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KINETICS OF HYDROGEN RELEASE FROM LUNAR SOIL

Roberta Bustin, Principal Investigator

Arkansas College

Batesville, Arkansas 72501

Everett K. Gibson, Jr. and David S. McKay, NASA Technical Officers

NASA Johnson Space Center

Houston, Texas 77058

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KINETICS OF HYDROGEN RELEASE FROM LUNAR SOIL

With increasing interest in a lunar base, there is a need for extensive examination of possible lunar resources. Hydrogen will be needed on a lunar base for many activities including providing fuel, making water, and serving as a reducing agent in the extraction of oxygen from its ores. Previous studies have shown that solar wind has implanted hydrogen in the lunar regolith (Becker, 1980) and that hydrogen is present not only in the outer layer of soil but to considerable depths, depending on the sampling site (Bustin and Gibson, 1990). If this hydrogen is to be "mined" and used on the lunar surface, a number of questions need to be answered. How much energy must be expended in order to release the hydrogen from the soil? What temperatures must be attained, and how long must the soil be heated? This study was undertaken to provide answers to practical questions such as these.

EXPERIMENTAL

Hydrogen was determined using a Pyrolysis/GC technique (Carr *et al.*, 1987) in which the hydrogen was released by heating the soil sample contained in a quartz tube in a resistance wire furnace, followed by separation and quantitative determination using a gas chromatograph with a helium ionization detector. Heating times and temperatures were varied, and particle separates were studied in addition to bulk soils. The typical sample size was 10 mg of lunar soil. All of the soils used in the study were mature soils with similar hydrogen abundances. Pre-treatments with air and steam were used in an effort to find a more efficient way of releasing the hydrogen.

RESULTS AND DISCUSSION

TEMPERATURE DEPENDENCE

Even though much of the solar wind hydrogen is trapped within 200 Å of the surface (Carter, 1985), the hydrogen appears to be tightly bound. Using bulk lunar soil 15021,2 and with heating times up to six minutes, no hydrogen was released at temperatures less than 300°C. For six-minute heating intervals, one-third of the total hydrogen released was evolved by 500°C, and two-thirds of the total had been evolved by 625°C. Prolonged heating at these low temperatures did not result in evolution of all the hydrogen present. For example, only about two-thirds of the total hydrogen present was released during 30 minutes of heating at 600°C. All of the hydrogen was not released until temperatures of 900°C to 1000°C were reached. Data for Figures 1 and 2 were obtained by heating the sample, allowing it to cool, injecting the evolved gases into the GC, and reheating the sample, each time using a heating interval 15 seconds longer than the previous heating time; the run was terminated after the three-minute heating interval. Using this method of heating the bulk soil, less than half of the total hydrogen present was released at temperatures of 700°C and 800°C. Even with fine-grained soil (<20µm), only about half of the total hydrogen present was released at 700°C, and about 70% was released at 800°C.

RATE OF RELEASE

As Figures 3a and 3b show, the majority of the hydrogen released at any temperature came off quickly. Continuous heating for three minutes at 900°C or above appeared to be sufficient to remove all the hydrogen from most samples. However, acceptable efficiency for hydrogen recovery can be achieved using even shorter heating times. As shown in Figure 4, almost 80% of the total hydrogen present was released at 1000°C with only a one-minute heating interval. Beginning with a heating interval of 15 seconds and heating 15 seconds longer each interval, 75% of the hydrogen released came off during the first four heating intervals (a total of 2.5 minutes of heating) for temperatures of 800°C or above. If the delay caused by the heating of the quartz sample holder could have been eliminated, even shorter heating periods would have been adequate. From an energy standpoint, short heating times are certainly an advantage even though high temperatures are required in order to remove all the hydrogen from a sample.

