

## **An Investigation of the Desorption of Hydrogen from Lithium Oxide using Temperature Programmed Desorption and Diffuse Reflectance Infrared Spectroscopy**

J. P. Kopasz and C. E. Johnson (Argonne National Laboratory) and J. Ortiz-Villafuerte (Escuela Superior de Fisica y Matematicas, Mexico)

### **OBJECTIVE**

The addition of hydrogen to the purge stream has been shown to enhance tritium release from ceramic breeder materials; however, this added hydrogen can lead to increased costs in the tritium purification system. The objective of this work is to develop an understanding of the interactions between hydrogen and lithium oxide surfaces so that we can take full advantage of the observed enhancement of tritium release caused by hydrogen addition without incurring high costs in the tritium purification plant.

### **SUMMARY**

A combination of Temperature Programmed Desorption (TPD) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is being used to investigate the desorption of hydrogen from lithium oxide. Initial studies have indicated that there are four different types of hydroxyl groups which can be observed on a lithium oxide surface. The particular species present vary depending on the temperature and hydrogen pressure of the system. Under some conditions where hydrogen is present in the purge gas surface hydride species have been observed. This suggests heterolytic adsorption of hydrogen has occurred.

### **PROGRESS AND STATUS**

#### Introduction

Lithium oxide is one of the leading candidates for use as a tritium breeding material in a fusion reactor. Many experiments have demonstrated the relative ease of tritium recovery from this material. Tritium release is particularly facile when a purge gas containing hydrogen, typically at levels of about 0.1%, is used. However, addition of hydrogen to the purge has a penalty associated with it when one gets to the tritium purification process. A large amount of hydrogen in the purge will necessitate a larger tritium purification unit, and therefore larger costs. In order to optimize tritium release while minimizing the amount of hydrogen necessary in the purge one must have a better understanding of the tritium desorption step and the interactions of hydrogen with the lithium oxide surface.

One method typically used to study surface desorption processes is Temperature Programmed Desorption (TPD). In this technique a gas is adsorbed on the sample, the sample is then heated at a constant rate and the gas desorbed from the sample detected downstream by a technique such as mass spectrometry. From the shape and position of the desorption peak one can obtain information about the energetics of the desorption process.[1] One shortcoming of this technique is that there is no information on the identity or form of the species that is desorbing as it exists on the surface. For example, if a tritium atom exists on a lithium oxide surface there is the possibility that it exists as a triton ( $H^+$ ), or as a tritide ( $H^-$ ). When it desorbs into the gas phase (as HTO or HT) it now can react with hydrogen or water in the gas phase to form an equilibrium mixture of  $H_2$ , HT,  $H_2O$ , and HTO. At the mass-spectrometer downstream you will only detect the equilibrium mixture, and have no information about whether the desorbed species was  $T^+$  or  $T^-$ , or worse whether the species is being desorbed from your sample or from the support structure. When several peaks are observed in a TPD spectra, there is no information other than the energetics to help determine what the different peaks are due to (different surface species, diffusion and desorption of the same species, desorption from other surfaces). In addition, when there are several overlapping peaks it is sometimes difficult to determine the number of peaks present.

Diffuse reflectance infrared Fourier Transform Spectroscopy has been used to view hydroxyl groups on the lithium oxide surface [2]. Different infrared absorptions were observed in the OH region, indicating different types of OH groups present on the surface. However, no energetic information was obtained regarding the desorption of these hydroxyl groups. In an effort to gain information about the species present on the surface and how they relate to peaks in the TPD spectra we have turned to a study of hydrogen adsorption and desorption from lithium oxide using a combination of TPD and diffuse reflectance infrared spectroscopy.

### Experimental

Temperature Programmed Desorption measurements were performed using an apparatus described previously.[3] Hydrogen or deuterium were dried by passing the high purity gas through a commercial deoxygenating unit. Hydrogen (deuterium) was adsorbed on the sample at  $250^\circ\text{C}$  for a period from 3 to 24 hours. The purge gas was then changed and the temperature increased linearly while the outlet gas stream was continuously monitored by mass spectroscopy.

Diffuse reflectance Fourier Transform Infrared spectroscopy measurements were performed on a commercial lithium oxide powder (Alfa) using a Bomem spectrometer equipped with a diffuse reflectance attachment (Harrick Scientific DRA-Praying Mantis). The samples were contained in a

vacuum chamber equipped for diffuse reflectance (Harrick Scientific) with ZnSe windows and equipped with an internal heater. Experiments were performed by exposing the sample to Ar+0.1%H<sub>2</sub> or Ar+0.1%D<sub>2</sub> at various temperatures and recording the infrared spectra. Kinetic experiments were performed by switching the purge gas then recording the spectra at specific time intervals.

