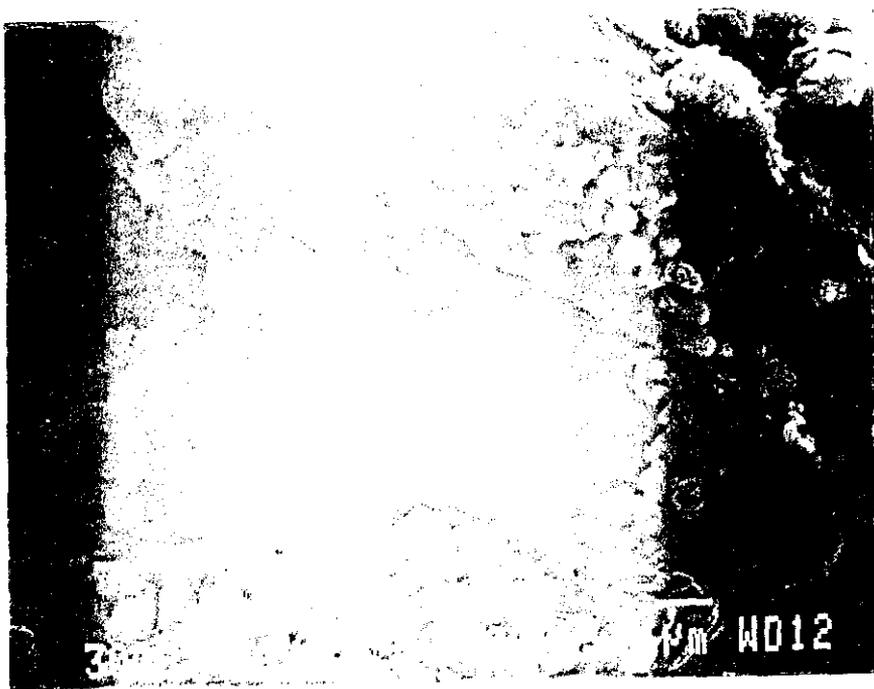
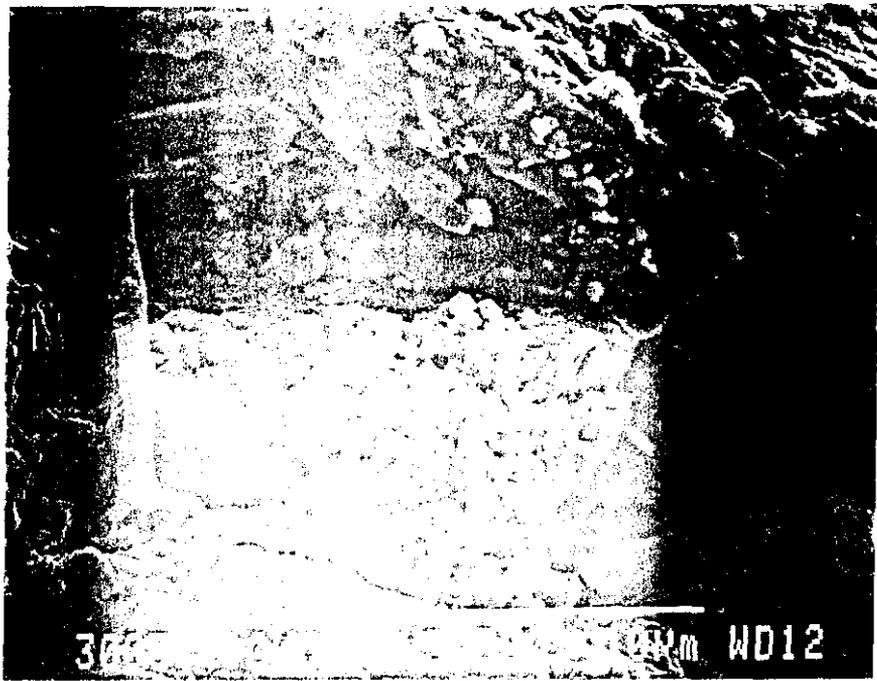
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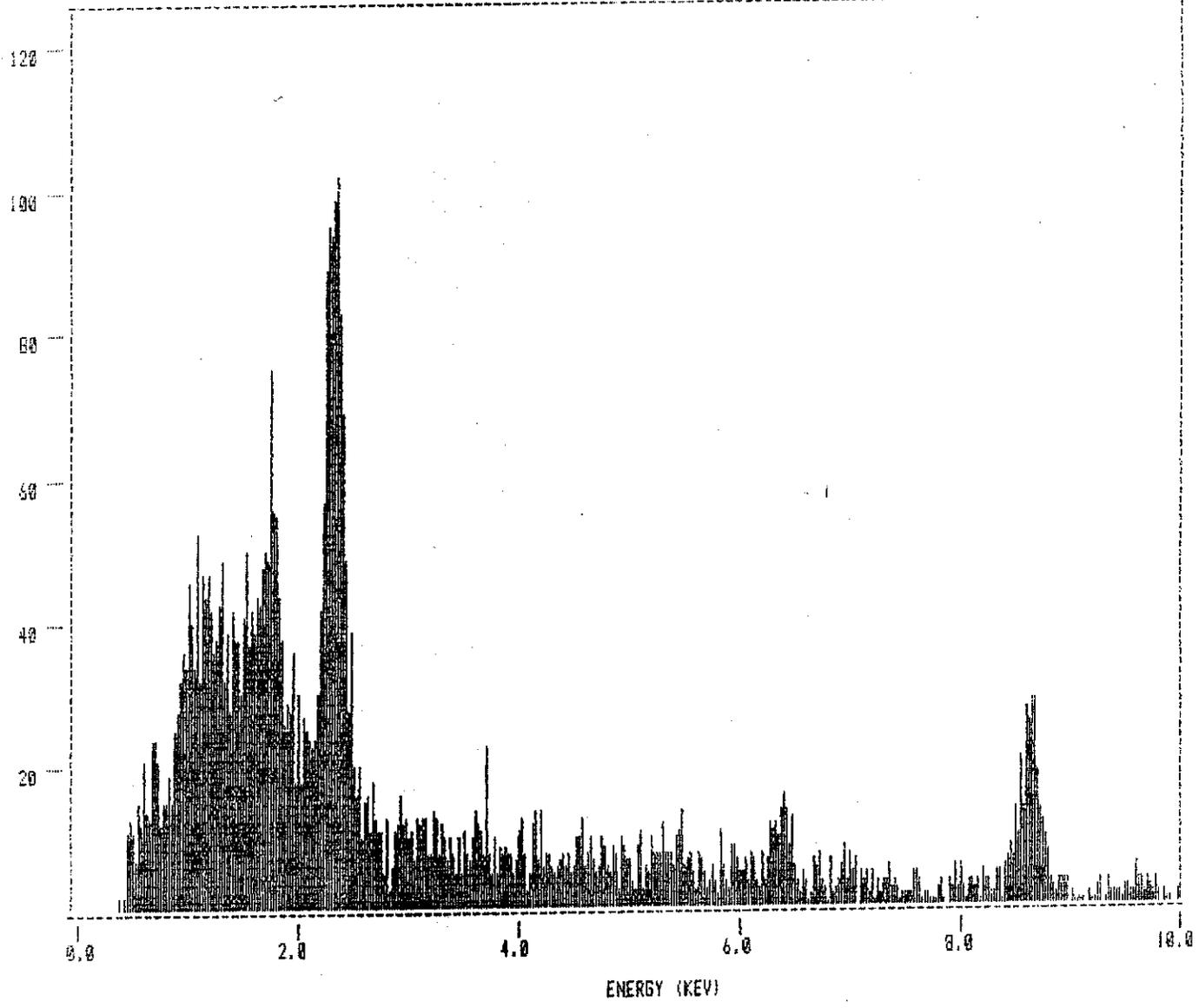
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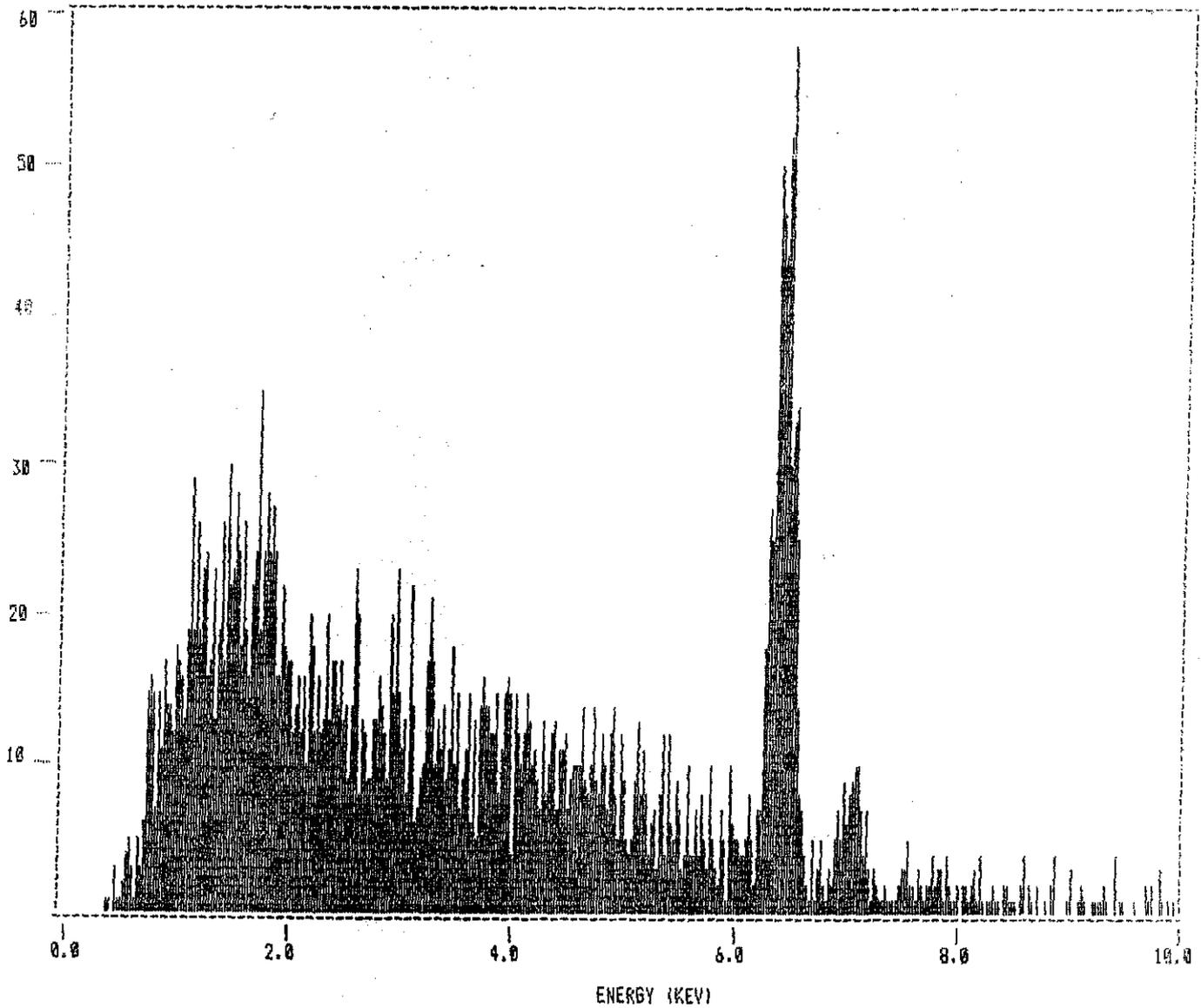
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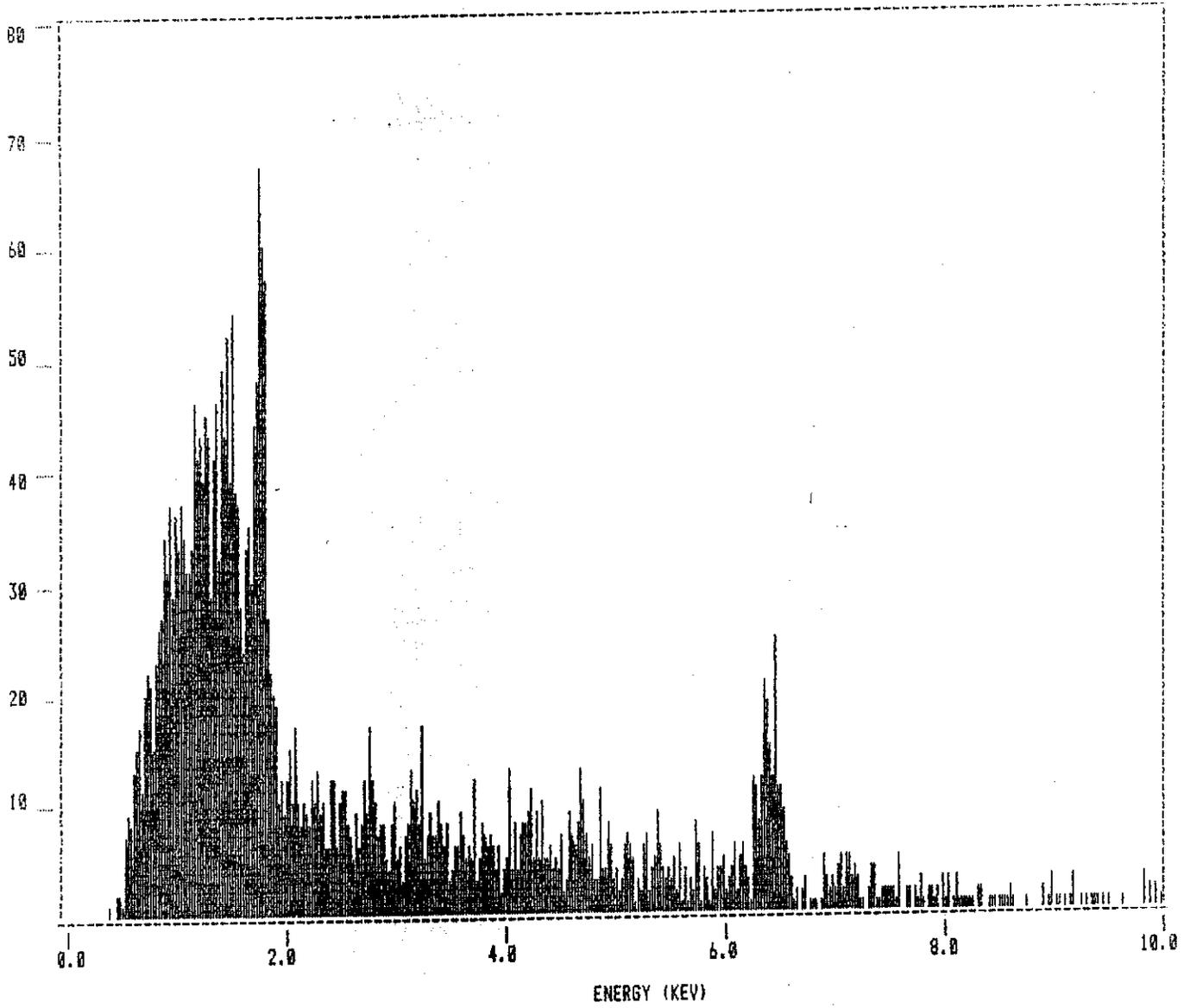
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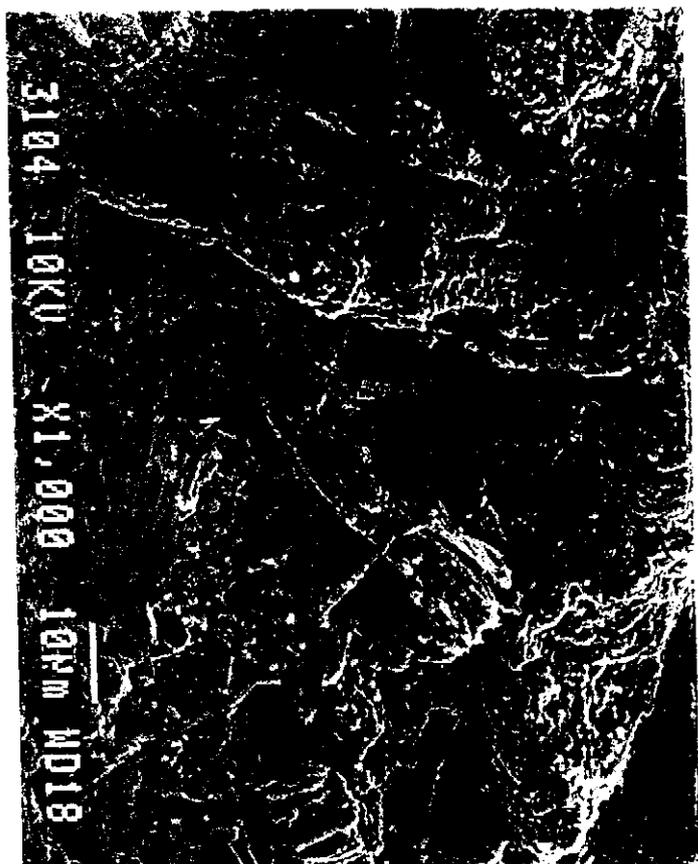
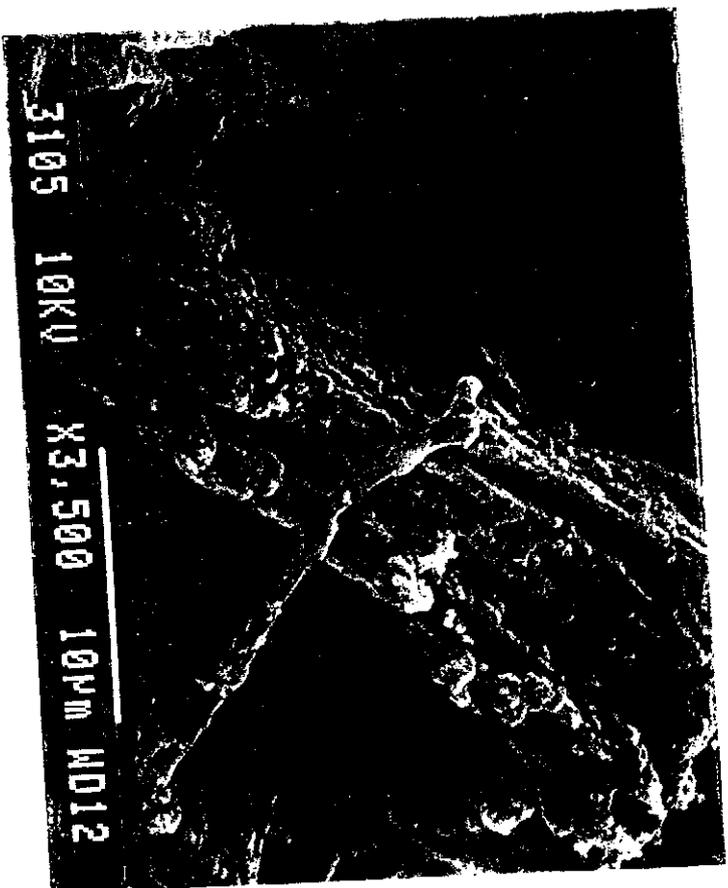
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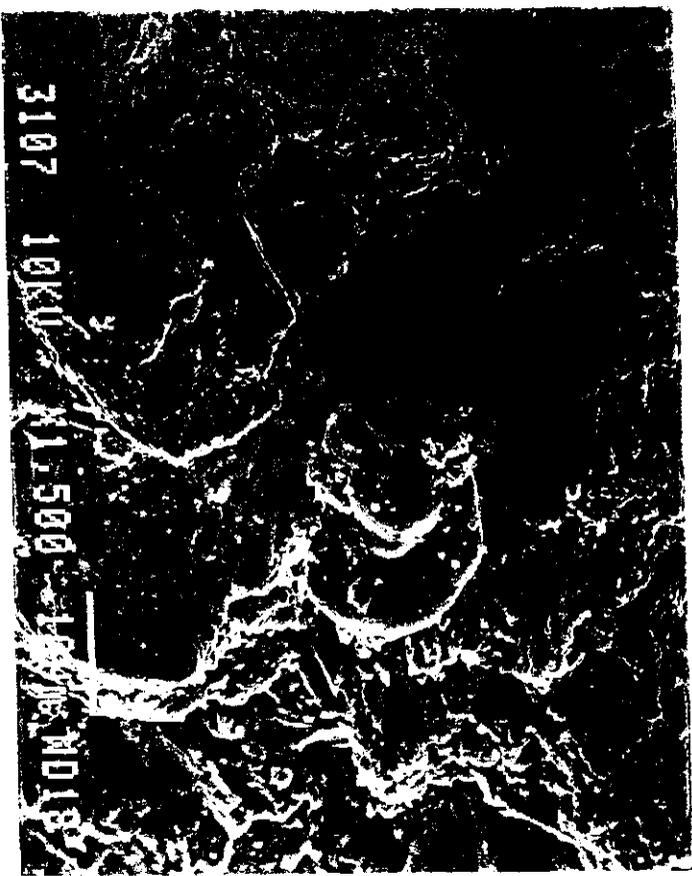