KINETICS

A previous study on release of hydrogen from particle separates (Bustin and Gibson, 1990) showed that, in addition to the hydrogen in the surface layer, lunar soil particles contain hydrogen which has become embedded within the particle as the particle has grown during micrometeorite action on the lunar surface. Figures 3a, 3b, 5, and 6 show that the release of hydrogen from lunar soil does not follow a simple rate-law expression. This is apparently due to the release of the two different "kinds" of hydrogen, surface-correlated and volume-correlated hydrogen. Evolution of the surface hydrogen involves mainly desorption from the surface, whereas evolution of volume-correlated hydrogen involves a more complicated mechanism including diffusion through the particle to the outer layer, followed by desorption from the surface. The first hydrogen released is probably the surface hydrogen. It appears to be released very quickly, particularly at high temperatures. The evolution of both kinds of hydrogen appears to follow first order kinetics; however, the rate constants are different for these two (Table 1). Desorption of hydrogen from a nickel surface has been shown to be first order (Petermann, 1972); thus, it is not surprising that desorption of hydrogen from lunar soil follows first order kinetics. For both bulk soil and <20μm soil, the distinction between the two kinds of hydrogen release is more pronounced at higher temperatures. More data points are desirable during the first few seconds of heating; however, points taken before 15 seconds are not very meaningful because of the time required to heat the quartz sample tube.

COMPARISON OF BULK AND <20μm SOILS

Most of the comparison studies were done with bulk soil 75121,6 and <20μm and bulk soil 15021,2. Particle separates were not available for soil 75121,6. It was used in some of the studies because of the limited amount of bulk soil 15021,2; however, both of these soils were mature and had similar hydrogen abundances, making it possible to compare results from the two. Soil 15021,2 (bulk and <20μm) was used in the comparisons in Figures 7 and 8. A total of 1.6 times as much hydrogen was released from the <20μm soil, and it was given off much quicker than from the bulk soil.

For example, at a temperature of 600°C, three times as much hydrogen had been released from the <20µm soil as from the bulk soil. Because of the large surface area, more of the hydrogen present in the <20µm soil is probably surface hydrogen. This might explain why there is a clearer distinction between the two kinds of hydrogen release in the <20 µm soil than in the bulk soil (Figures 5 and 6). Using the Arrhenius Plot in Figure 9, the activation energy for the release of hydrogen from bulk soil 75121,6 was found to be 8.05 kJ/mol. A much lower value of 3.51 kJ/mol was obtained for the <20µm soil 15021,2 (Figure 10). This is not surprising since hydrogen comes off quicker and at a lower temperature in the <20µm soil.

All of these observations point to the desirability of physically separating the small particles from the rest of the soil prior to heating. Carter (1985) describes a practical way to accomplish this by vibratory screening followed by direct gaseous classification using turboscreening. The energy requirement for releasing the hydrogen could be cut significantly if such a preliminary screening was practical.

ATTEMPTS TO INCREASE EXTRACTION EFFICIENCY BY PRETREATMENT OF SOIL

In an effort to find a more efficient way of releasing the hydrogen, pre-treatment of soil with both air and with steam was attempted.

Pre-treatment with air was an attempt to react the hydrogen in the soil with oxygen in order to remove the hydrogen more efficiently (higher percentage removal at a lower temperature). Two methods were used. In the first procedure, the soil was heated in an open crucible in a furnace. The second method involved placing the soil in an alumina sample boat, putting the boat in a glass tube, and allowing air to flow through the tube. Heating times from five minutes to 24 hours were tried. No significant difference was detected at a temperature of 400°C. (Results were almost the same when the sample was heated in air or in vacuum at 400°C, followed by the routine determination at 900°C.) There was a slight decrease (up to 15%) in the values from routine determinations at 900°C when the samples had been preheated overnight at approximately 250°C. While this could be interpreted to mean that some hydrogen was removed with oxygen at a temperature below that normally required for hydrogen evolution, it was not a significant amount, and more tests would have to be run before a definitive conclusion could be reached.

A sample was preheated in steam by putting it in a small alumina crucible which was then placed in a Parr bomb containing about 0.5 mL of water in the bottom of the Teflon container. The bomb was then placed in an oven so that steam could be produced. Extraction efficiency did not seem to be improved by preheating samples with steam. In several instances, larger than expected values of hydrogen were found, probably because the steam reacted with some metallic iron in the soil, producing hydrogen which was then adsorbed on the surface of the soil to be evolved during a subsequent determination.)