Pseudo TPD-DRIFTS experiments were performed by exposing the sample, then slowly raising the temperature manually from 200 to 400°C while sampling the purge gas downstream of the sample with the mass spectrometer and recording the infrared spectra at discrete times during the temperature increase. Ar +0.1%D<sub>2</sub> was passed over the sample at 115-120°C for 16 h. The purge gas was then switched to Ar+0.1%H<sub>2</sub>, and the temperature of the sample slowly increased to 400°C. The gas was continuously sampled by mass spectrometry and diffuse reflectance spectra were recorded at specific temperatures during the TPD run. Diffuse reflectance spectra were recorded at temperatures of 157, 174, 200, 225, 250, 275, 308, 322, 347, 361, 374, and 395°C.

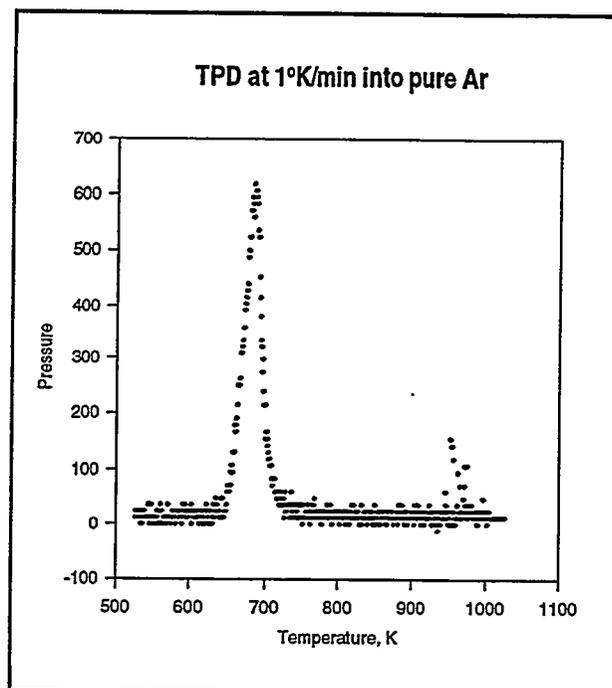


Figure 1

## Results and Discussion

### TPD

For TPD experiments into a purge gas of pure Ar, one narrow peak was observed for temperature ramps up to 750°C at heating rates of 2, 5 and 10 K/min. For a heating rate of 1K/min one peak with what might be a second small peak near the temperature limit of the experiment was observed. (Fig 1) The main peak is narrow, and attempts to obtain an activation energy for this peak which is self-consistent using line-shape analysis and plots of  $\ln(T_m^2/H)$  vs.  $1/T$  have been unsuccessful. The activation energy calculated from the plots of  $\ln(T_m^2/H)$  vs.  $1/T$  is 88 kJ/mol while that obtained from line-shape analysis is about a factor of two higher. This suggests desorption into pure Ar is not a

simple first-order desorption process.

TPD experiments performed in a purge gas of Ar+0.1% H<sub>2</sub> exhibit more than one peak in the desorption spectra. The main peak occurs at temperatures close to those seen in pure Ar, however additional peaks occur at higher temperatures and at temperatures near the maximum temperature for the experiment. (Fig.2) For the main peak plots of  $\ln(T_m^2/H)$  vs  $1/T$  gives an activation energy of 102.5 kJ/mol (24.5 kcal/mol); however, line shape analysis again gives a much higher activation energy for this peak. This suggests that the mechanism for desorption of this species is not a simple first-order desorption. For the second peak seen a self-consistent activation energy of 73 kJ/mol is obtained from line shape analysis and plots of  $\ln(T_m^2/H)$  vs  $1/T$ . The other peaks were too close to the temperature limit for the experiment to be able to obtain activation energies from these methods.

## DRIFTS

Diffuse reflectance infrared Fourier transform spectra of a lithium oxide powder after exposure to a purge gas of Ar+0.1%D<sub>2</sub> at 365°C is shown in Fig. 3. Several different absorptions are observed for OH and for OD. Under different conditions, other peaks appear more prevalent. From deconvolutions of these curves it appears that there are four different OH absorptions at 3657, 3604, 3480 and 3400 cm<sup>-1</sup>.