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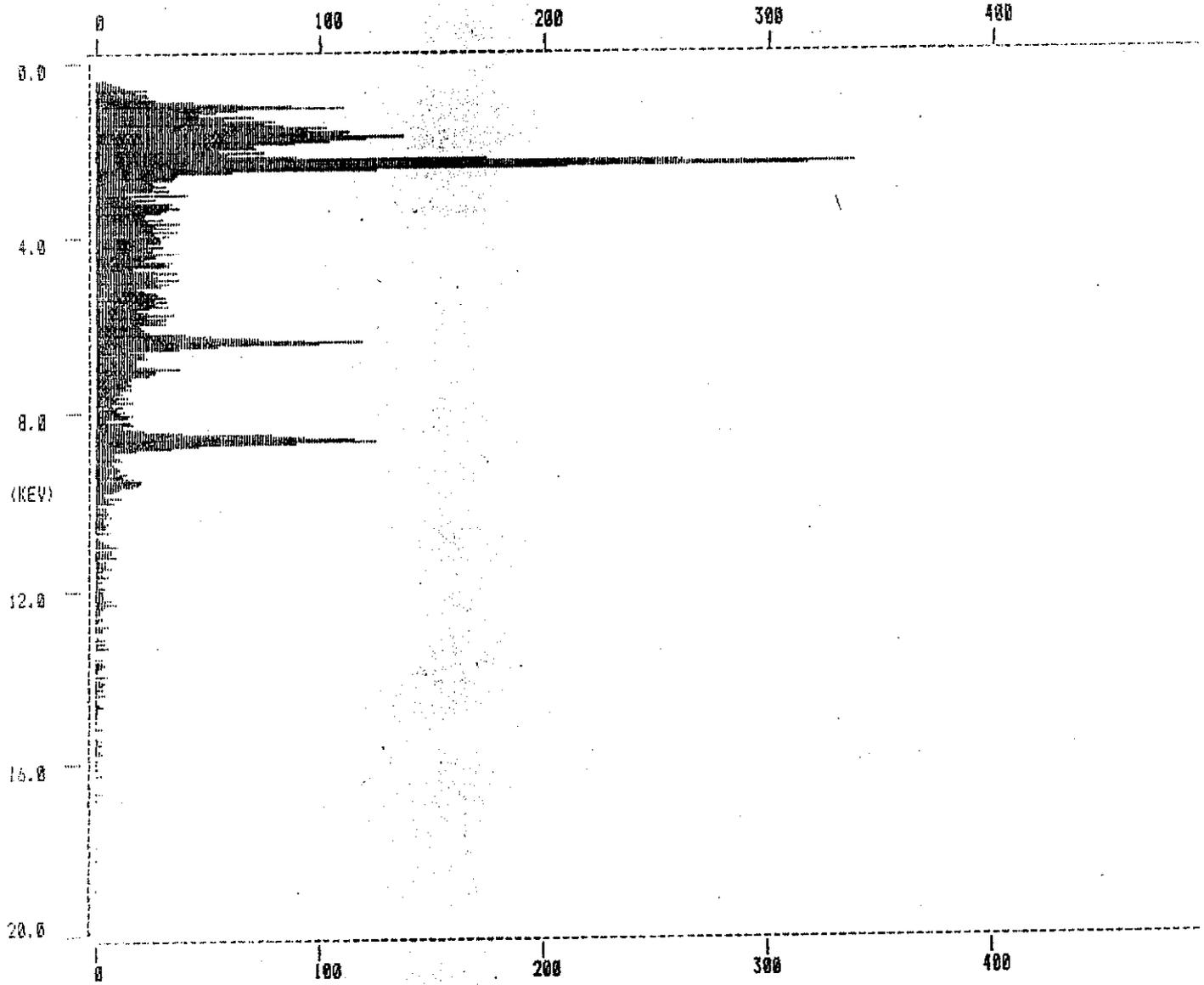
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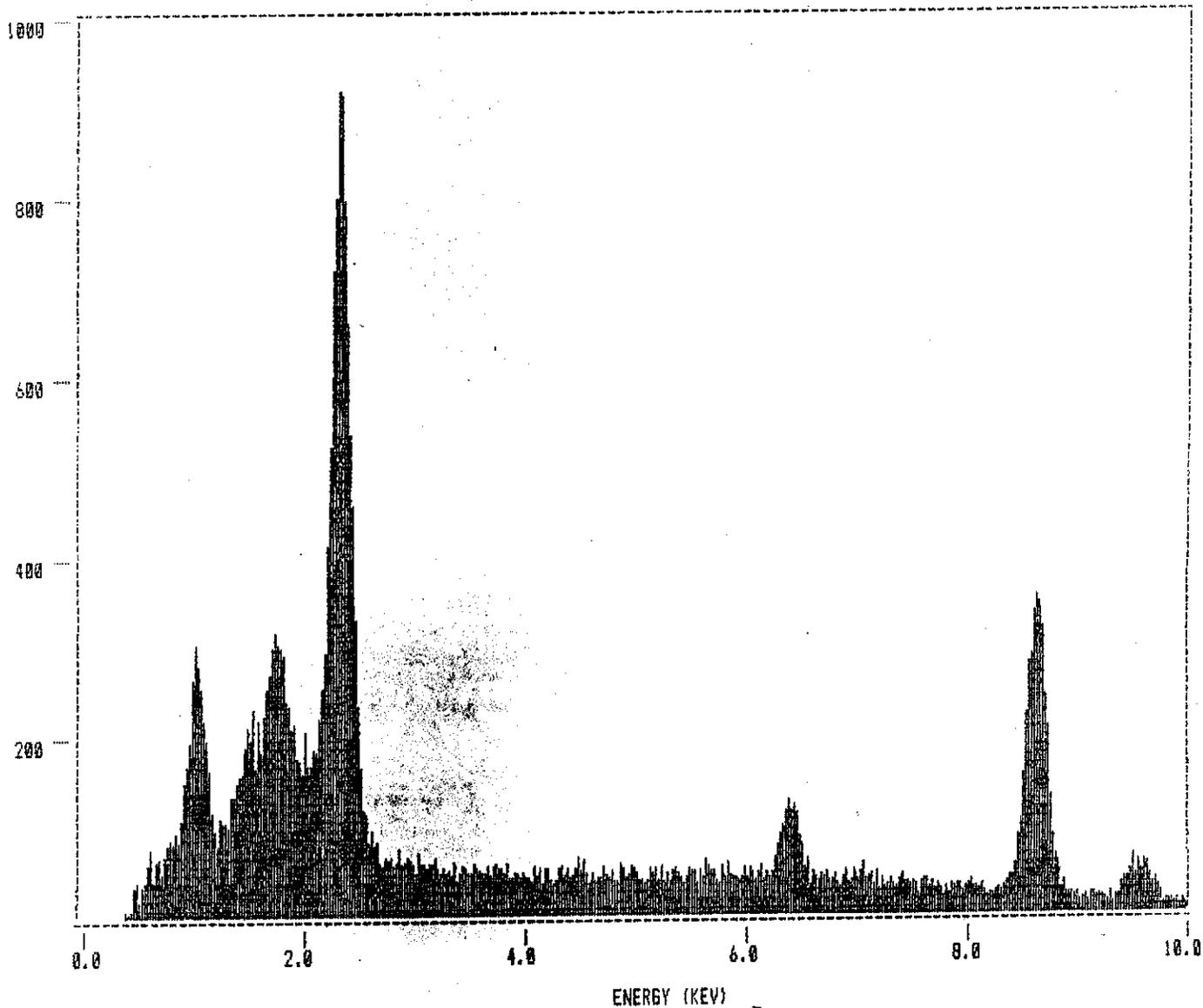
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ATTACHMENT 2

**SOME ASPECTS OF DISSOLUTION
OF PHOSPHATE ROCK**

MEMORANDUM

Date: November 17, 1995

To: M. Kalin, Boojum Research VIA FAX 861-0634

From: Grant Ferris 4 pages

Re: Phosphate Rock / AMD Drum Experiments

Dissolution experiments have been conducted with samples of phosphate rock used in the AMD drum experiments conducted by Boojum Research. The objective of these kinetic experiments was to ascertain specific rate constants for phosphate dissolution at different pH values. Determination of the phosphate dissolution rate constants provides a quantitative basis on which to compare and evaluate performance data from the AMD drum experiments.

The experiments were done in 125 mL acid-leached polypropylene bottles containing 0.5 g of phosphate rock in dilute aqueous H_2SO_4 adjusted to pH 3.0, 5, or 6.5. Samples of the aqueous phase were removed from the bottles after 10, 30, 60, and 120 minutes of reaction time. Dissolved orthophosphate concentrations were determined for each sample using the Hach Phosphover reagent and DREL 2000 spectrophotometer.

Dissolution profiles for the phosphate rock at pH 3, 5, and 6.5 are shown in Figure 1. The rate of orthophosphate dissolution was the greatest at pH 3.0, and about one order of magnitude higher than that which occurred at the higher pH values. In each case, dissolution rates decreased with reaction time as expected from the hyperbolic rate law for mineral dissolution (Stumm and Morgan 1981. Aquatic Chemistry, John Wiley, New York):

$$(1) \frac{dC}{dt} = K_p t^{0.5}$$

The integrated form of the rate law yields:

$$(2) C_t = C_0 + 2K_p t^{0.5}$$

where C_t is the concentration of a dissolved species at time t , C_0 is the dissolved species concentration at time 0, and K_p is the rate constant. Since the concentration of dissolved phosphate in the dilute H_2SO_4 used in the experiments was zero, equation 2 becomes:

$$(3) C_t = 2K_p t^{0.5}$$

Linear plots of the experimental data according to equation 3 yielded dissolution rate constants (normalized to the mass of phosphate rock) of 0.01125 $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$ at pH 3.0, and 0.001875 $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-0.5}$ at pH 5.0 and 6.5. Using these rate constants, the expected weathering rate of phosphate rock in the AMD drums may be calculated as follows.

