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CATALYTIC GASIFICATION OF GRAPHITE OR CARBON.
Quarterly Report: January 1, 1986-March 31, 1986

H. Heinemann

March 1986

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QUARTERLY REPORT

January 1, 1986 - March 31, 1986

CATALYTIC GASIFICATION OF GRAPHITE OR CARBON

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I. Task Description for FY 1986

This program is designed to study the basic chemistry of the reaction of carbonaceous materials with water in the presence of catalysts to produce hydrocarbons and/or synthesis gas. Relatively low temperatures are being used. Earlier work has shown that a combination of KOH and a transition metal oxide, such as NiO, constitutes catalysts superior to either component alone. It is an objective of the present task to identify the optimum ratio of the components and to determine the existence and composition of a potential catalytic compound, e.g. a potassium nickelate. The applicability of the reactions thus far studied with graphite to char, coke and possibly coal will be investigated. Improvements in kinetics will be sought and the effect of added gases, such as H_2S , CO and O_2 will be researched.

II. Highlights

- 1) Steam gasification of five chars has been carried out in the presence of a mixture of potassium and nickel oxides as catalyst. The steady state rate of hydrogen production after 60 minutes at 620°C is highest for a N. Dakota Husky lignite and is twice as high as the next char, Western Kentucky. The order is N. Dakota > W. Kentucky > Illinois #6, low temp. > Illinois #6, high temp. > Montana. All chars gasified at a rate at least one order of magnitude greater than graphite.

- 2) Conversion after six hours at 620°C and atmospheric pressure varied from about 50% for Western Kentucky to 20% for Montana char and 5% for graphite.
- 3) Initial hydrogen production for the Ni-K catalyst was more than twice that for either component alone in the case of Illinois #6 char. Gasification rates declined more rapidly for the Ni-K catalyst than for NiO or KOH alone, but the total amount gasified during the first six hours was vastly greater for Ni-K.
- 4) Gasification was observed in the environmental cell of an electron microscope and though data are still being evaluated, it is apparent that the wetting behaviour of the Ni-K catalyst and its attack on carbon is distinctly different from that observed for Ni alone and for KOH alone.
- 5) X-ray photon electron spectra of graphite surfaces exposed to oxygen and water gave support to the existence of quinone type species. Added to water, KOH enhances the formation of these quinones. Surface wettability appears to be a crucial parameter in the reaction sequence.

III. Progress of Studies

a) Flow Reactor Work Kinetic Studies of Various Carbon Sources

During the current quarter the study of the gasification of various chars with steam catalyzed by mixtures of potassium and nickel was continued. The results obtained with five different chars and graphite are shown in this report. The identification and pretreatment of the carbon sources used is summarized in Table 1.

Figure 1 shows the steady state rate for steam gasification after 60 minutes at 620°C for the six carbon sources studied. In general, the rate of gasification of the five chars studied is at least one order of magnitude higher than that of graphite. After 18 hours all the char samples had deactivated to values equal or lower than that of graphite. Also there are differences in activity among the five different chars studied. Insufficient evidence is available, so far, to determine the reason of this difference. Part of future work will be dedicated to study these differences.

Figure 2 shows the percentage of carbon conversion after six hours at 620°C and atmospheric pressure for all the samples studied. The conversion was determined by dividing the number of moles of H₂ produced by two times the initial number of moles of carbon. In the case of char samples, it was assumed that the sample was comprised of carbon. The

total conversion listed must, therefore, be lower than the actual conversion. In the case of the char samples, conversions up to 50% were obtained after six hours. This is an order of magnitude higher than the conversion of graphite during the same period. It should be mentioned, however, that in previous experiments graphite conversions of 20% were obtained when the reaction was carried out for a period of one week.

In the case of Illinois #6 char, the carbon conversion obtained with a mixture of potassium and nickel oxides (Figure 3) is almost nine times higher than that of nickel alone. Figure 3 further shows that the rate of reaction with a catalyst mixture of potassium and nickel oxides is higher than the sum of the rates of each of the components alone plus the uncatalyzed reaction. This again demonstrates the existence of a cooperative effect between potassium and nickel for the steam gasification of carbon, a conclusion previously obtained in the case of graphite.

A different behavior is seen in the case of the Montana subbituminous char (Figure 4). Here the rate of reaction for nickel alone is similar to that of a mixture of nickel and potassium. It is possible that this is due to the interaction of nickel with alkaline metal salts already present in the char. Further work is being done to test this hypothesis. It appears that different chars show different activities with different catalysts, though no catalyst so far has exhibited better activity than the Ni-K oxides.