SUMMARY

Although very small samples (10 - 20 mg) were used in this study, results can be extrapolated to large samples. For example, temperature is very important. High temperatures (900°C - 1000°C) are required for the release of all the hydrogen present in a sample; the same results are not obtained simply by heating longer at a lower temperature. However, two-thirds of all hydrogen present could be released at 600°C by heating for 30 minutes. From 60 - 80% of the total hydrogen released at temperatures of 800°C or above comes off quickly (within 1.5 minutes for the sample sizes used here). Both the fact that a significant amount of the hydrogen comes off at a considerably lower temperature than that required for complete hydrogen extraction (600°C compared to 900°C) and the fact that the hydrogen is released quickly are encouraging from an energy standpoint.

The kinetics of hydrogen release are complicated by the presence of two "types" of hydrogen, hydrogen present on the surface released by simple desorption and hydrogen present in the interior of the particle which must diffuse to the surface before being desorbed. Desorption from the surface appears to occur by first order kinetics with an activation energy of 8.05 kJ/mol for bulk soil 75121,6 and 3.51 kJ/mol for <20μm soil 15021,2.

Large-scale studies need to be done in order to work out the details of extracting hydrogen from actual lunar soil. However, results from this study show that such extraction is feasible from an energy standpoint.

TABLE 1. Rate Constants for Hydrogen Release. (k = rate constant for the surface-correlated hydrogen; k' = rate constant for the volume-correlated hydrogen)

	Bulk Soil 75121.6		≤20μm Soil 15021.2	
	k	k'	k	k'
700° C	0.335	0.309	0.424	0.256
800°C	0.907	0.572	0.725	0.162
900°C	1.802	0.422	0.889	0.149
1000°C	1.100	0.117	1.224	0.107

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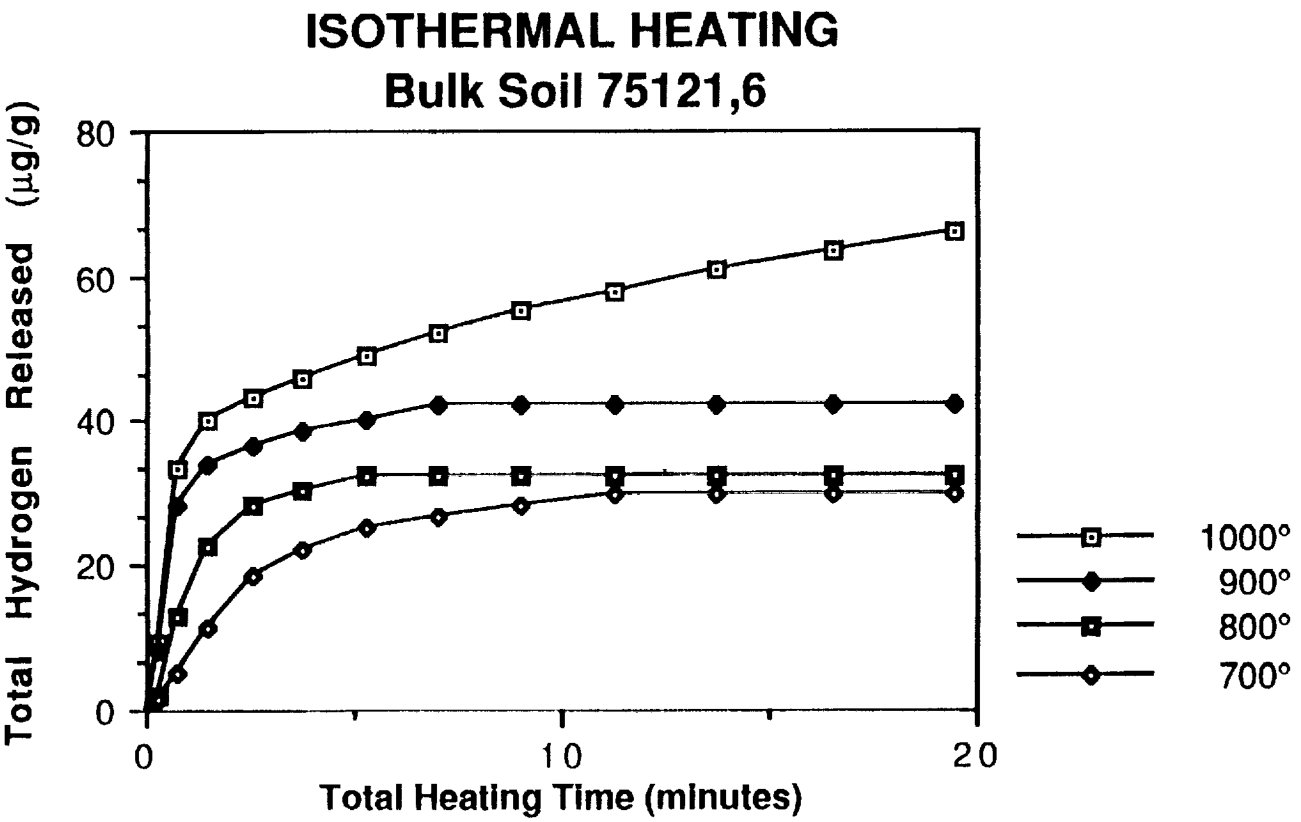