The weathering rate of phosphate rock (R) relates generally to the water flux through the drum (Q), mass of phosphate rock exposed to weathering (m), and amount of orthophosphate released per unit mass of phosphate rock (C):

$$(4) R = QmC$$

The value C is described by equation 3. Thus, equation 4 becomes:

$$(5) R = Qm2K_p t^{0.5}$$

From the dimensions of the phosphate rock AMD drums, and meteoric precipitation in the Toronto region (956 mm per year), the yearly water flux Q is estimated to be 154.88 $\text{L}\cdot\text{yr}^{-1}$. As each of the treated AMD drums was amended with 3.6 L of phosphate rock (density of 1.74 $\text{kg}\cdot\text{L}^{-1}$), the value of m is 6264 g. The really difficult parameter to estimate is t, the reaction time over which phosphate dissolution occurs. Conceptually, t is equivalent to the water transit time through the drums (τ):

$$(6) t = \tau = M/Q$$

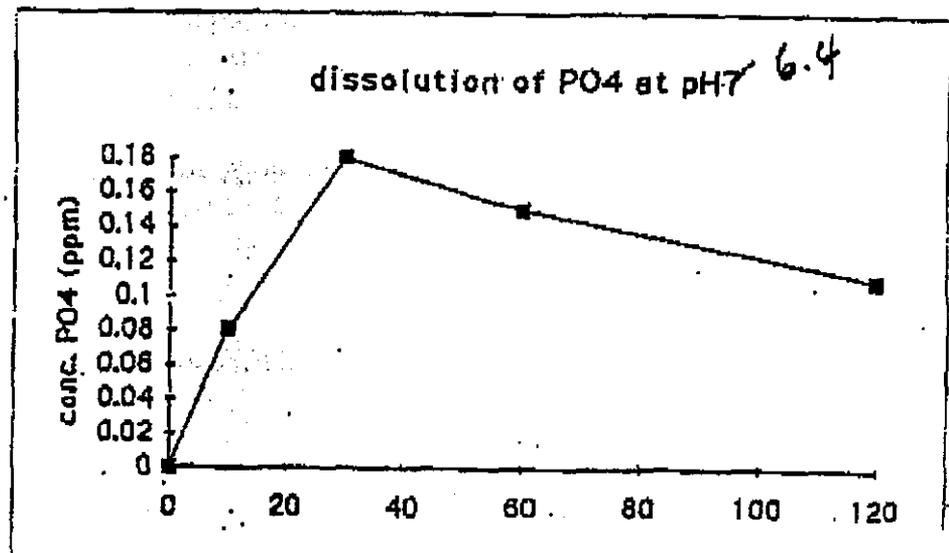
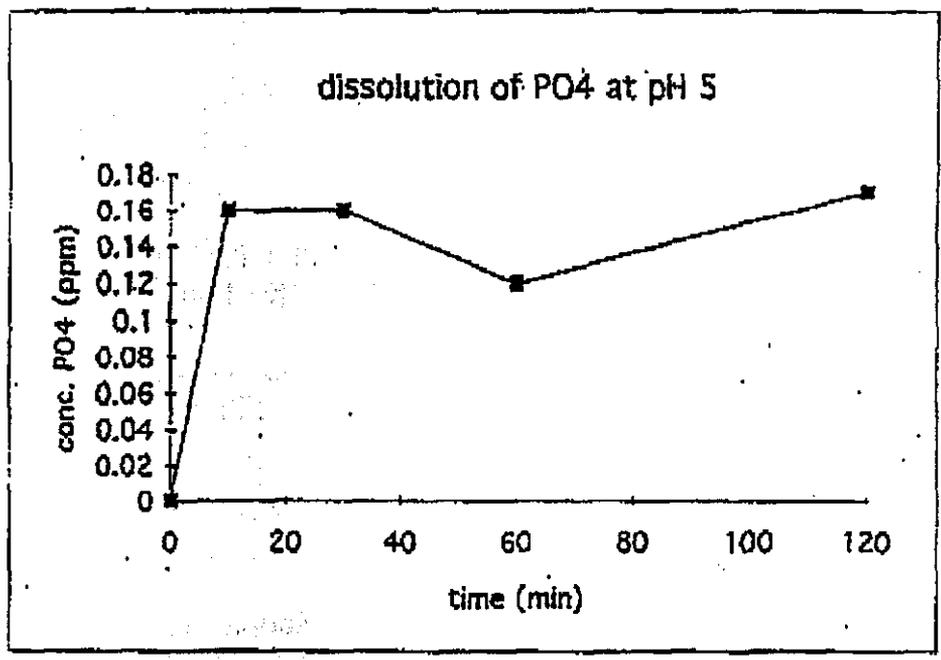
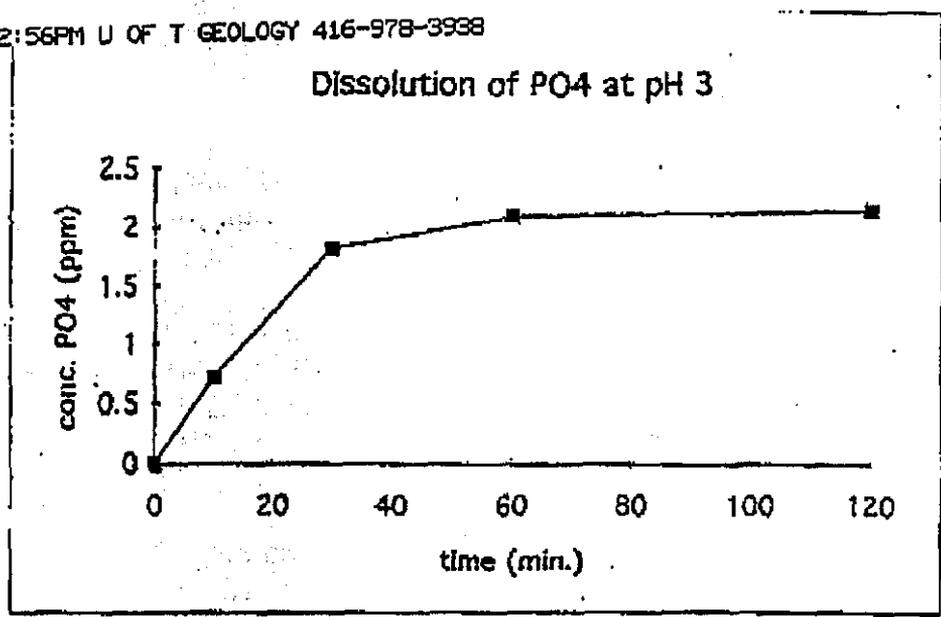
where M is the volume of water in transit through the drum (effectively some fraction of the void volume V, i.e., $M = \alpha V$). Measured void volumes for the drums are around 20 L, so t must be something less than 0.129 years. Because the drums are highly porous (around 50 %), the transit time for the infiltrating water was probably fairly short. In view of this, and the rapid decrease in phosphate dissolution after 60 minutes (Figure 1), t is assumed to be around 120 minutes. This yields a value of 0.0354 L (35.4 mL) for M (perhaps not unreasonably as the drums must have been dry for some periods of time throughout the year).

If t is taken at 120 minutes and used in equation 5, one finds that 242.4 g of orthophosphate would have been dissolved on a yearly basis at pH 3.0. Similarly, at pH 5.0 or 6.5, only 40.5 g of orthophosphate would have been dissolved on a yearly basis. Assuming a phosphate content of 49% in the phosphate rock, and a duration of 2.75 years for the AMD drum experiments, a total loss of 1360 g of phosphate rock would be expected at pH 3.0, while a loss of 227 g should have occurred at pH 5.0 or 6.5.

The actual amounts of phosphate rock recovered from the AMD drums at the end of 2.75 years of operation corresponded to a loss (depending on the treatment) of between 500 g (layered on top) and 1000 g (throughout the drum). These values are close to those calculated from the dissolution experiments. The lower amount (500 g) corresponds to weathering at a higher pH (meteoric water pH was between 6 and 6.9), whereas the higher amount (1000 g) conforms with weathering under reduced pH conditions (as might be expected from the oxidation of pyrite within the waste rock in the drum).

Since the amount of phosphate rock used in the AMD drums are close to calculated amounts for phosphate rock weathering, it would appear that very little phosphate was actually retained as an insoluble FePO_4 mineral coating on waste rock inside the drums. If and where FePO_4 mineral precipitation occurred, it would depend primarily on the amount of dissolved orthophosphate in the water passing through the drum. Phase equilibria diagrams may be used to address this issue in greater detail. Examples will follow.

FIGURE 1



MEMORANDUM

Date: November 20, 1995

To: M. Kallin, BooJum Research

VIA FAX 861-0634

/ Pages

From: Grant Ferris

Re: Your Fax

Magarete,

I have sent you another memo report by fax with relevant phase equilibrium diagrams. You have all the information you need to further refine my calculations of dissolved orthophosphate concentrations at various points inside the AMD drums. You might want to do this just to get a more precise picture of what happened.

Your action plan seems appropriate. Following my return from Sweden, I will make arrangements to complete the SEM work on samples from series 2 and 3 drums. I will also consider whether the information we have collected thus far can be related to the pyrite surface area of the waste rock.

For your information, I have talked with Dave Koren at CANMET. I must admit that I am not pleased with the time frame they've suggested.

I return December 4. A floppy disk with copies of memo reports is in the mail (MS Win/Word 1.1).

MEMORANDUM

Date: November 20, 1995

To: M. Kalin, Boojum Research

VIA FAX 861-0634

4 Pages

From: Grant Ferris

Re: Phosphate Rock / AMD Drum Experiments

A mineral coating consisting of iron and phosphate was identified by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) on rock samples from treated drum A3. These precipitates were not found in any of the control drums (A1, B1, C1), nor were they present in samples from treated drum A2. (Note: corresponding SEM micrographs and EDS spectra were previously forwarded to Boojum by M. Berezowsky).

Mineral phase equilibrium diagrams can be used to relate the presence (or absence) of iron phosphate mineral coatings on rocks from the AMD drums to the dissolution of phosphate rock, employed in the treatment of 2 and 3 series drums. Specifically, Figure 1 shows the relationship for the solubility of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (strengite) expressed in terms of dissolved orthophosphate or ferric iron concentration (moles L^{-1}) as a function of pH. The plot shows clearly that the solubility of the iron phosphate mineral decreases as pH goes up. Moreover, as between pH 2.2 and 7.2 (pK_1 and pK_2 for phosphoric acid), the main dissolved orthophosphate species is H_2PO_4 .

As outlined in a memo report of November 17, 242.4 g of orthophosphate would have been dissolved on a yearly basis at pH 3.0, whereas 40.5 g of orthophosphate would have been dissolved at pH 5.0 or 6.5. These amounts, allowing for a yearly through-put of water of 154.86 L, correspond to orthophosphate concentrations of 1.65×10^{-2} and 2.75×10^{-3} M, respectively. Both of these values fall well within the iron phosphate stability field, as shown in Figure 1, suggesting that phosphate precipitation may have occurred; however, several other factors need to be considered additionally. These include stability relationships between iron phosphate and iron oxides (i.e., the most insoluble mineral phase should dominate), as well as factors controlling dissolved orthophosphate concentrations in the drum.

When iron oxides are present (or may precipitate owing to the introduction of dissolved ferric iron into solution through, for example, the oxidative dissolution of pyrite), the solubility of iron phosphate may be greatly altered (Figure 2). At low pH, iron phosphate is more insoluble than amorphous iron oxide and controls the solubility of dissolved orthophosphate; however, at

pH values above 3.0, amorphous iron oxide becomes dominant owing to its insolubility (i.e., dissolved iron precipitates as amorphous iron oxide, leaving orthophosphate in solution). Thus, orthophosphate will be released into solution as iron phosphate is converted into amorphous iron oxide at pH values above 3.0. Again, the estimated concentrations of dissolved orthophosphate from the dissolution experiments (1.65×10^{-2} at pH 3.0 and 2.75×10^{-3} M at pH 5.0/6.5) fall within the iron phosphate stability field, suggesting further that phosphate precipitation may have occurred.

The phase equilibrium diagrams emphasize the importance of dissolved orthophosphate concentrations on the formation of iron phosphate precipitates in the drums. As emphasized in the November 17 memo report, the transit time of water through the AMD drums effectively determines dissolved orthophosphate concentrations as this is the reaction time over which phosphate rock dissolution occurs. In 2 series drums, where the phosphate rock is distributed throughout the waste rock, the transit time is estimated at 120 minutes. In these drums, the estimated concentrations of dissolved orthophosphate (1.65×10^{-2} at pH 3.0 and 2.75×10^{-3} M at pH 5.0/6.5) corresponding to *EXIT* concentrations. Concentrations within the drum must have been somewhat lower. In this context, it is important to note that even a 10 fold decrease in dissolved orthophosphate concentration at meteoric water pH will favor the formation of amorphous iron oxide instead of iron phosphate. Thus, the phosphate will be lost from the drum. This is consistent with the SEM/EDS work that has, so far, not detected iron phosphate precipitates in 2 series samples.

In 3 series drums, where phosphate rock was layered on top of the waste rock, the dissolution reaction time was shorter; however, all of the phosphate rock was exposed to the meteoric water prior to infiltrating through the waste rock. Thus, the estimated concentrations of dissolved orthophosphate (1.65×10^{-2} at pH 3.0 and 2.75×10^{-3} M at pH 5.0/6.5) correspond to *INTERNAL* concentrations favorable to the precipitation of iron phosphate. Again, this is consistent with SEM/EDS results that reveal iron phosphate coatings on rocks from drum A3.