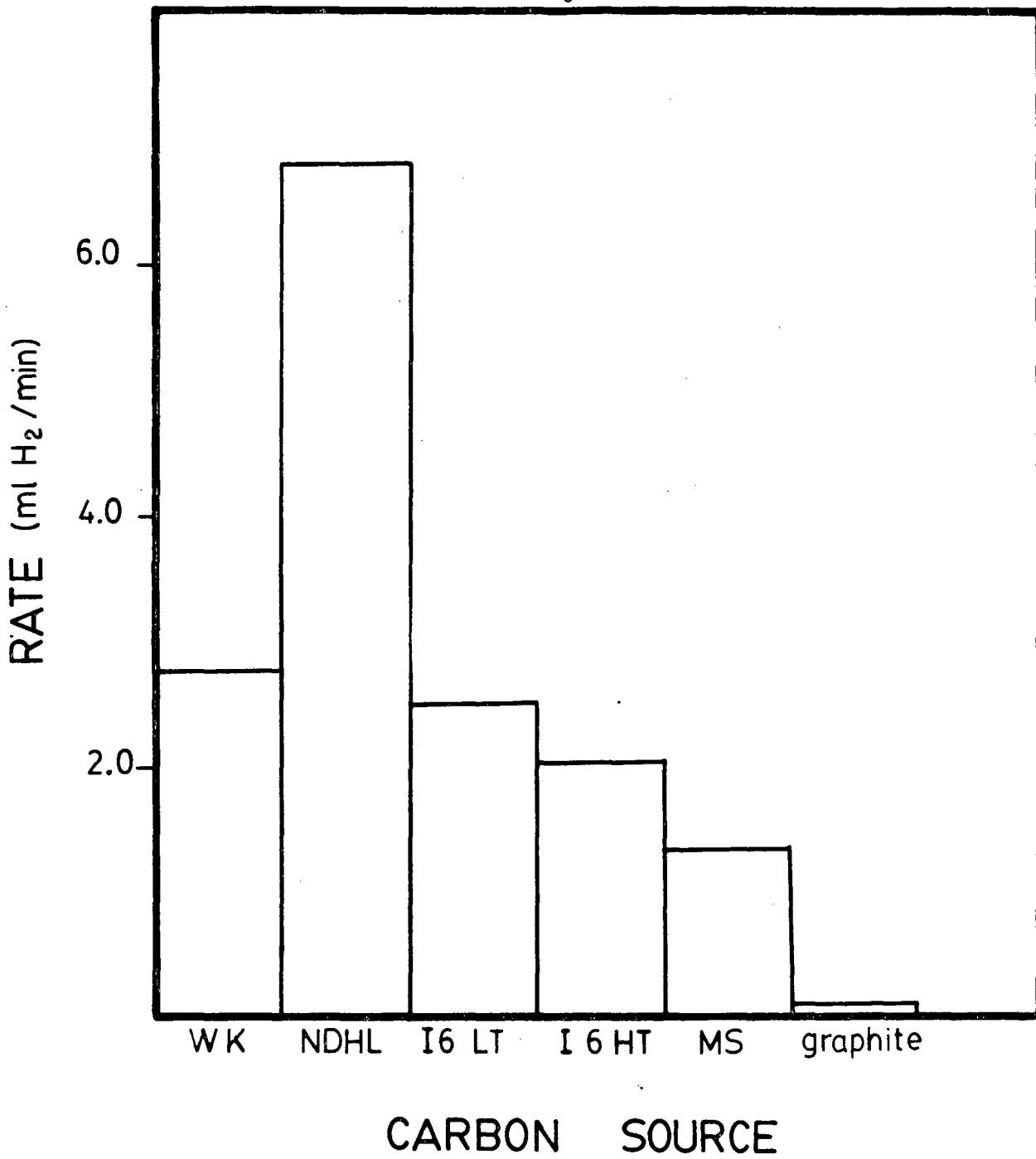
b) Controlled Atmosphere Electron Microscopy (CAEM) Studies

During this quarter, CAEM studies of the catalytic activity of mixtures of potassium and nickel oxides on the steam gasification of natural graphite have been undertaken in collaboration with Dr. Terry Baker of Exxon Research and Engineering Corp. The analysis of the results is not yet complete, but qualitatively, this mixture tends to wet the graphite edges extremely well. It attacks the surface by an edge recession mode. This behavior is completely different from that of nickel alone and of KOH alone where the sample is gasified by a channeling mode.

Table 1: Carbon Sources

<u>Name</u>	<u>Type</u>	<u>Prep.</u>
Western Kentucky Washed (WK)	HV. B. Bituminous	Unknown
North Dakota Husky (NDM)	Lignite	Partial Steam Gasification T=1196K
Illinois N-6 Low Temp.(I6LT)	HV. C. Bituminous	Pregasifier Heater T<670K
Illinois N-6 High Temp.(I6HT)	HV. C. Bituminous	Heated in He T>1273K
Montana (MS)	Subituminous	Partial Steam Gasification T<1200K