Figure 1. Isothermal Heating Curves for Bulk Soil 75121,6.

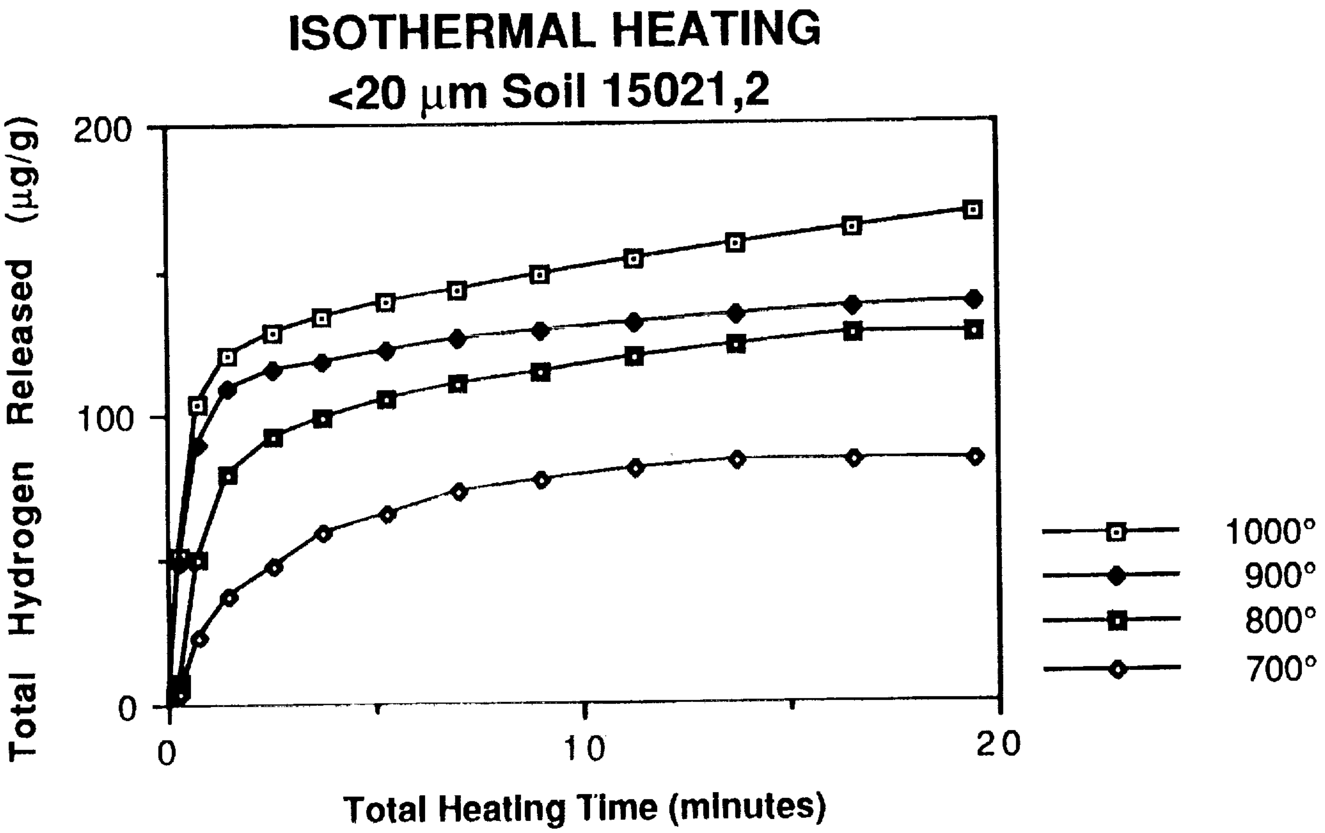

Figure 2. Isothermal Heating Curves for <20 µm Soil 15021,2.