Chart1

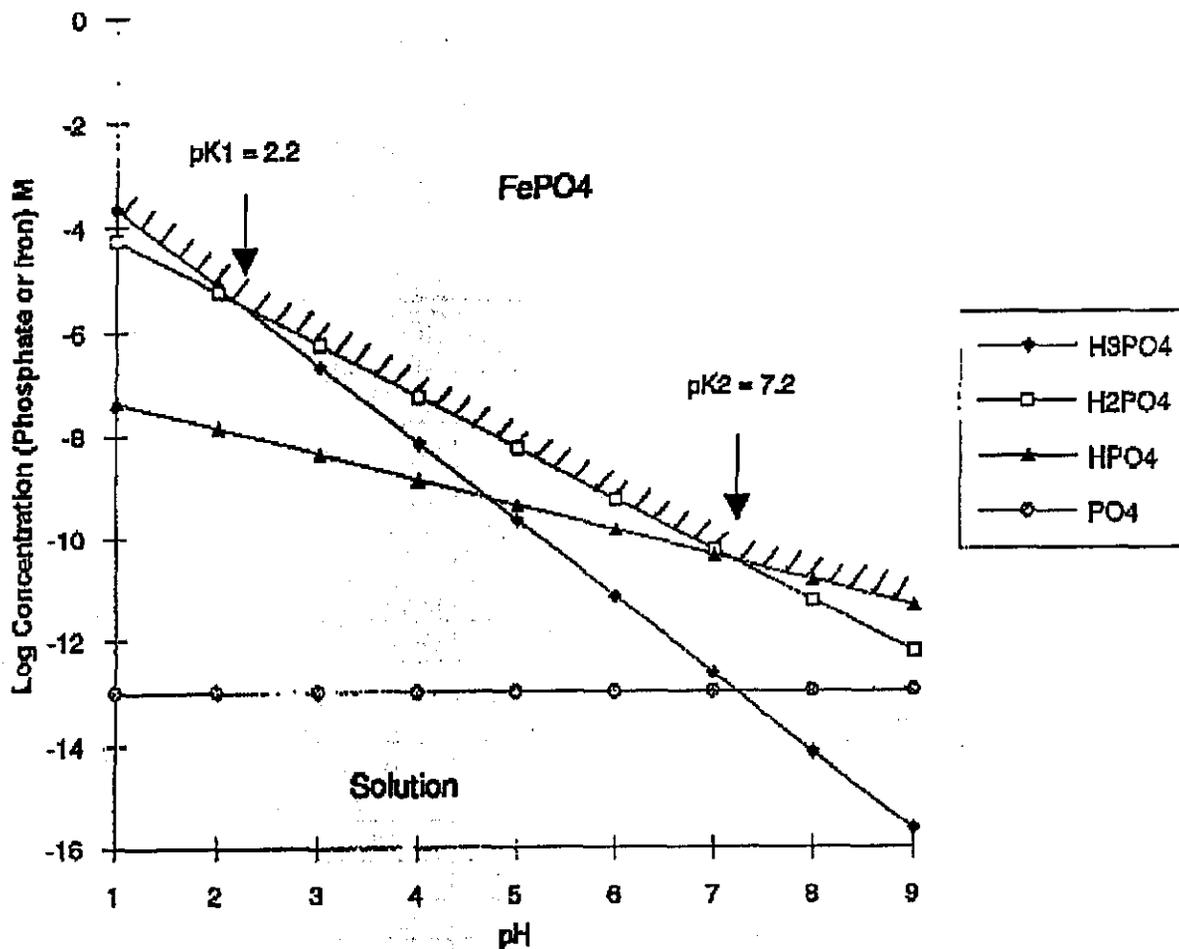


Figure 1

P040X.XLC

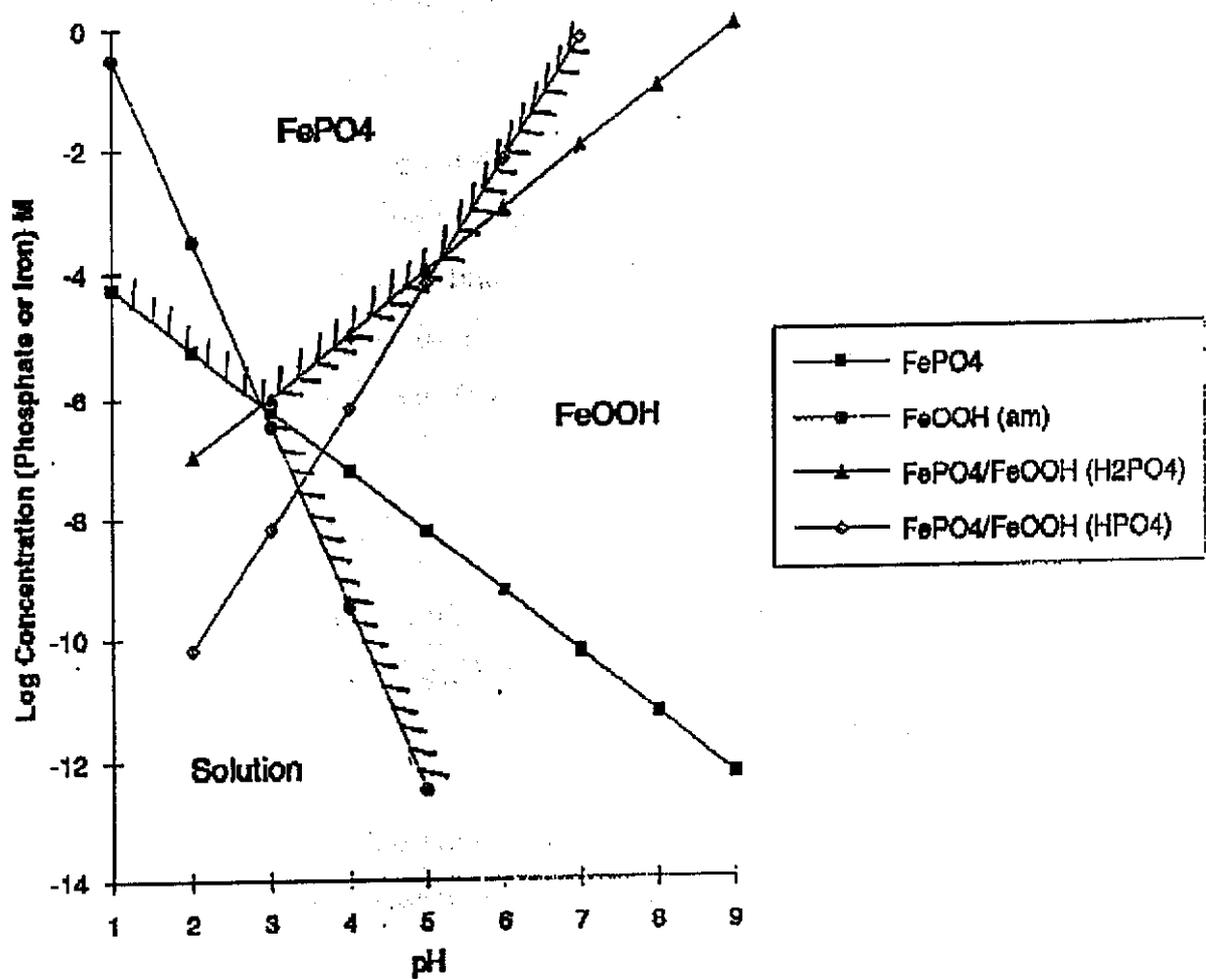


Figure 2

ATTACHMENT 3

**RESULTS OF LAST WATER SAMPLES
SUBMITTED FOR CHEMICAL ANALYSIS**

Notes on Chemistry of Waste Rock Drum Effluents Collected May 11, 1995

For reference:

- A drums = low pyrite fresh
- B drums = high pyrite fresh
- C drums = low pyrite old
- D drum = background rock
- E drums = high pyrite old

For each series:

- Drum 1 = control, no phosphate rock
- Drum 2 = phosphate rock mixed
- Drum 3 = phosphate rock top only

Rain Water

The only elements exceeding 1 mg/L in the sample from the rainwater drum were Ca (6.65 mg/L), K (8 mg/L), Na (1.34 mg/L) and S (4.2 mg/L).

Phosphate Rock Drum

Water which passed through a layer of phosphate rock had elevated concentrations of Ca (33.6 mg/L), Na (2.91 mg/L) and S (16.2 mg/L) compared to rain water indicating some dissolution and release of materials. Very little P was present (0.09 mg/L) as expected. This would only be released at a lower pH.

Control Drums

The effluents of control drums were characterized by high concentrations of Zn (59-110 mg/L), Ca (25-42 mg/L), Mg (7-30 mg/L) and S (53-155 mg/L). Smaller

but relevant concentrations of Al (1.5-8.4 mg/L), Cu (0.8-32 mg/L), Fe (0.2-8.4 mg/L), Mn (2.0-6.7 mg/L), Na (6.0-7.8 mg/L). Of these elements Mn and Na concentrations were similar across rock types indicating a similar source and if present, similar removal mechanisms. Sodium is very soluble and except through ion exchange can not be readily be removed from solution. Mn is notoriously difficult to remove from AMD.

Effluent Fe, Cu and Al concentrations exhibited considerable differences between rock types. The high pyrite old (C-1) had the highest Al, Cu and Fe concentrations, indicative of release of metal from oxidation and products of previous oxidation. A little P was present in the control drum effluents (<0.06-0.24 mg/L) indicating the presence of some P in the rock materials and its release in low pH conditions found within the drum.

Drums with Phosphate Rock

In the presence of phosphate rock, the effluents were characterized by substantial reductions in concentrations of Al, Cu, Fe, Mn and Zn. For the fresh rock drums, these elements were reduced by around 90 % or more regardless of whether the phosphate rock was placed throughout the drum or in the top part only. This indicates that both treatments inhibit the oxidation of pyrite and release of these metal ions or that they are released locally but reprecipitated within the drums. For the drums with weathered rocks, the drums with phosphate rock throughout (C-2, E-2), the treatment was as effective as with the drums with fresh unweathered rock whereas the drums with phosphate rock in the top part only exhibited much less reduction in concentration of these elements in the effluent. This indicates that in these drums, the low pH remobilized these metals from precipitates in the lower part of the drums. In the drums with fresh rocks, presumably such precipitates were absent. It is worthy of note that in these two drums, effluent concentrations of some elements (Ca, K, S, Sr and Zn) were greater than in the control drums

suggesting that local oxidation had occurred. Phosphate concentrations were below detection limits in most drums with phosphate rock indicating that none was released or, if so, precipitating with metal ions.

Summary

Overall, the presence of phosphate rock in the drums substantially reduced the concentrations of metal ions (Al, Cu, Fe, Mn and Zn) in drum effluents. This inhibition was most effective for the drums with fresh (unweathered) waste rock where phosphate rock throughout the drum or in the top part only worked equally well. With weathered waste rock, the presence of phosphate rock throughout the drum was required to maintain low metal concentrations in the effluent. Phosphate was absent in effluent of drums treated with phosphate rock indicating no dissolution or precipitation of phosphate with metal ions released within the confines of the drum.

Sampling date: May 11, 1995

ASS#	5762 WRD A-1 low pyrite fresh no PR	5763 WRD A-2 low pyrite fresh PR mixed	5764 WRD A-3 low pyrite fresh PR layer	5765 WRD B-1 high pyrite fresh no PR	5766 WRD B-2 high pyrite fresh PR mixed	5767 WRD B-3 high pyrite fresh PR layer	5768 WRD C-1 low pyrite >4y weather. no PR	5769 WRD C-2 low pyrite >4y weather. PR mixed	5770 WRD C-3 low pyrite >4y weather. PR layer	5771 WRD D-1 non acid genera- ted rock	5772 WRD E-1 high pyrite >4y weather. no PR	5773 WRD E-2 high pyrite >4y weather. PR mixed	5774 WRD E-3 high pyrite >4y weather. PR layer	5775 WRD Red Drum PR only	5776 WRD Rain Water
Al	1.52	<0.025	0.03	2.01	0.031	0.071	8.42	0.048	1.93	3.19	0.037	<0.025	0.043	<0.025	<0.025
B	0.01	0.03	0.04	0.02	0.03	0.04	0.01	0.04	0.04	<0.01	0.02	0.02	0.03	0.03	0.03
Ba	0.015	0.009	0.008	0.014	0.008	0.011	0.008	0.009	0.007	0.011	0.016	0.007	0.009	0.017	0.007
Ca	40.3	80.6	78.4	42.4	71.8	97.5	38.8	138	265	35	25	51.9	150	33.6	6.65
Cd	0.42	0.026	0.036	0.669	0.025	0.094	0.311	0.082	0.252	0.431	0.28	0.013	0.503	<0.003	<0.003
Co	0.042	0.011	0.016	0.035	0.008	0.017	0.033	0.036	0.031	0.047	0.033	0.006	0.081	<0.005	<0.005
Cr	<0.005	0.005	0.006	0.007	0.006	0.007	0.006	0.008	0.005	<0.005	0.007	<0.005	0.006	0.008	<0.005
Cu	7.06	0.054	0.06	1.84	0.037	0.191	32.1	0.52	23.9	19.1	0.804	0.054	1.34	0.022	<0.003
Fe	1.62	0.22	0.137	1.25	0.109	0.315	8.45	0.462	0.687	4.94	0.223	0.064	0.332	0.043	0.052
K	<4	<4	<4	<4	<4	<4	<4	8	9.9	8.3	<4	<4	7.1	<4	8
Mg	23.7	15.1	15	25.8	12.9	15.5	30.9	26	27.3	22	7.13	8.12	20.1	1.6	1.23
Mn	3.98	1.08	1.09	6.7	1.49	2.54	3.77	3.14	4.9	4.61	2.05	0.371	3.87	<0.005	0.015
Na	6.36	14.7	4.47	7.75	3.92	5.27	5.47	4.9	6.02	4.67	6.11	3.71	5.25	2.91	1.34
Ni	0.02	0.01	0.02	0.03	0.01	0.02	0.02	0.03	0.04	0.02	0.01	<0.01	0.04	<0.01	<0.01
P	0.14	0.08	<0.06	0.08	0.06	<0.06	0.38	<0.06	0.24	0.26	<0.06	<0.06	<0.06	0.09	<0.06
Pb	<0.025	<0.025	<0.025	0.083	<0.025	0.026	0.071	0.029	<0.025	0.044	0.063	<0.025	<0.025	<0.025	<0.025
S	105	72.6	72.4	119	68.3	99.1	155	149	275	127	53.2	45.3	200	16.2	4.2
Sr	0.105	0.604	0.616	0.086	0.542	0.662	0.061	0.951	1.58	0.059	0.053	0.405	0.901	0.319	<0.02
Zn	65.3	6.23	7.05	85	8.23	16.9	84.5	31.3	59.7	101	46.8	5.11	119	0.075	0.04

ATTACHMENT 4

**SEM EDX ANALYSIS
OF ENCRUSTMENT LAYERS**

IMAGETEK
Analytical Imaging

ANALYSIS OF SAMPLES PERD COL.3 #6 AND PERD COL.9#4

Samples PERD COL.3#6 (P36) and PERD COL.9#4 (P94) were examined by scanning electron microscopy (SEM) and chemically analysed using X-ray microanalysis (EDX).

SAMPLE P94.

Small fragments of P94 (1-5mm) were examined by SEM (see fig.1). The surface of the fragments were typically covered in fine grain (<10micron) material. Backscattered electron imaging revealed no significant segregation of different elemental species across the sample surface.

EDX of the fragments showed that for elements in the range Na to U, Fe represented between 5 and 15% of the sample composition. See figs 2-6 for sample spectra.

The glutaraldehyde fixed sample of P94 was washed in distilled water then taken through an ethanol series before being air dried. With the exception of the removal of some fine grain material, the morphology and chemistry of the fixed sample was the same as for the dry P94.

SAMPLE P36.

Sample P36 was found to be predominantly an agglomerate of large grains (1-10mm) cemented together by a fine grained matrix material. For examination by SEM a portion of the agglomerate was fractured and the fracture surface examined. Figure 7 is an electron micrograph of the fracture surface. The micrograph clearly shows a single large grain encrusted by the matrix material. Figure 8 is a micrograph of the interface between the grain and the matrix. The matrix appears to consist of both crystalline and extensive amorphous or extremely fine grain material. Figure 9 is a backscattered electron micrograph of the same region.

EDX of the matrix material and the grain (spectra collected from points A and B, fig.9) are presented in figures 10 and 11 respectively. The grain is composed predominantly of Ca and P with less than 5% of Fe. However, the matrix material is approximately 35-40% Fe. Spectra taken from other areas of the matrix material are presented in figure 12-16. Examination of the spectra show that while there are significant variations in the presence and amount of elements like Si, K, Al and S - P is present in all the spectra and the Fe content is in the range 25 to 40% in all cases.

Examination of the glutaraldehyde fixed sample showed no significant differences from the dry P36. No bacteria were observed in the sample examined.

FIGURE 1.