Figure 1



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Figure 2

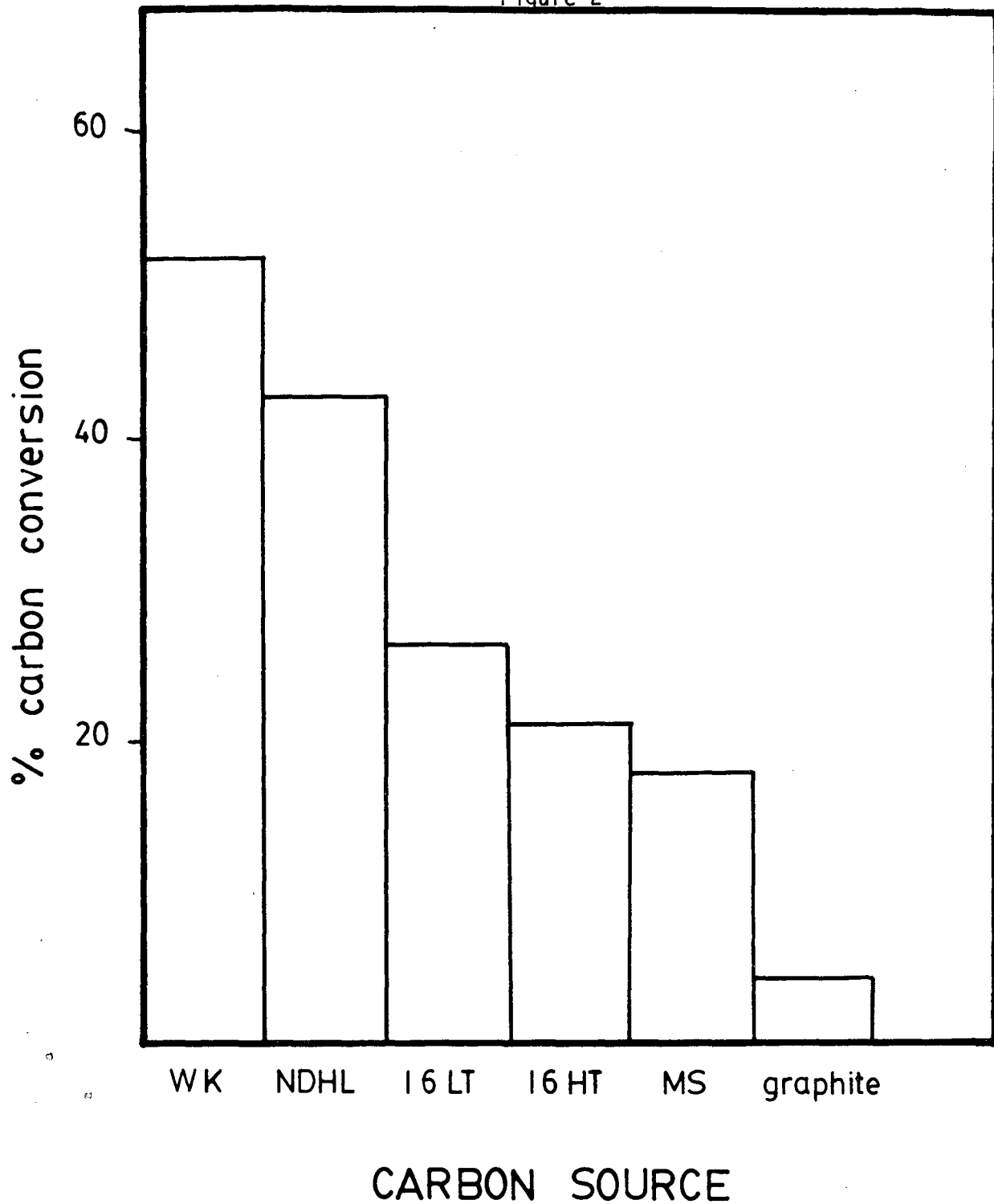


Figure 3

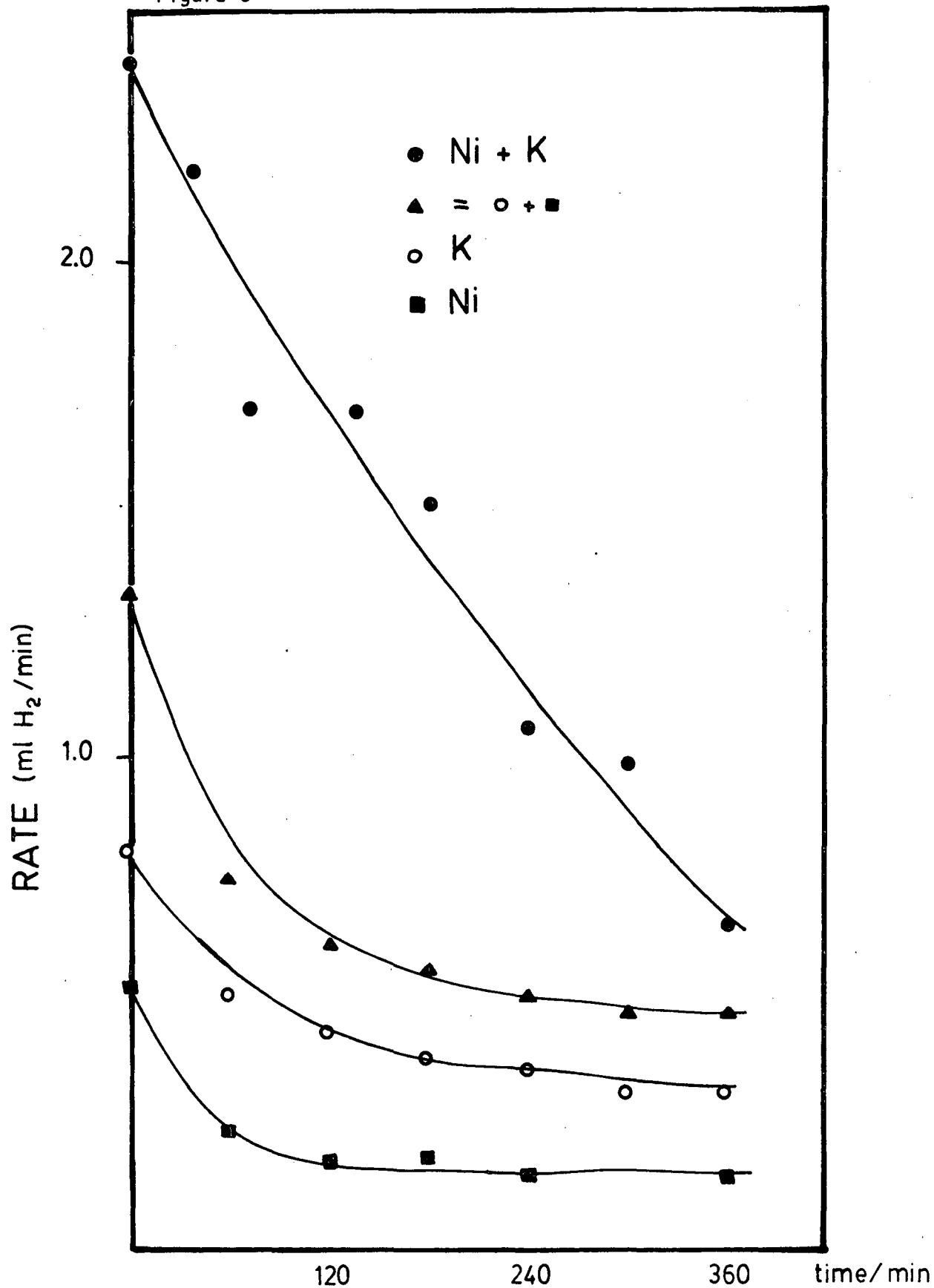
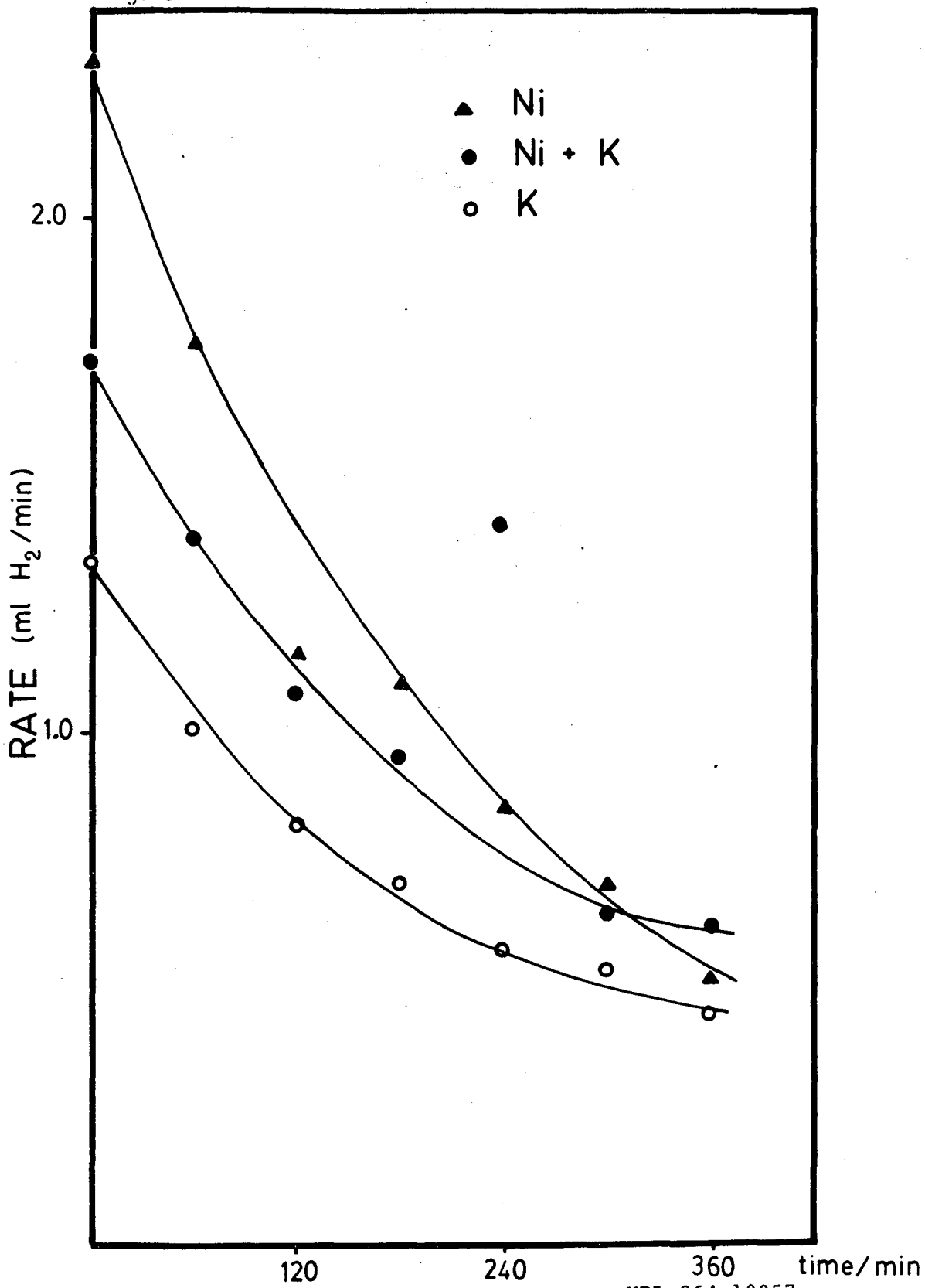