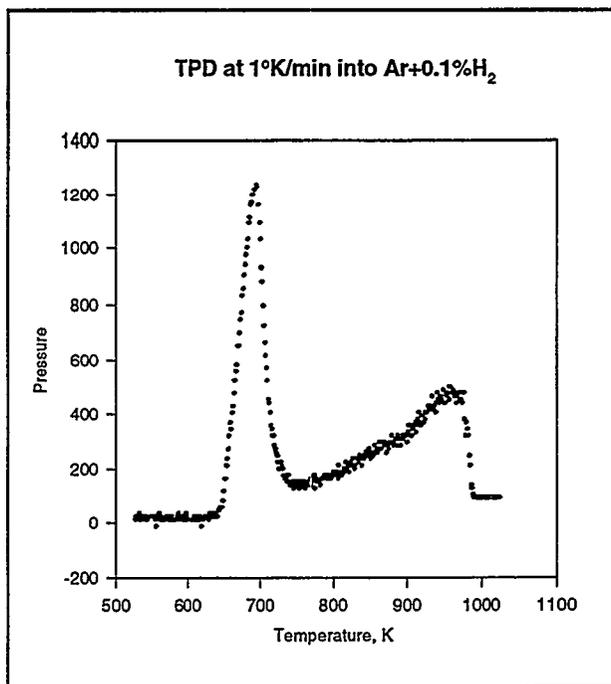


Figure 2

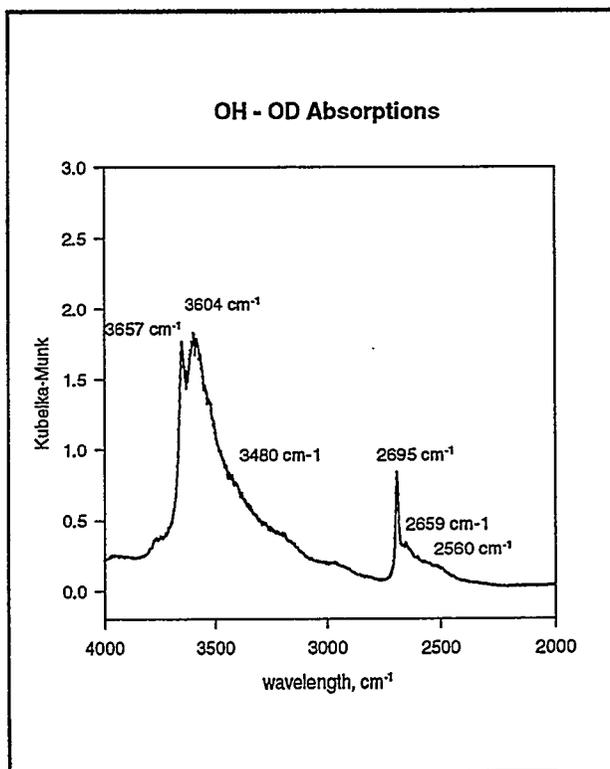
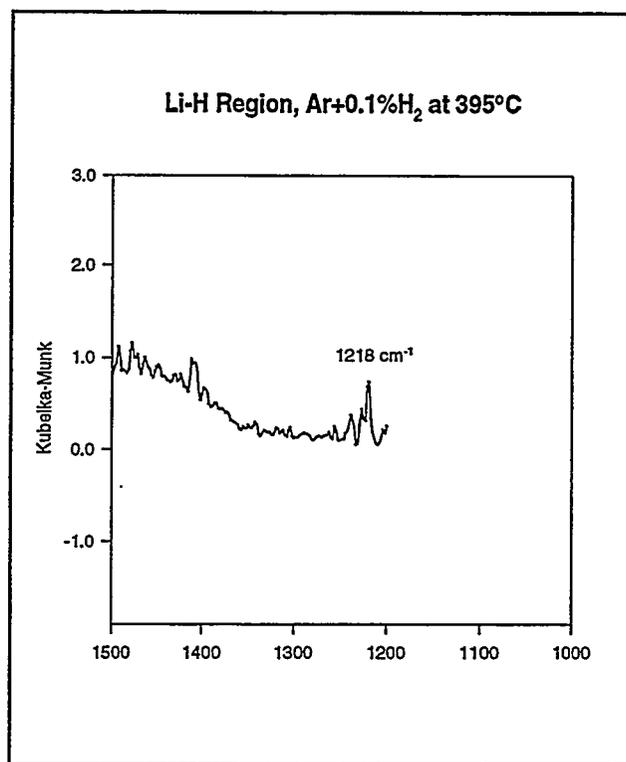