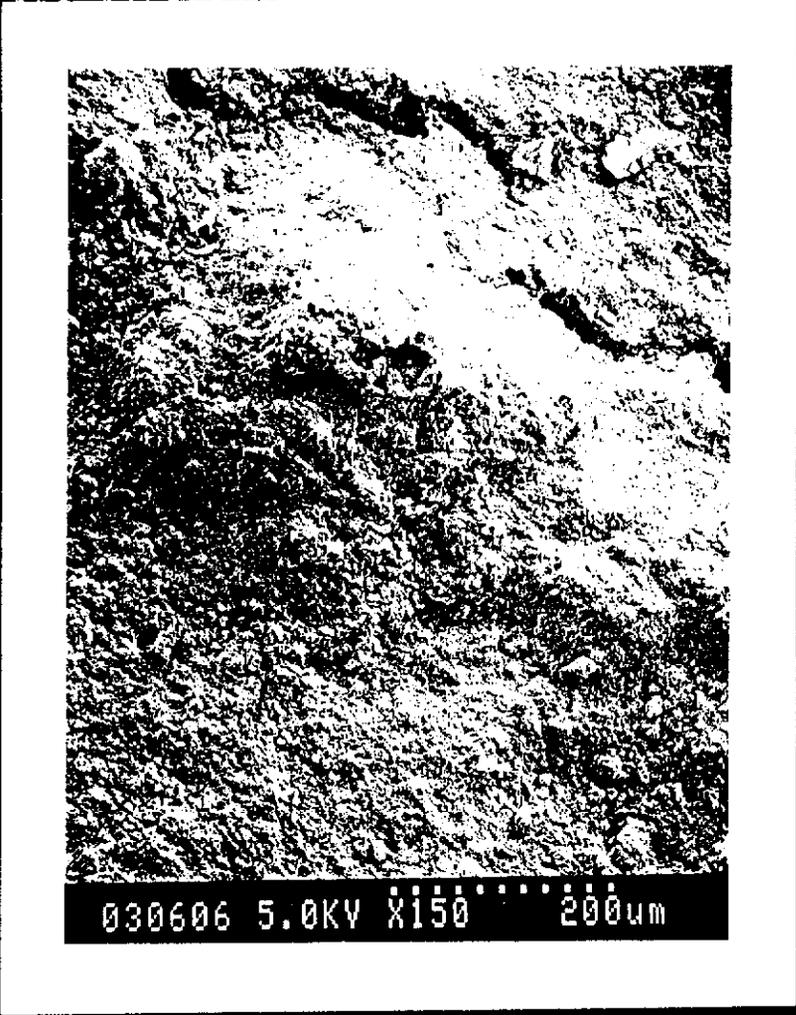
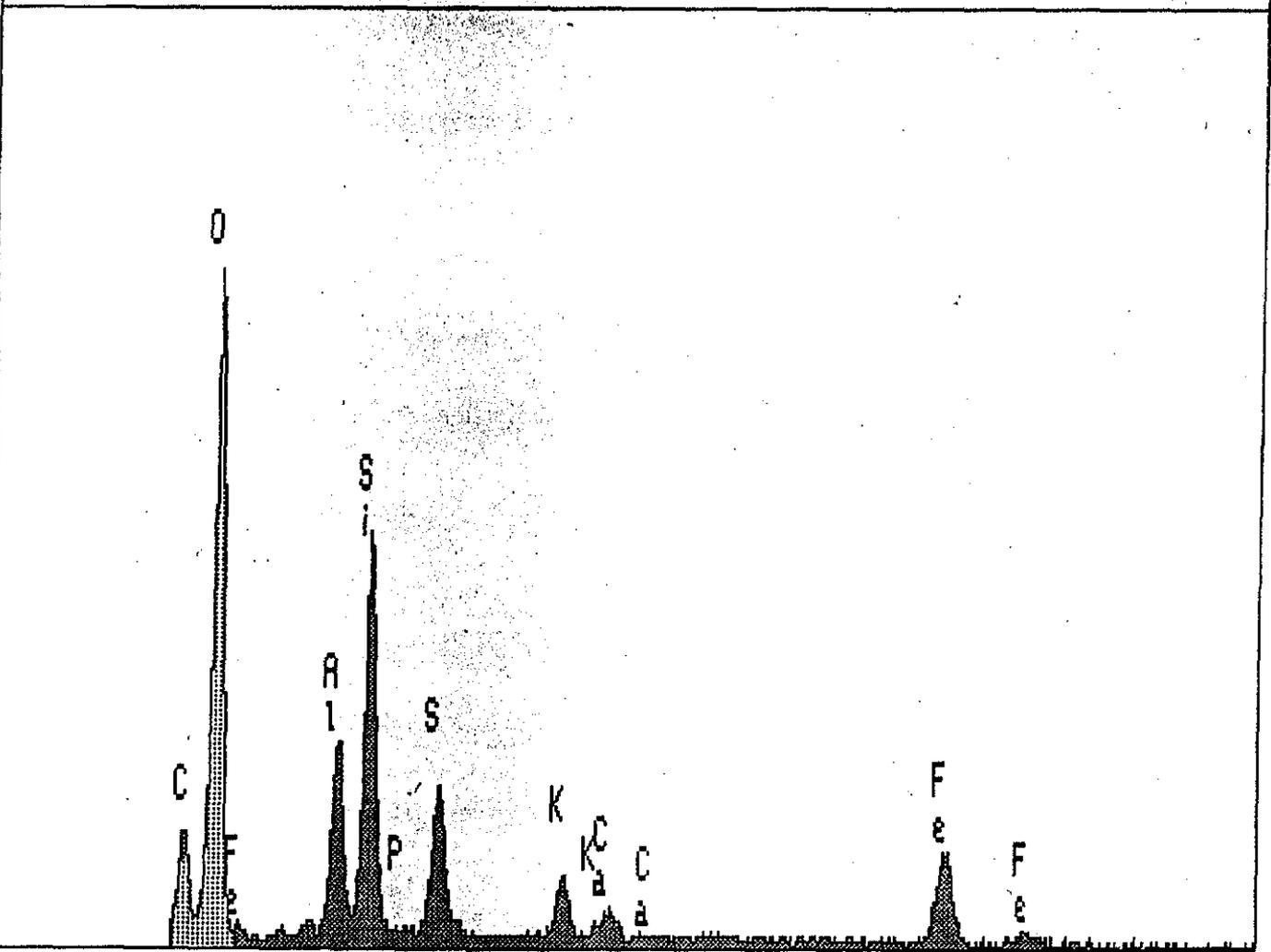


FIGURE 2.

X-RAY: 0 - 20 keV
Live: 50s Preset: 50s Remaining: 0s
Real: 78s 36% Dead



3.800 keV 8.9 >
FS= 4K ch 200= 94 cts
MEM1: PERD COL. 9 SAMPLE 4 SPEC#1

Spectrum file : NC91

PERD COL.9 SAMPLE 4 SPEC#1

LIVETIME(spec.)= 50

ENERGY RES AREA
- 6.7 85.54 39340

TOTAL AREA= 84840

.....
Peak at .50 keV omitted?
FIT INDEX=10.90

ELMT	APP.CONC	ERROR (WT%)
CaK : 0	.943	.109
AlK : 0	6.554	.185
SiK : 0	10.613	.175
ClK : 0	-.068	.083* < 2 Sigma*
P K : 0	.288	.137
TiK : 0	.289	.103
FeK : 0	8.328	.323
NaK : 0	.204	.068
S K : 0	4.572	.147
K K : 0	2.181	.123
MnK : 0	.081	.140* < 2 Sigma*
CrK : 0	.124	.122* < 2 Sigma*
NiK : 0	.191	.222* < 2 Sigma*
AsK : 0	.559	.621* < 2 Sigma*

ZAF CALCULATIONS

.....[4 iterations]

20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

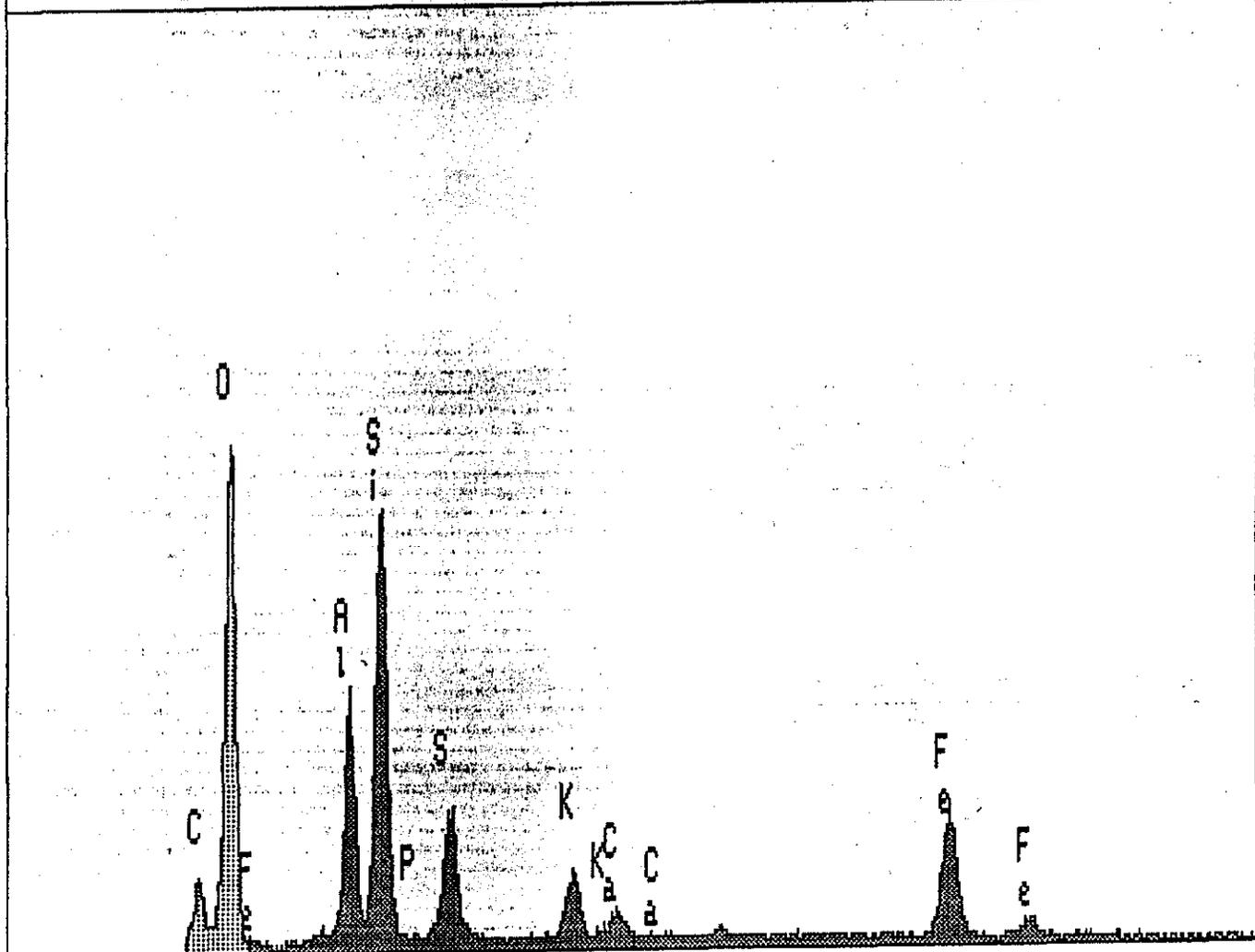
Spectrum: PERD COL.9 SAMPLE 4 SPEC#1

* INITIAL START-UP *

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT +-	Error	ATOM. %
CaK : 0	.819	2.333 +-	.270	1.922
AlK : 0	.721	18.427 +-	.521	22.553
SiK : 0	.638	33.732 +-	.555	39.653
ClK : 0	.601	< .165 +-	.083	
P K : 0	.643	.910 +-	.433	.970
TiK : 0	.778	.754 +-	.267	.520
FeK : 0	.848	19.906 +-	.772	11.769
NaK : 0	.604	.683 +-	.227	.981
S K : 0	.605	15.334 +-	.494	15.794
K K : 0	.812	5.451 +-	.307	4.603
MnK : 0	.819	< .281 +-	.140	
CrK : 0	.842	< .245 +-	.122	
NiK : 0	.844	< .444 +-	.222	
AsK : 0	.749	<1.241 +-	.621	
TOTAL		97.530		100.000

X-RAY: 0 - 20 keV
Live: 50s Preset: 50s Remaining: 0s
Real: 78s 36% Dead



3.800 keV 8.9 >
FS= 4K ch 200= 106 cts
MEM1: PERD COL.9 SAMPLE 4 SPEC#2

Spectrum file : NC92

PERD COL.9 SAMPLE 4 SPEC#2

LIVETIME(spec.)= 50

ENERGY RES AREA

- 6.4 86.38 38504

TOTAL AREA= 86222

.....
Peak at .50 keV omitted?

FIT INDEX= 8.91

ELMT	APP.CONC	ERROR(WT%)
CaK : 0	.890	.110
AlK : 0	7.621	.193
SiK : 0	11.819	.183
ClK : 0	.069	.080* < 2 Sigma*
P K : 0	.138	.132* < 2 Sigma*
TiK : 0	.363	.109
FeK : 0	11.331	.364
NaK : 0	.104	.060* < 2 Sigma*
S K : 0	4.184	.141
K K : 0	2.461	.129
MnK : 0	.036	.152* < 2 Sigma*
CrK : 0	.056	.133* < 2 Sigma*
NiK : 0	.466	.241* < 2 Sigma*
AsK : 0	.038	.664* < 2 Sigma*

ZAF CALCULATIONS

....[4 iterations]

20.00 kv TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: PERD COL.9 SAMPLE 4 SPEC#2

* INITIAL START-UP *

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT +-	Error	ATOM. %
CaK : 0	.830	1.930 +-	.239	1.605
AlK : 0	.709	19.334 +-	.490	23.888
SiK : 0	.627	33.931 +-	.525	40.267
ClK : 0	.614	< .160 +-	.080	
P K : 0	.636	< .265 +-	.132	
TiK : 0	.789	.829 +-	.250	.577
FeK : 0	.854	23.883 +-	.768	14.255
NaK : 0	.560	< .120 +-	.060	
S K : 0	.603	12.497 +-	.421	12.994
K K : 0	.823	5.379 +-	.282	4.586
MnK : 0	.825	< .305 +-	.152	
CrK : 0	.854	< .265 +-	.133	
NiK : 0	.841	< .482 +-	.241	
AsK : 0	.750	< 1.328 +-	.664	
TOTAL		97.783		100.000