Figure 4



c) X-ray Photoelectron Spectra (XPS)
of the Graphite Surface

Previous temperature controlled desorption (TDS) experiments carried out under ultra high vacuum (UHV) conditions after exposing a clean graphite surface to O_2 , CO, CO_2 or H_2O gave some useful information about the chemistry and nature of the species existing on the graphite edges. In particular, the adsorption of oxygen at room temperature leads to a strongly bound surface complex $C_S(O)$, identified as a quinone group, which decomposes to give CO at temperatures higher than $800^\circ C$ (quarterly report October-December 1985). On the other hand, CO exposure at room temperature gives rise to a carbonyl species desorbing molecularly at $250^\circ C$. Water vapor adsorption gave mostly the quinone group on the surface, with simultaneous release of hydrogen. Only a few hydrogen atoms form CH bonds on the surface.

The aim of this XPS study was to bring additional evidence to the assignment of the features observed by TDS. The C_{1S} photoelectron peak energy is very sensitive to the oxidation state of the surface carbon atoms and can shift up to 7 eV when highly oxidized. The O_{1S} peak, on the other hand, seems to be less sensitive to its environment, but can shift as much as 3 eV from one compound to another. By recording XPS spectra after exposing the graphite sample to different gases, one should then be able to get information about the nature of the surface species.

1. Oxygen Adsorption

The graphite sample was exposed to 250 torr of oxygen at 530°C for five minutes. At this temperature, the graphite is expected to start burning at a slow rate, and one may populate a high number of active sites with quinone groups. Figure 5 shows the XPS C_{1s} spectra taken on the clean surface, and after the oxygen treatment. Computerized data acquisition allowed calculation on the difference spectrum. Within the limit of detection of the apparatus, no significant change in the spectra is observed, showing that even at this condition of exposure, the number of quinone species on the surface is much less than the total number of available sites. The O_{1s} signal, however, is not hidden by any substrate peak and easily observable (Figure 6). The peak maximum is at about 532 eV and rather broad. The decomposition of these quinone groups into gaseous CO can be monitored by recording the spectra after flashing the sample at different temperatures. The results are consistent with the earlier TDS experiments, since most of the surface oxygen comes off between ca 500 and 1000°C. No significant change in the O_{1s} binding energy is observed as the amount of oxygen decreases.

2. CO Adsorption

Exposure to 400 torr of CO for one minute at room temperature gives the same O_{1s} signal but at far less intensity than after oxygen exposure (Figure 7). The O_{1s} electron binding energy is therefore the same for both types of species (carbonyl and quinone). The sticking coefficient of CO on graphite is, however, much less than that of oxygen.

3. H₂O Adsorption

The clean graphite sample from the UHV chamber was wetted with liquid water for about one minute. After drying, it was put back into the UHV chamber and the C_{1s} XPS spectrum was recorded (Figure 8). Contrary to the adsorption of oxygen, a signal could be extracted from the difference spectrum and the carbonaceous compound formed after water adsorption shows a binding energy shift of about 2 eV. However, the spectrum is quite broad and can result from the super position of several peaks with energy shifts ranging from 1 to 3 eV. This energy range is more characteristic of phenol, ether or carbonyl groups, than carboxyl groups. On heating the sample, this difference gets smaller and eventually vanishes, while no fine structure or frequency shift occurs.

The O_{1s} signal (Figure 9) is very intense after the wetting and shows that wetting leads to many more surface species than exposure to oxygen, even at 500°C. The binding energy is now 533 eV, i.e. higher than for the quinone. By heating the sample, the peak position shifts down to lower binding energies and ends up at 532 eV for temperatures higher than 500°C. This is consistent with the fact that one expects mostly quinone groups to be stable on the surface at this temperature. The peak intensity eventually vanishes at high temperatures.