Figure 3

Corresponding OD peaks have been observed at 2695, 2659, and 2570  $\text{cm}^{-1}$  upon exposure to  $\text{D}_2$  (the OD peak corresponding to the OH peak at 3400  $\text{cm}^{-1}$  has not yet been observed, probably due to the very low intensity of this OH peak under the conditions investigated). These absorptions indicate that there are four different OH species on the surface. We propose that these different OH groups are due to OH groups with different coordination numbers, 2, 4, 6 and 8. The strength of the OH bond, and therefore the OH vibration frequency, will depend on the electron density on the oxygen. As the electron density on the oxygen is reduced by coordination to Li atoms in the lattice the O-H bond strength should decrease, decreasing the frequency of the absorption. This is similar to the effect seen for IR absorptions of terminal versus bridging carbonyl groups.

Under certain conditions we have seen infrared absorptions in the region where a Li-H stretch is expected. These infrared absorptions at 1245 to 1212  $\text{cm}^{-1}$  are shifted to slightly lower frequencies than that observed for lithium hydride (1280  $\text{cm}^{-1}$ ). The hydride absorption in the infrared was generally seen at temperatures of about 380°C and higher. Confirmation that this is a Li-H absorption by isotopic substitution with deuterium has not been possible since the deuterium peak would be shifted to a position beyond the absorption edge. However, these absorptions have only been seen in a purge gas containing hydrogen. At 395°C with a purge gas of Ar+0.1% hydrogen an absorption is observed at 1218  $\text{cm}^{-1}$ , when the purge gas is changed to pure Ar this peak disappears. (Figs. 4 and 5), giving a strong indication that this absorption is due to the presence of a Li-H species on the surface. The presence of an Li-H species on the surface suggests that hydrogen is adsorbed on the surface heterolytically to form  $\text{H}^+$  (OH $^-$ ) and  $\text{H}^-$  (Li-H). Quantum mechanical calculations indicate this type of heterolytic adsorption is expected on some lithium oxide surfaces.[4]

Preliminary kinetic studies have been performed. The decomposition of



**Figure 4**

the hydroxyl species was followed at 400°C by recording the spectra at about 10 minute intervals (see Fig. 6). The preliminary data for the decomposition of the main peak at 3657  $\text{cm}^{-1}$  appears consistent with a first order desorption which is an order of magnitude slower than that reported for the decomposition of bulk LiOH, however more data are needed. The decompositions of the secondary peaks do not appear to follow first-order processes. The secondary hydroxyl peaks tend to remain constant until the peak at 3657  $\text{cm}^{-1}$  has decayed substantially before they start to decay. This complicated kinetics may be the reason for the difficulty interpreting the sharp peaks seen in the TPD curves and requires more study.

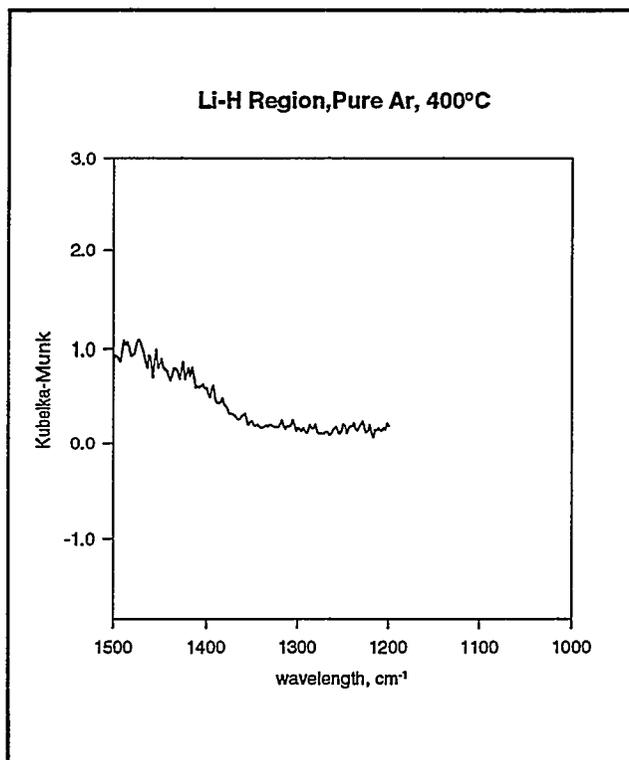


Figure 5

#### DRIFTS-TPD

As part of a preliminary study to determine the applicability of a combined TPD-DRIFTS experiment a pseudo TPD experiment was performed while recording the diffuse reflectance infrared spectra at discrete times during the temperature increase. Limitations in the apparatus relegated the experiment to a maximum temperature of 400°C and resulted in a heating ramp which was not quite linear so no quantitative information regarding the activation energies could be obtained. However, the results do provide some qualitative answers and indicate that the technique of combined TPD-DRIFTS should be pursued. The pressure-time curve for mass 18 during the temperature ramp is shown in Fig. 7.