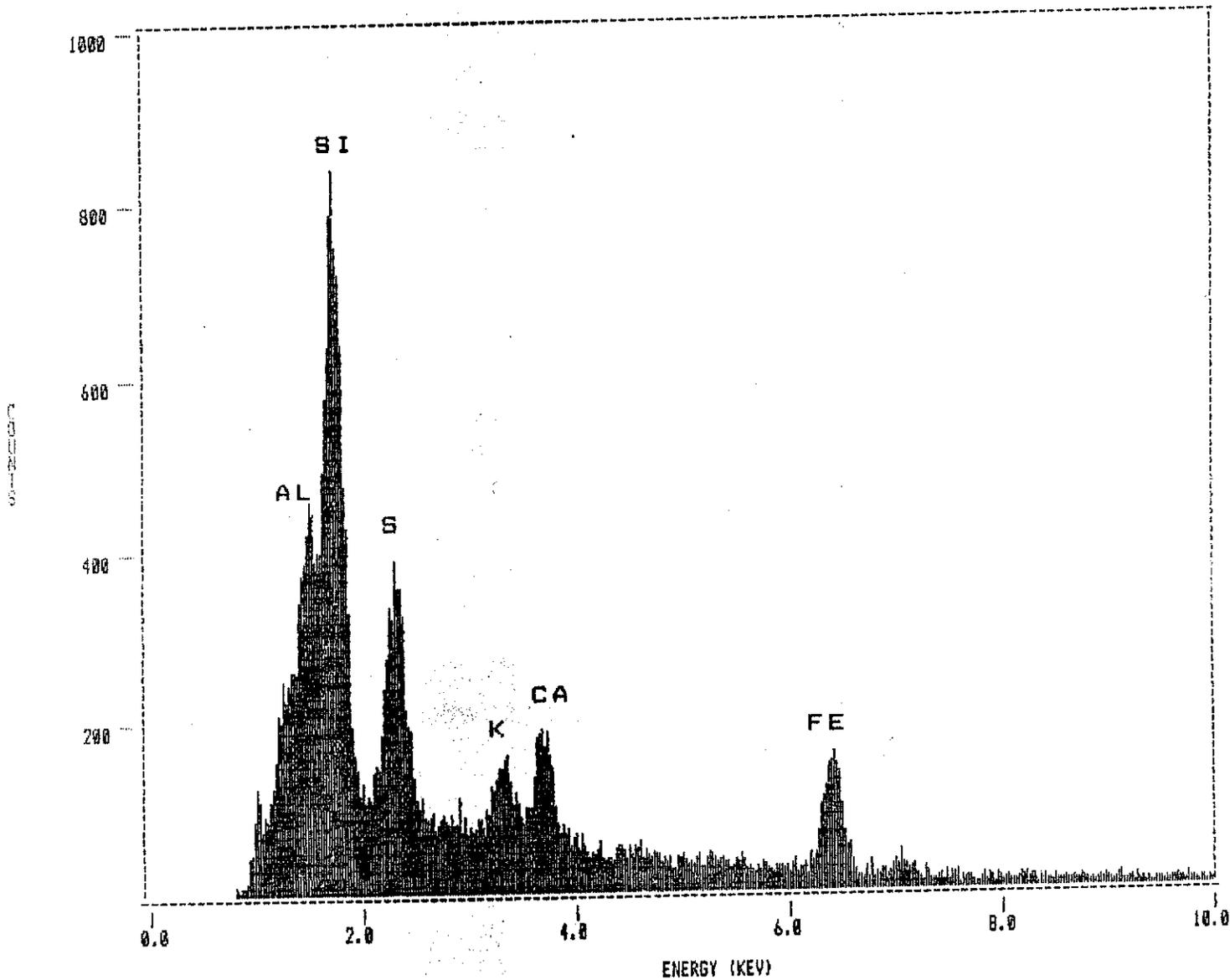
PERD COL.9 SPEC#1

SPECTRUM LABEL

SPECTRUM FILE NAME

████████

████████ NCCI



8 PIGITI

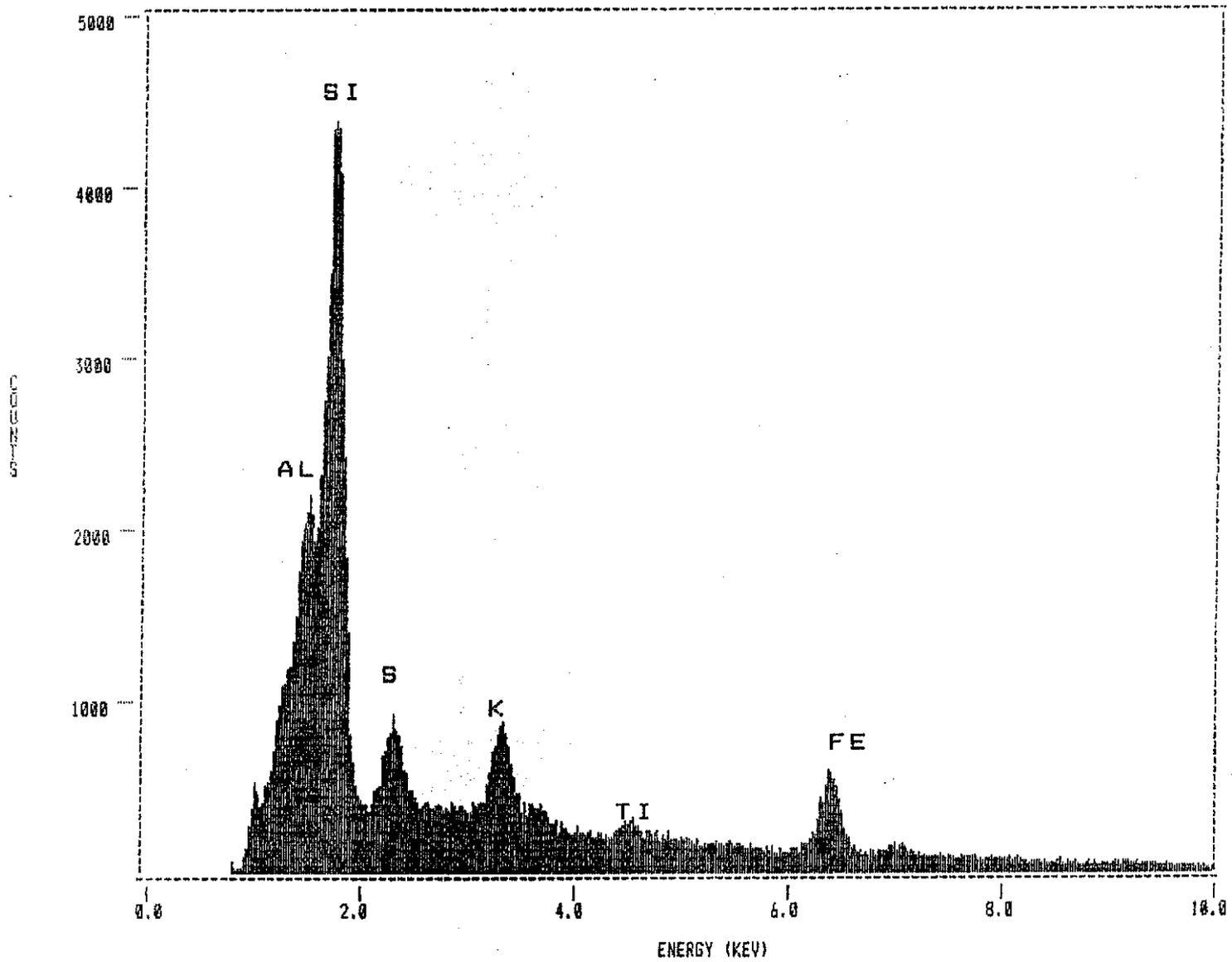
PERD COL.9 SPEC#2

SPECTRUM LABEL

SPECTRUM FILE NAME

██████

██████ NCC1



YPIGJTI

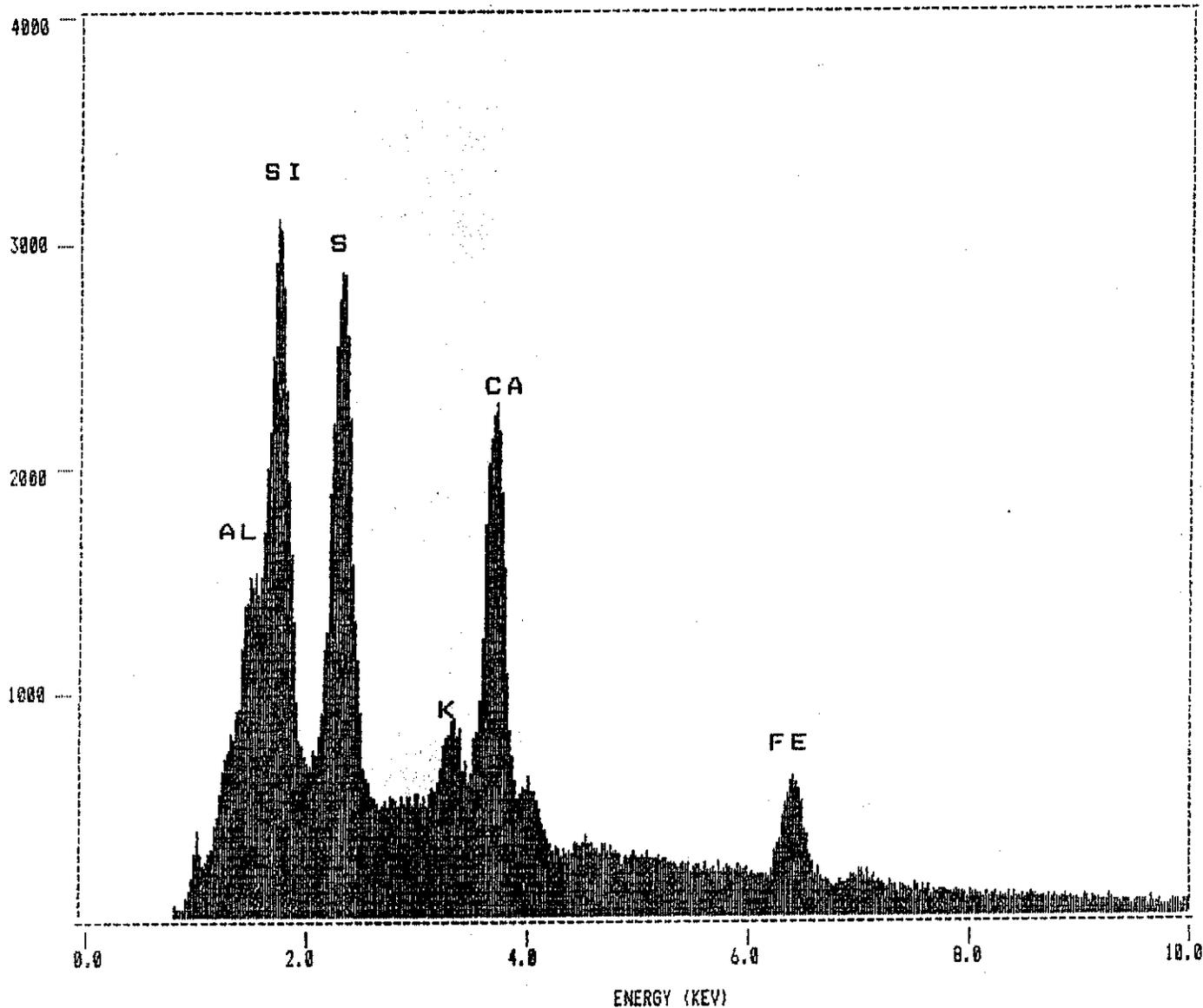
PERD COL.9 SPEC#3

SPECTRUM LABEL

SPECTRUM FILE NAME

XXXX

XXXX NCD1



γ PIGTI

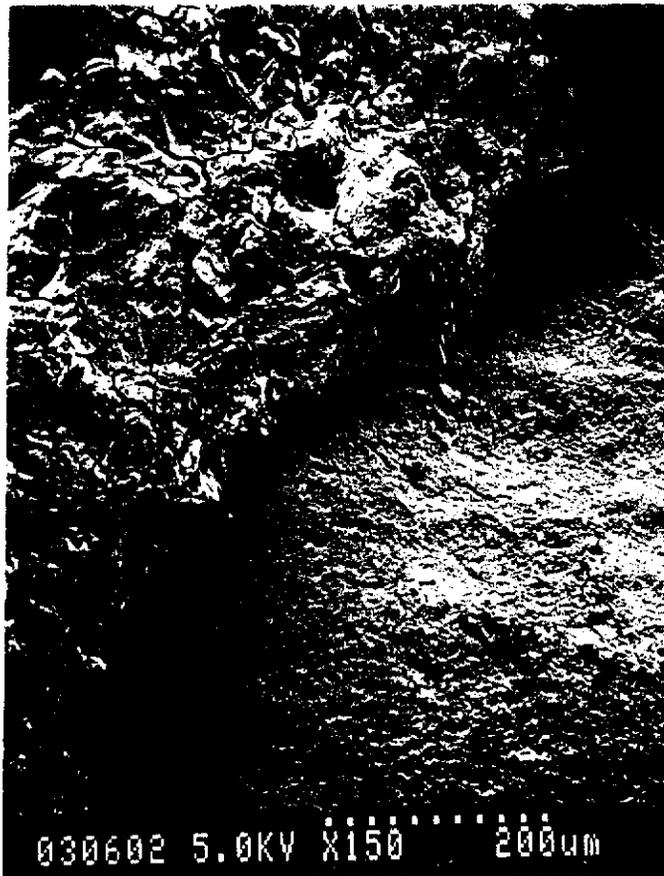
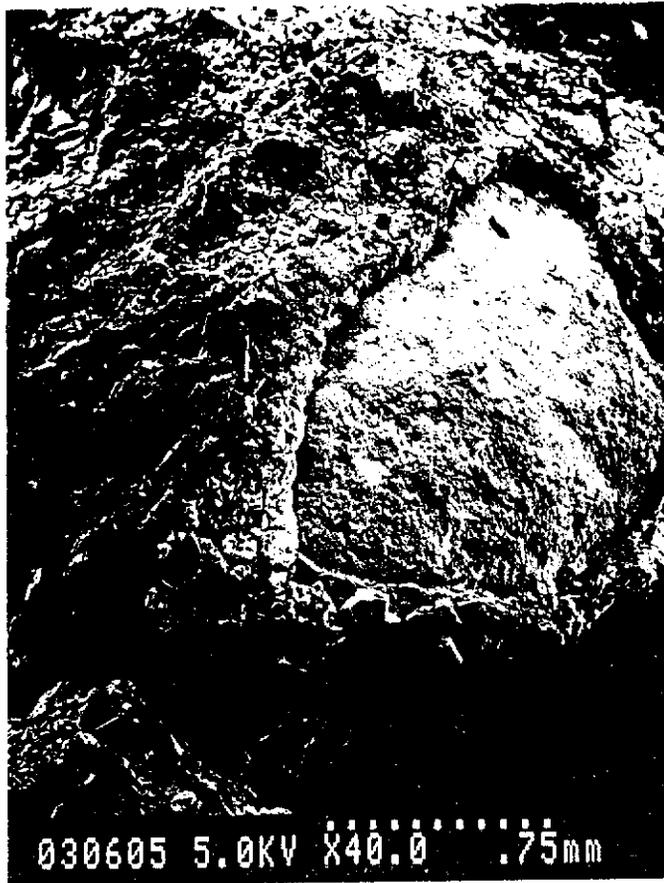
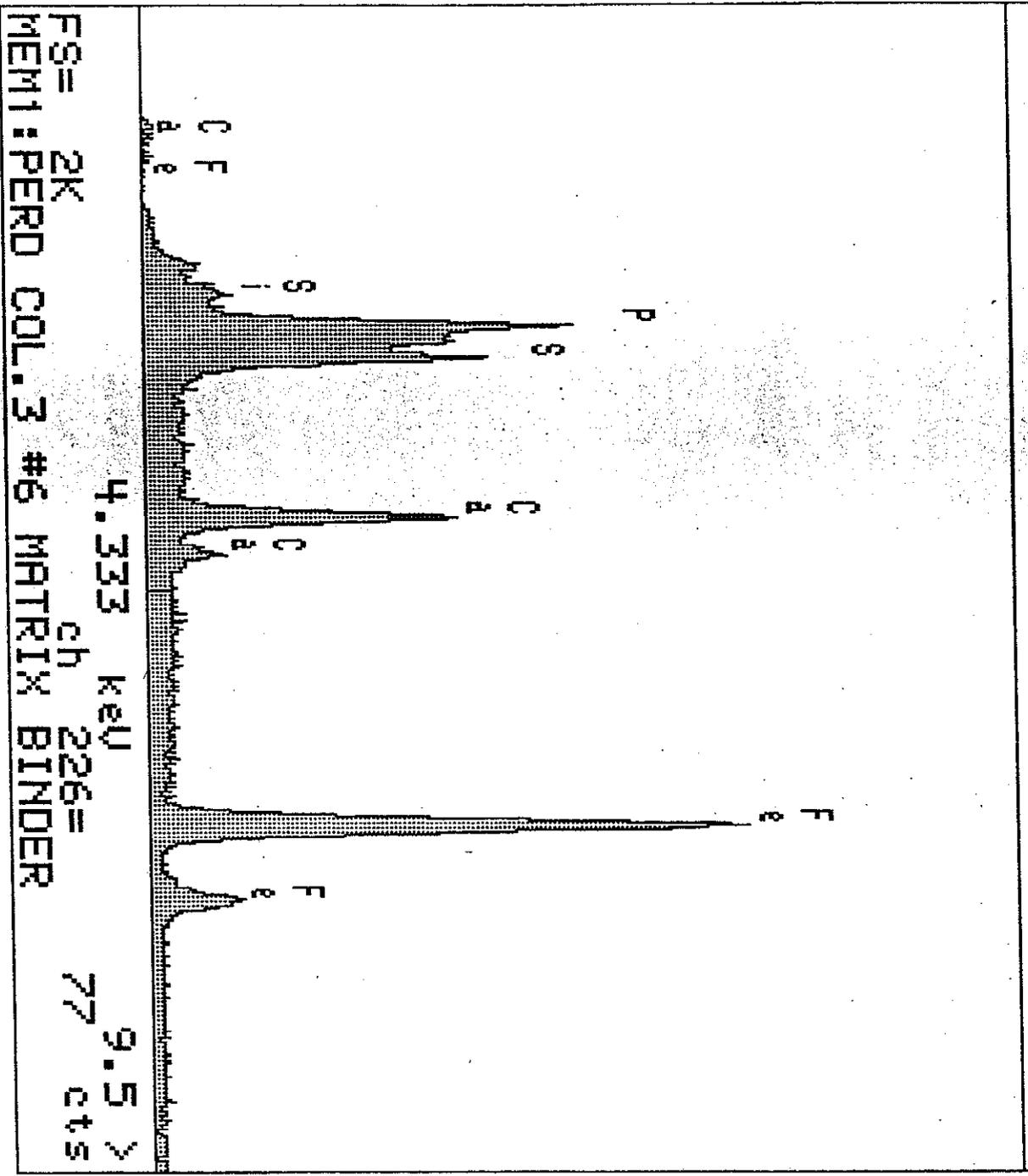


FIGURE 9.