The nature of the species responsible for the O_{1s} signal at 533 eV after water wetting is not understood yet, but it is interesting to observe that if the surface is wetted first with a solution of KOH in

water before rinsing it with distilled water, the O_{1s} XPS peak is less intense and shifted towards lower binding energy at 532 eV, corresponding to the quinone species. Exposing the clear surface to vapor pressure of water gives almost no signal.

The fact that KOH changes the surface species on the graphite edges is not surprising since it is known to be a good catalyst for many of its reactions, and in particular the hydrogasification. The exact nature of both species which give different O_{1s} binding energies is not known yet, but one can reasonably assume that the one which gives rise to highest binding energy peak at 533 eV can be an acidic function which can be neutralized by KOH. This would explain the loss in peak intensity as well.

Finally, the dramatic difference in the XPS signal after exposing the graphite to water vapour pressure, as compared to wetting it with liquid water, shows the importance of the wettability, i.e. the sticking probability of the water molecule to the graphite surface on the hydrogasification reaction.

Further experiments are in progress to understand in more details the wetting process, and the role of KOH in determining the nature of the surface species.

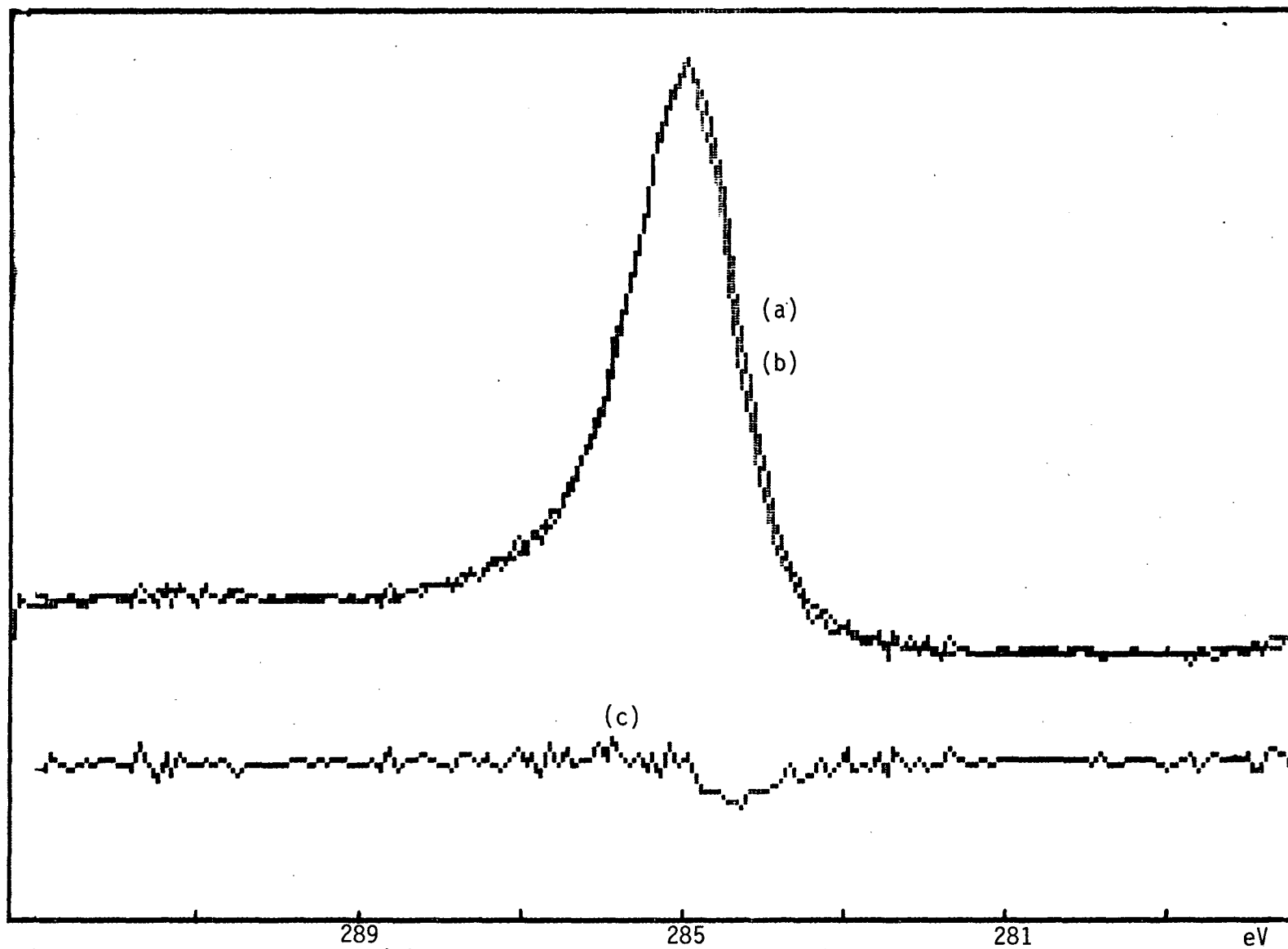
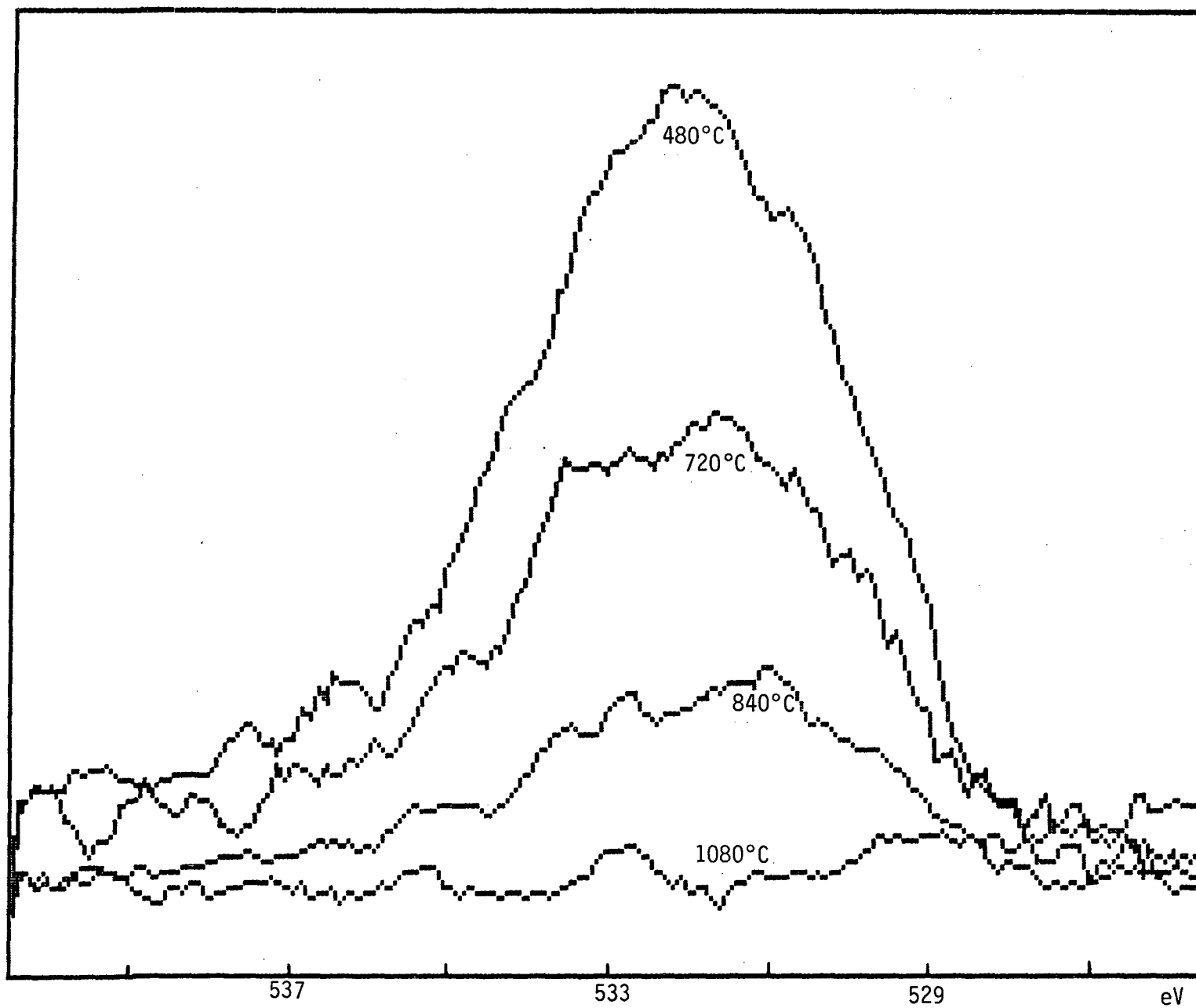