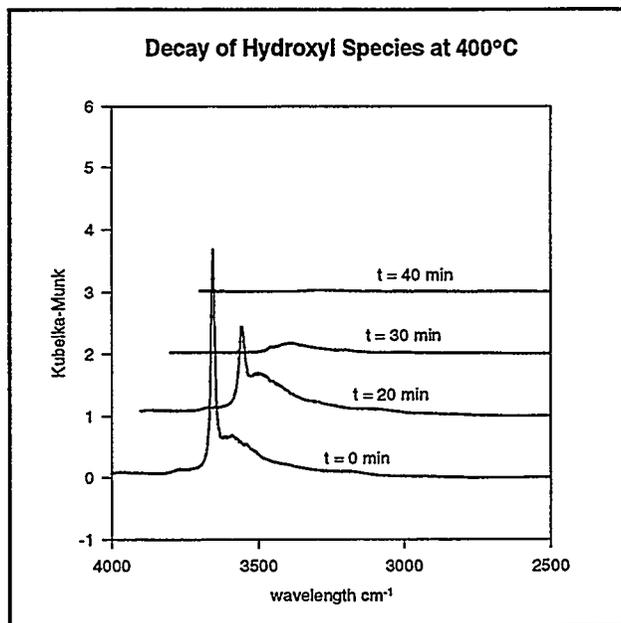


Figure 6

Identical curves were obtained for mass 17 and 19. The infrared spectra show no changes in the spectra until after the desorption peak has started in the TPD. While the desorption peak is rising in the TPD a decrease is seen in the OH absorption intensity at  $3657\text{ cm}^{-1}$ . After the TPD peak has reached its maximum, the OH peak at  $3657$  has disappeared in the infrared spectra (Fig. 8,  $395^\circ\text{C}$  curve). At this point, a Li-H peak is seen in the infrared. ( Fig. 9,  $395^\circ\text{C}$  curve )

The combination of the TPD curve and the DRIFTS results suggest that the TPD peak observed at about  $663\text{K}$  ( $390^\circ\text{C}$ ) is due mainly to removal of the OH species seen in the infrared at  $3657\text{ cm}^{-1}$  from the surface. The observation of this species at the surface and the observed change in the concentration of this species with time indicate that the rate controlling mechanism for the disappearance of this peak is not bulk diffusion. If bulk diffusion was the rate controlling process, one would expect the surface concentration to be near zero and for there not to be an appreciable change in the surface concentration of this species during the TPD peak. The combination of the TPD and DRIFTS also indicates that the hydride species is not observed until the OH species at  $3657\text{ cm}^{-1}$  is absent. One possible explanation is that these hydroxide groups occupy the sites at which  $\text{H}^-$  adsorbs.