FIGURE 10.

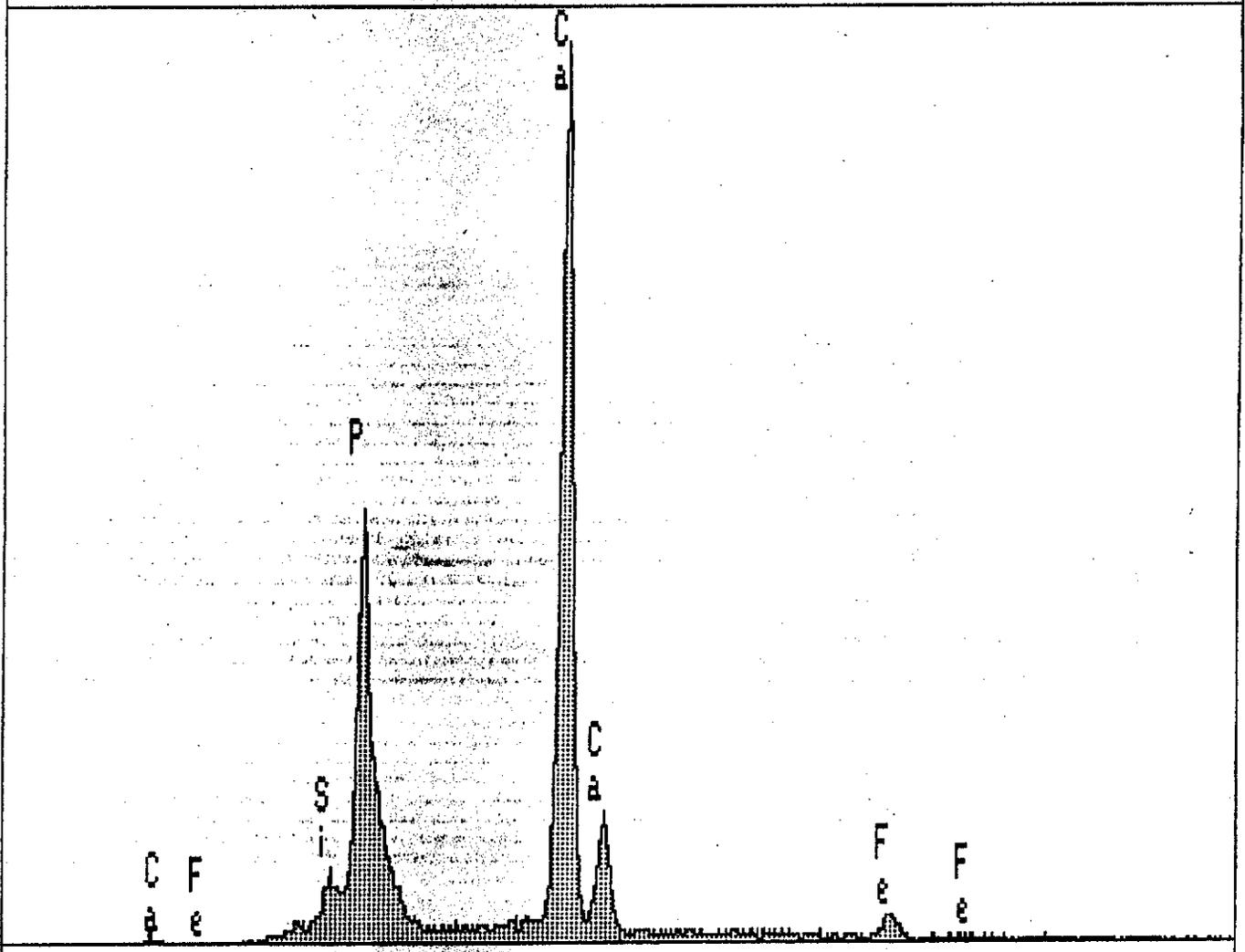
X-RAY: 0 -- 20 keV 50 s Preset: 33% Dead 50 s Remaining: 0 s
Live: 75 s
Real: 75 s



FS= 2K 4.333 keV 9.5 >
MEM1: PERD COL. 3 #6 MATRIX BINDER ch 226= cts

FIGURE 11.

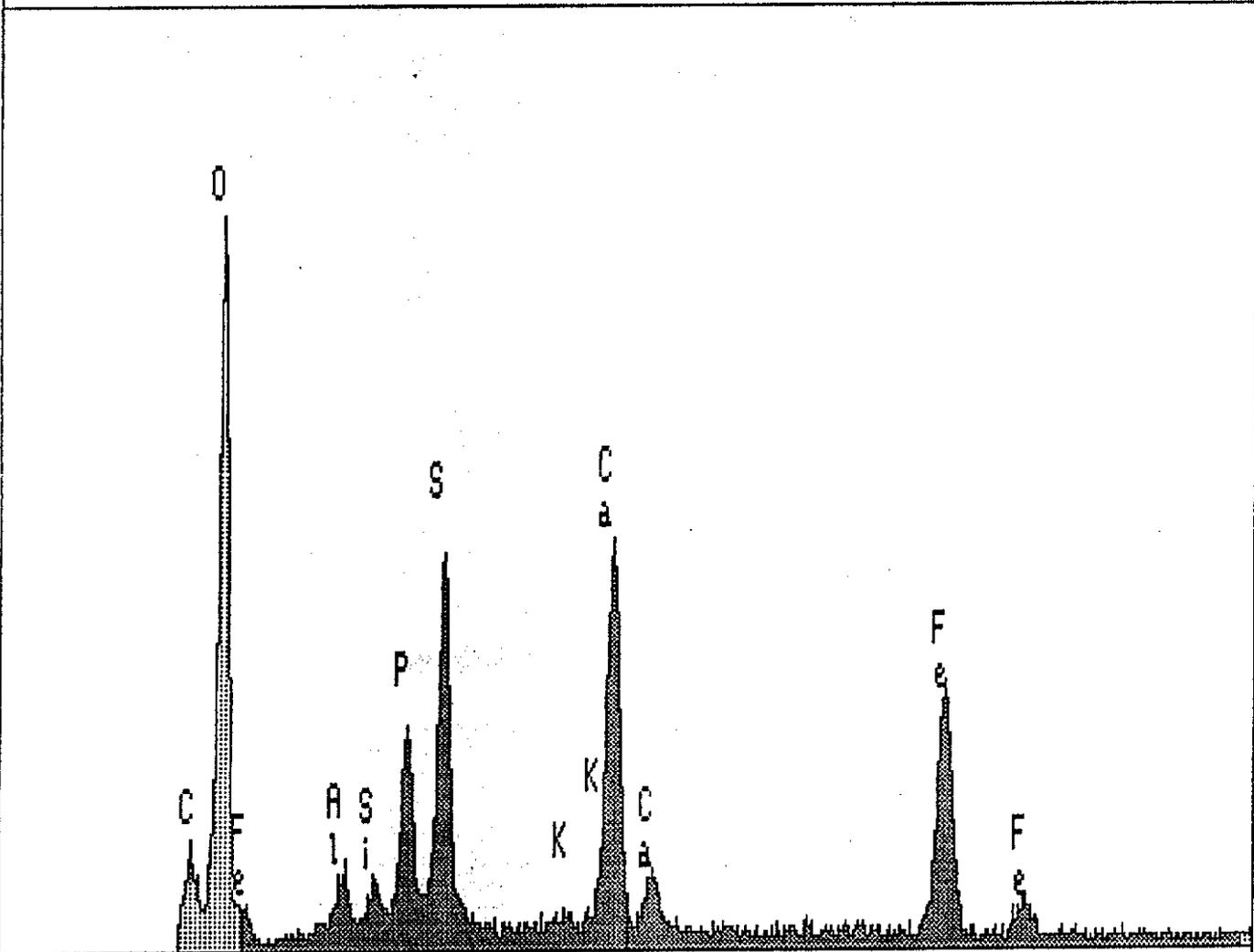
X-RAY: 0 - 20 keV
Live: 50s Preset: 50s Remaining: 0s
Real: 78s 36% Dead



4.152 keV 9.3 >
FS= 4K ch 217= 104 cts
MEM1:PERD COL.3 #6 CLEAN SURFACE.

FIGURE 12.

X-RAY: 0 - 20 keV
Live: 50s Preset: 50s Remaining: 0s
Real: 68s 26% Dead



3.800 keV 8.9 >
FS= 2K ch 200= 139 cts
MEM1: PERD COL.3 SAMPLE 6 SPEC#1

Spectrum file : NC31

PERD COL.3 SAMPLE 6 SPEC#1

LIVETIME(spec.)= 50

ENERGY RES AREA
- 6.8 83.34 36905
TOTAL AREA= 63937.

.....
Peak at .50 keV omitted?
FIT INDEX= 4.23

ELMT	APP.CONC	ERROR(WT%)
CaK : 0	7.763	.181
AlK : 0	.943	.093
SiK : 0	.529	.077
ClK : 0	.110	.074* < 2 Sigma*
P K : 0	4.048	.181
TiK : 0	-.004	.085* < 2 Sigma*
FeK : 0	11.343	.349
NaK : 0	.120	.049
S K : 0	5.818	.156
K K : 0	.218	.086
MnK : 0	-.039	.131* < 2 Sigma*
CrK : 0	-.150	.114* < 2 Sigma*
NiK : 0	.179	.204* < 2 Sigma*
AsK : 0	-.223	.597* < 2 Sigma*

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

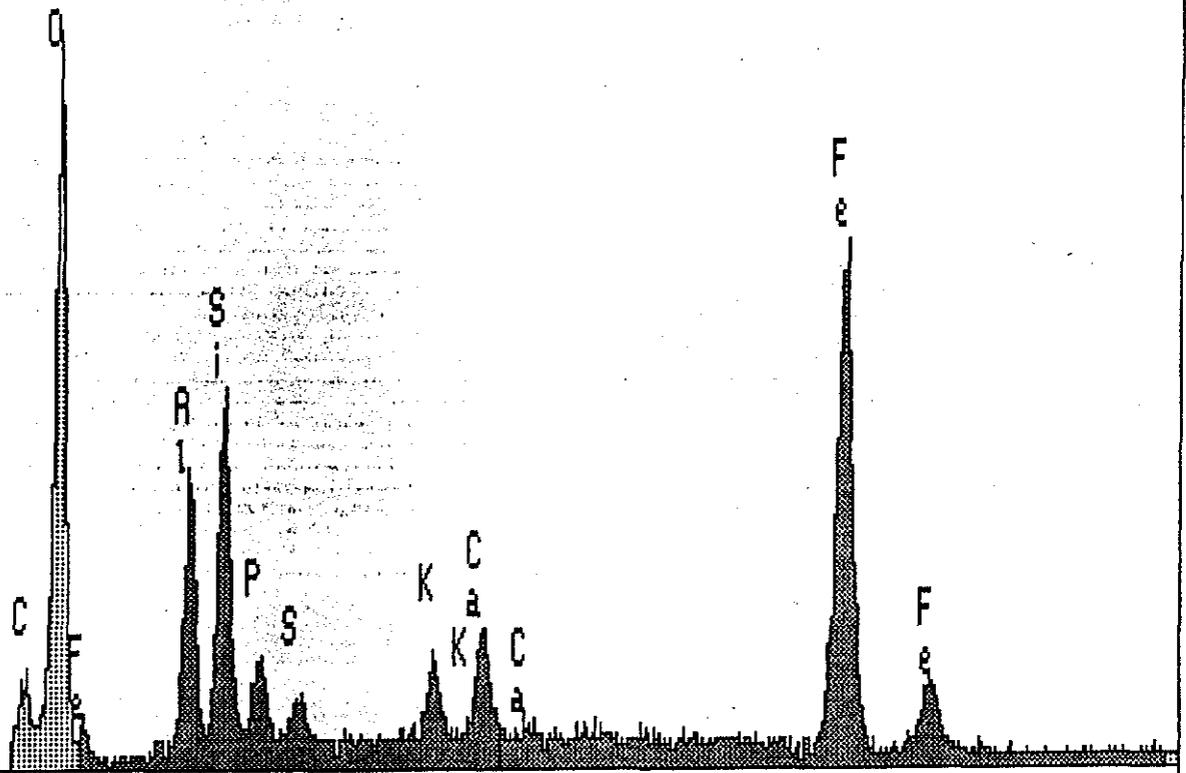
Spectrum: PERD COL.3 SAMPLE 6 SPEC#1

* INITIAL START-UP *

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT +-	Error	ATOM.%
CaK : 0	.912	23.031 +-	.537	22.566
AlK : 0	.580	4.398 +-	.433	6.402
SiK : 0	.671	2.133 +-	.310	2.982
ClK : 0	.683	< .147 +-	.074	
P K : 0	.955	11.461 +-	.511	14.532
TiK : 0	.773	< .169 +-	.085	
FeK : 0	.861	35.609 +-	1.095	25.038
NaK : 0	.418	.774 +-	.316	1.322
S K : 0	.752	20.928 +-	.562	25.635
K K : 0	.903	.653 +-	.257	.655
MnK : 0	.827	< .262 +-	.131	
CrK : 0	.858	< .229 +-	.114	
NiK : 0	.839	< .408 +-	.204	
AsK : 0	.768	<1.195 +-	.597	
TOTAL		98.986		100.000

X-RAY: 0 - 20 keV
 Live: 50 s Preset: 50 s Remaining: 0 s
 Real: 70 s 29% Dead



3.800 keV 8.9 >
 FS= 2K ch 200= 101 cts
 MEM1: PERD COL.3 SAMPLE 6 SPEC#2

Spectrum file : NC32

PERD COL.3 SAMPLE 6 SPEC#2

LIVETIME(spec.)= 50

ENERGY RES AREA
- 6.5 84.85 37333

TOTAL AREA= 65176

.....
Peak at .50 keV omitted?
FIT INDEX= 4.25

ELMT	APP.CONC	ERROR(WT%)
CaK : 0	1.983	.122
AlK : 0	4.139	.141
SiK : 0	4.355	.123
ClK : 0	-.009	.071* < 2 Sigma*
P K : 0	1.876	.141
TiK : 0	.201	.103* < 2 Sigma*
FeK : 0	20.493	.445
NaK : 0	.050	.045* < 2 Sigma*
S K : 0	.743	.087
K K : 0	1.343	.108
MnK : 0	.237	.146* < 2 Sigma*
CrK : 0	-.139	.127* < 2 Sigma*
NiK : 0	.192	.222* < 2 Sigma*
AsK : 0	-.642	.580* < 2 Sigma*