Figure 5: XPS C_{1s} spectra (a) Clean graphite surface
(b) After exposure to 250 torr of O₂ at 530°C for 5 minutes
(c) Difference spectrum



O_{1s} XPS spectra of the oxidize graphite surface after flash at different temperatures.

Figure 6

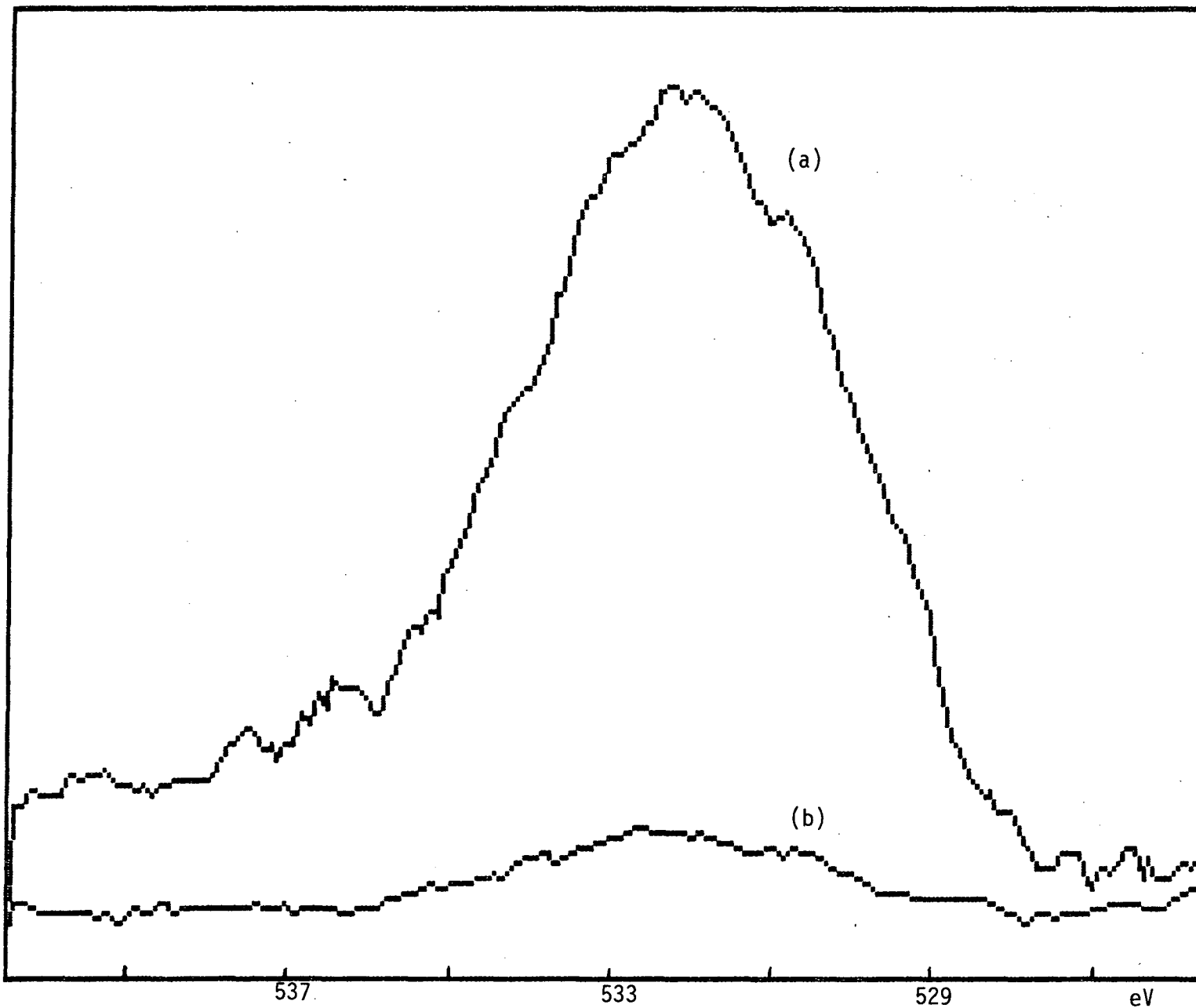


Figure 7: O_{1s} XPS spectra of graphite (a) O_2 250 torr, 530°C, 5 minutes
(b) CO 400 torr, room temp., 1 minute