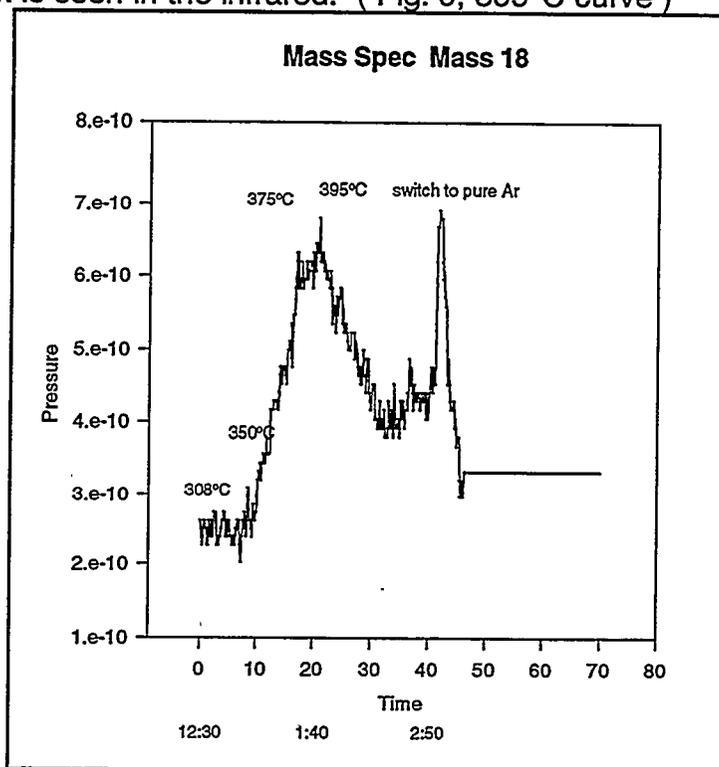


Figure 7

### Conclusions

Our studies have indicated that there are four different types of hydroxyl groups which can be observed on a lithium oxide surface. The particular species present vary depending on the temperature and hydrogen pressure of the

system. Under some conditions where hydrogen is present in the purge gas surface hydride species have been observed. This suggests heterolytic adsorption of hydrogen has occurred.

These studies indicate that the combination of temperature programmed desorption and diffuse reflectance infrared spectroscopy provides a valuable method for studying surface processes. The combination of these methods overcomes the shortcomings of the individual methods, and allows one to determine correlations between species observed on the surface and those detected in the gas phase downstream.

### Future Work

The current studies have been limited to temperatures below 400°C. Future work will investigate the surface interactions at temperatures up to about 700°C using the combination of diffuse reflectance infrared spectroscopy and temperature programmed desorption.

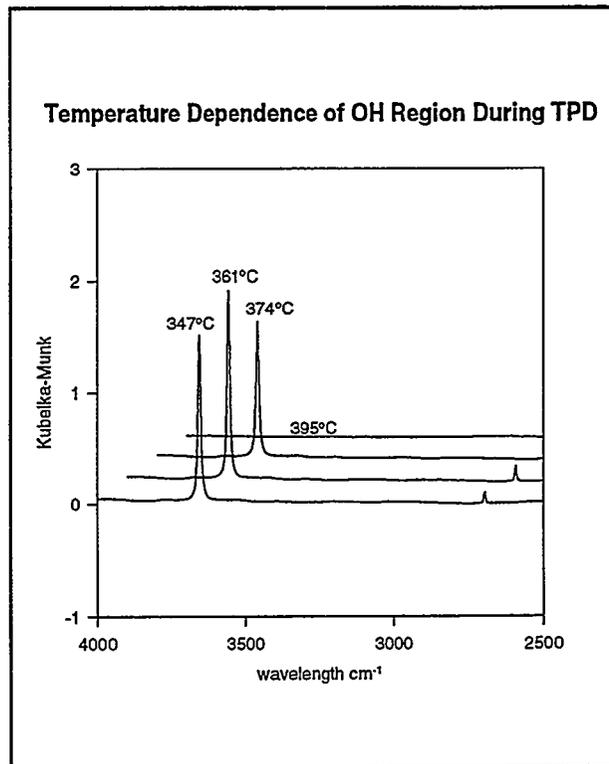


Figure 8

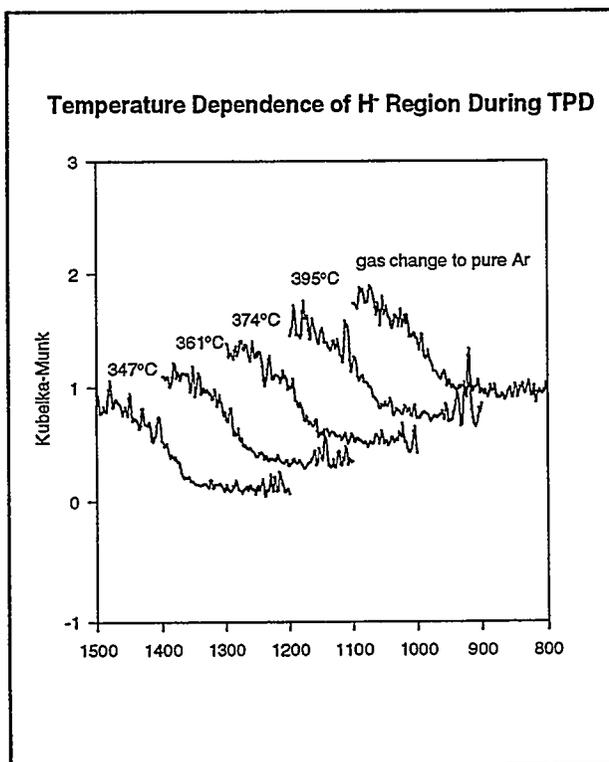


Figure 9

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