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: PERD COL.3 SAMPLE 6 SPEC#2

* INITIAL START-UP *

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT +-	Error	ATOM.%
CaK : 0	.928	4.619 +-	.284	4.472
AlK : 0	.555	16.118 +-	.550	23.181
SiK : 0	.561	16.775 +-	.474	23.172
ClK : 0	.703	< .142 +-	.071	
P K : 0	.709	5.723 +-	.429	7.170
TiK : 0	.861	< .207 +-	.103	
FeK : 0	.899	49.227 +-	1.068	34.201
NaK : 0	.392	< .090 +-	.045	
S K : 0	.635	2.528 +-	.295	3.059
K K : 0	.920	3.155 +-	.255	3.131
MnK : 0	.871	< .292 +-	.146	
CrK : 0	.949	< .254 +-	.127	
NiK : 0	.843	< .443 +-	.222	
AsK : 0	.775	<1.161 +-	.580	
TOTAL		98.145		100.000

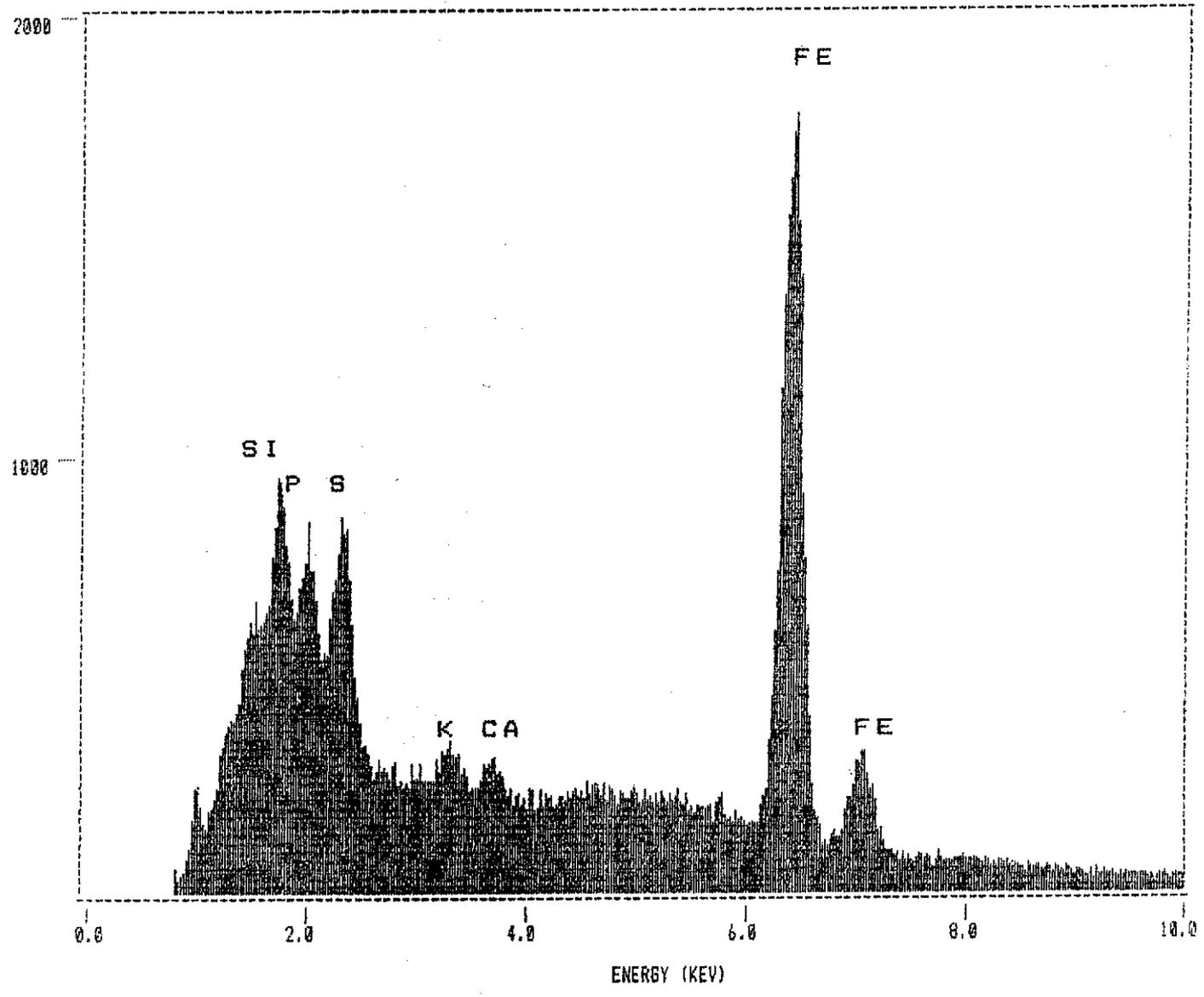
PERD COL.3 SPEC#1

SPECTRUM LABEL

SPECTRUM FILE NAME

██████

██████ NCC1



∞ PIGITI

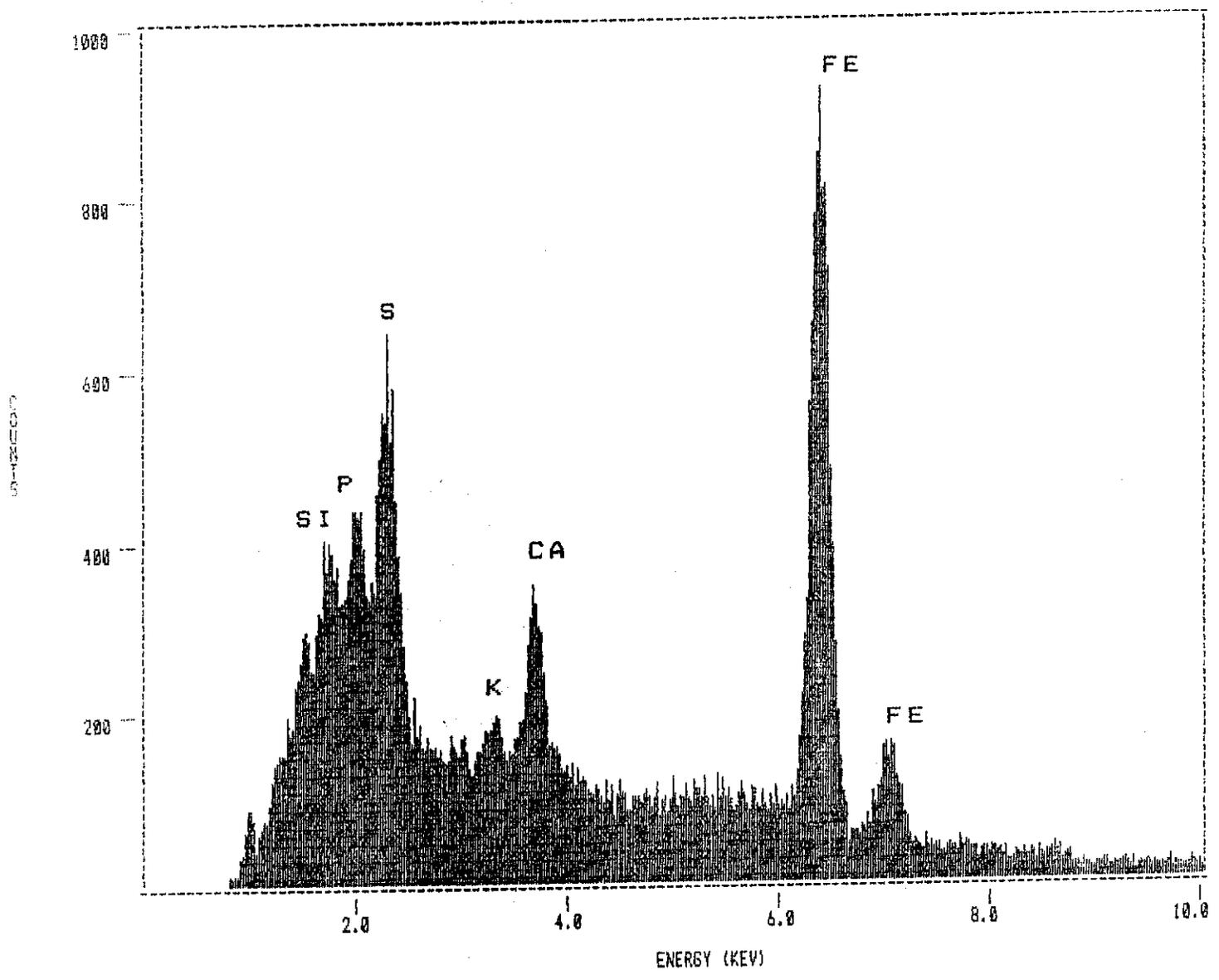
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SPECTRUM LABEL

SPECTRUM FILE NAME

PERD

PERD NCC1



γ PIGITI

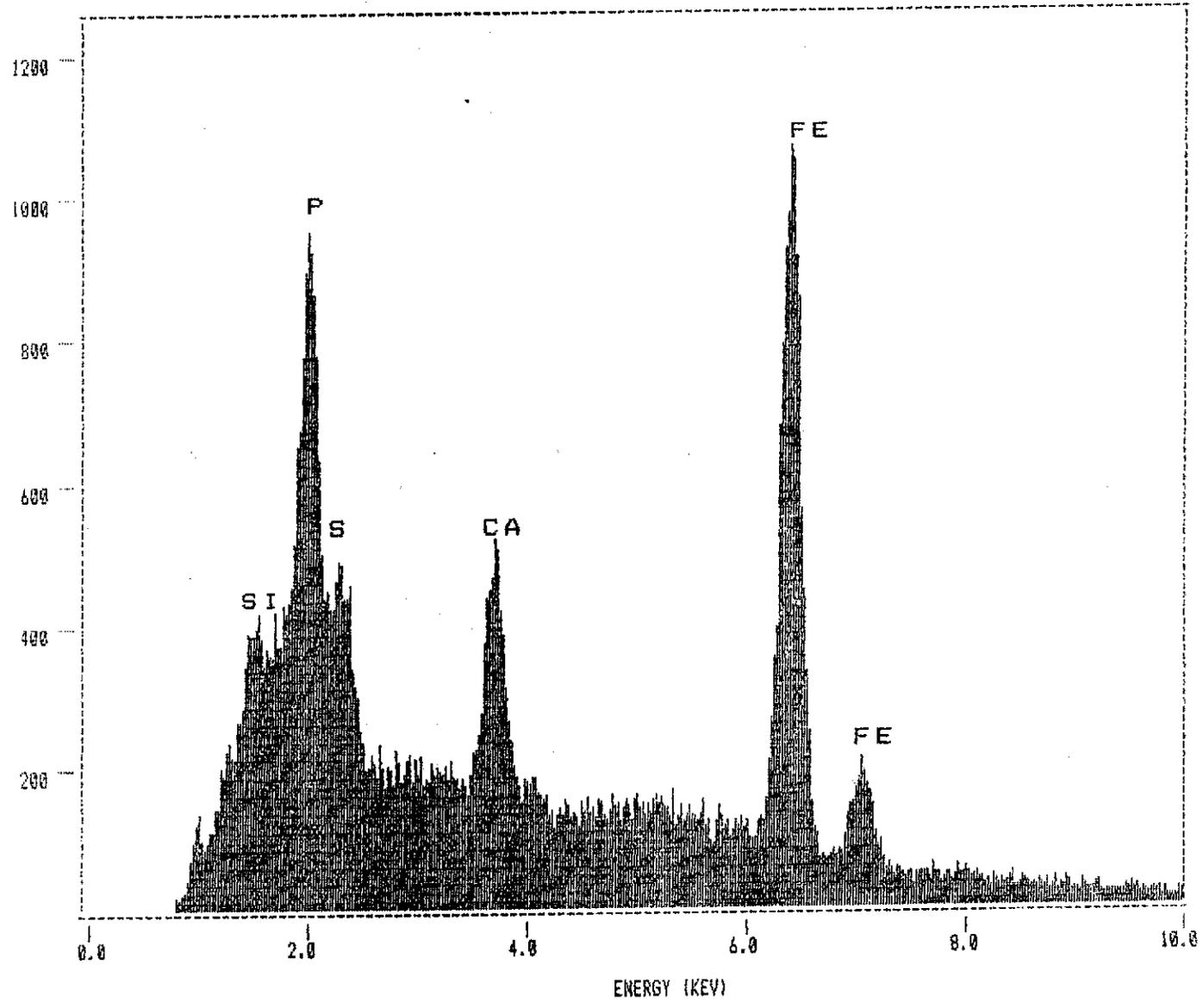
PERD COL.3 SPEC#3

SPECTRUM LABEL

SPECTRUM FILE NAME

~~XXXXXXXX~~

~~XXXXXXXX~~ NCC1



PIGITI

ATTACHMENT 5

EXPRESSION OF INTEREST

IN JOINT PROJECT

BY GERMAN RUHRKOHLE MONATALITH

**Der Rat von
Sachverständigen
für Umweltfragen
Dir.u.Prof. Dr. H. Wiggering**

Telefax

**- Eilt -
Bitte sofort vorlegen
- Urgent -
Please transmit immediately**

Absender/Sender:

Der Rat von Sachverständigen für Umweltfragen - 65180 Wiesbaden
Telefon (0611) 73 4210 Telefax (0611) 73 12 69

Telefax-Nr., Telefax No.:	von/from:	Telefon-Nr./Phone No.:
0611/73 12 69	SRU-Geschäftsstelle	0611/75 4221

Empfänger/Adresse:

**BOOJUM RESEARCH LIMITED;
468 Queen St. E., Suite 400
Toronto, Ont., M5A 1T7**

Telefax-Nr./Telefax No.:	an/Attn.:	Datum/Date:
001 416 861 - 0634	Prof. Margarete Kalin	09.01.1996
Anzahl der Seiten/ Number of pages: 1		Uhrzeit/Time:
		Telekopie Nr./Number of telecopy

Bei fehlenden Seiten unverzüglich Rückruf / If pages are missing, please call immediately.

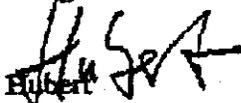
Betreff/Subject: Projekt Bergematerial/Phosphate

Liebe Margarete,

zunächst einmal die allerbesten Wünsche für das Jahr 1996. Auch ich hoffe, daß eine gute Zusammenarbeit in oben genanntem Projekt zustande kommt. Mittlerweile gab es Mitte Dezember und gestern Gesprächsrunden mit der Geschäftsführung der Ruhrkohle Montalith bezüglich der Durchführung des zwischen uns besprochenen Projektes. Die Montalith-Geschäftsführung signalisierte mir, daß sie großes Interesse an diesem Projekt haben und wir nun einen detaillierten Projektantrag einreichen sollten. Wir haben uns über eine Laufzeit von 2 Jahren und ein Projektvolumen von 150 bis 170.000 DM unterhalten. Nach Einreichen des Projektantrages muß dieser dann die Ruhrkohle-Finanzabteilung und noch einmal die Vorstandsebene durchlaufen, um endgültig bewilligt zu werden.

Ich werde mich - soweit ich eben Zeit finde - in den nächsten Wochen hinsetzen und diesen Projektantrag zusammenstellen. Sobald ich einen ersten Entwurf fertiggestellt habe, werde ich ihm Dir überfaxen bzw. zusenden mit der Bitte, diesen dann zu korrigieren bzw. zu ergänzen.

Mit ganz lieben Grüßen


Hilbert