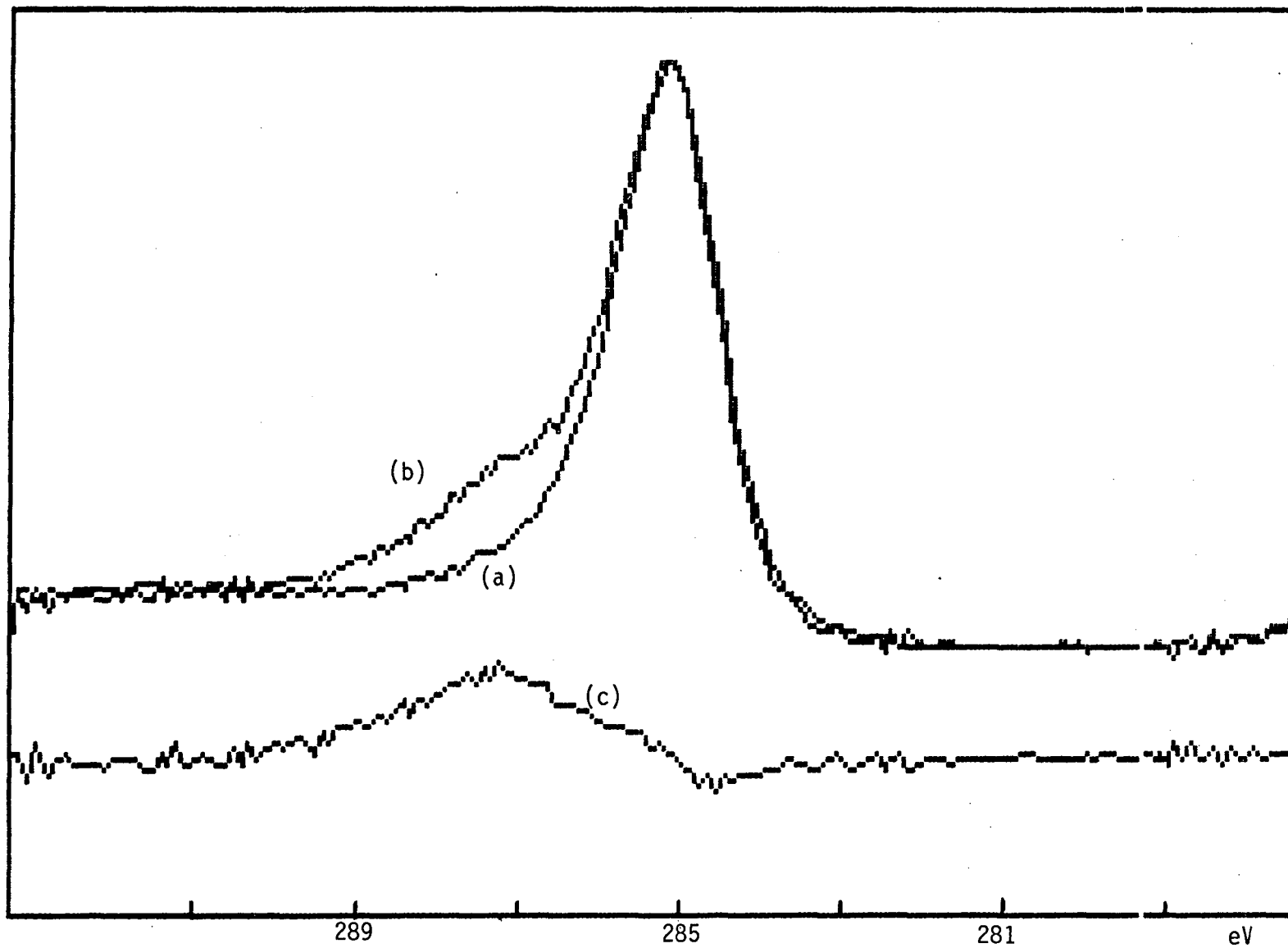


Figure 8: C_{1s} XPS spectra of graphite (a) clean (b) after wetting with H₂O (c) difference spectrum

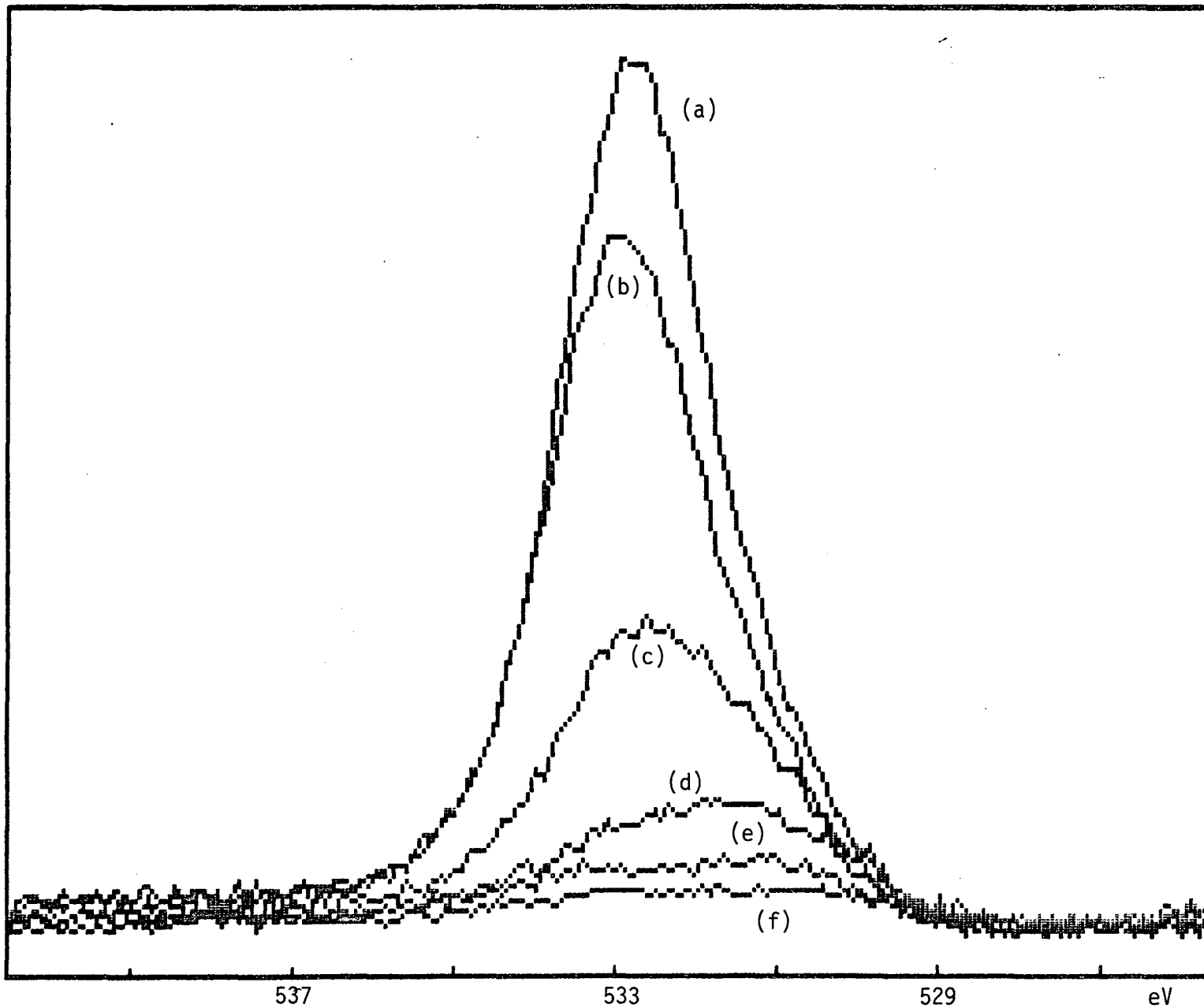


Figure 9: O_{1s} XPS spectra of graphite after wetting with water and flash at different temperatures (a) non flashed (b) 250°C (c) 320°C (d) 390°C (e) 530°C (f) 740°C

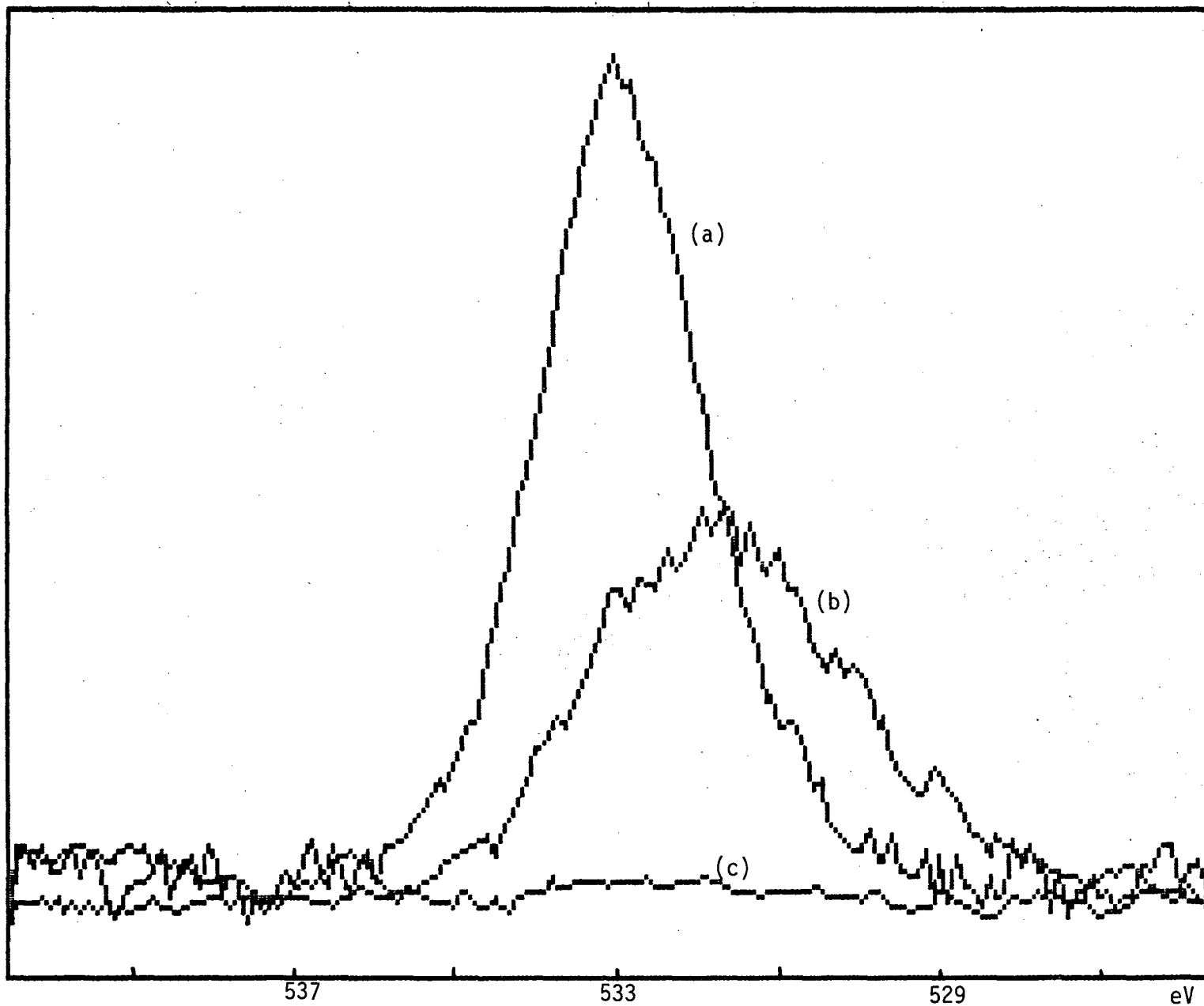


Figure 10: O_{1s} XPS spectra of graphite (a) after wetting with H_2O (b) after wetting with KOH (c) after exposure to H_2O vapor pressure for one minute

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