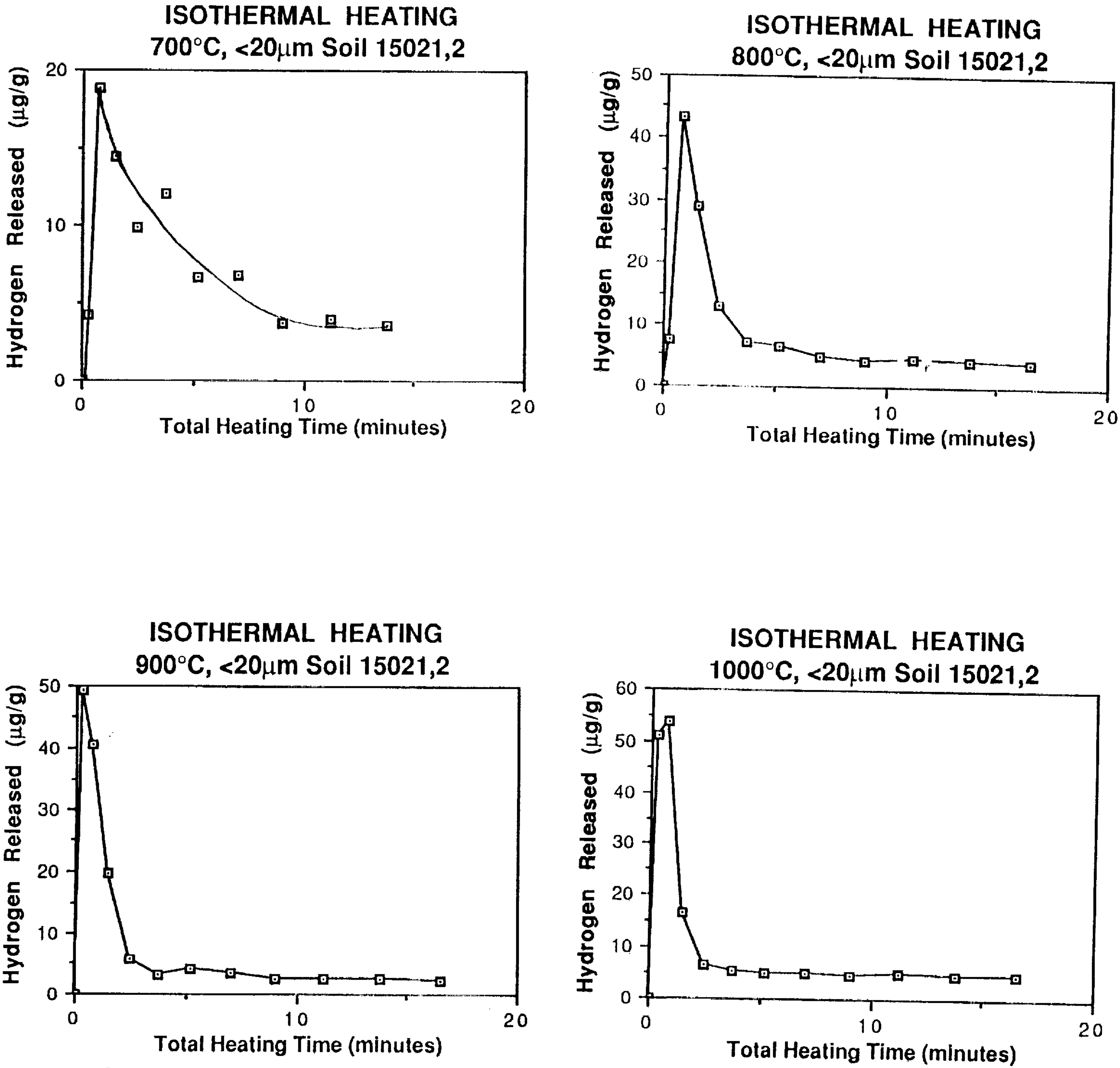

Figure 3a. Hydrogen Released from <20 μm Soil 15021,2 During Isothermal Heating. Figure 3b is a composite of the individual graphs in Figure 3a.

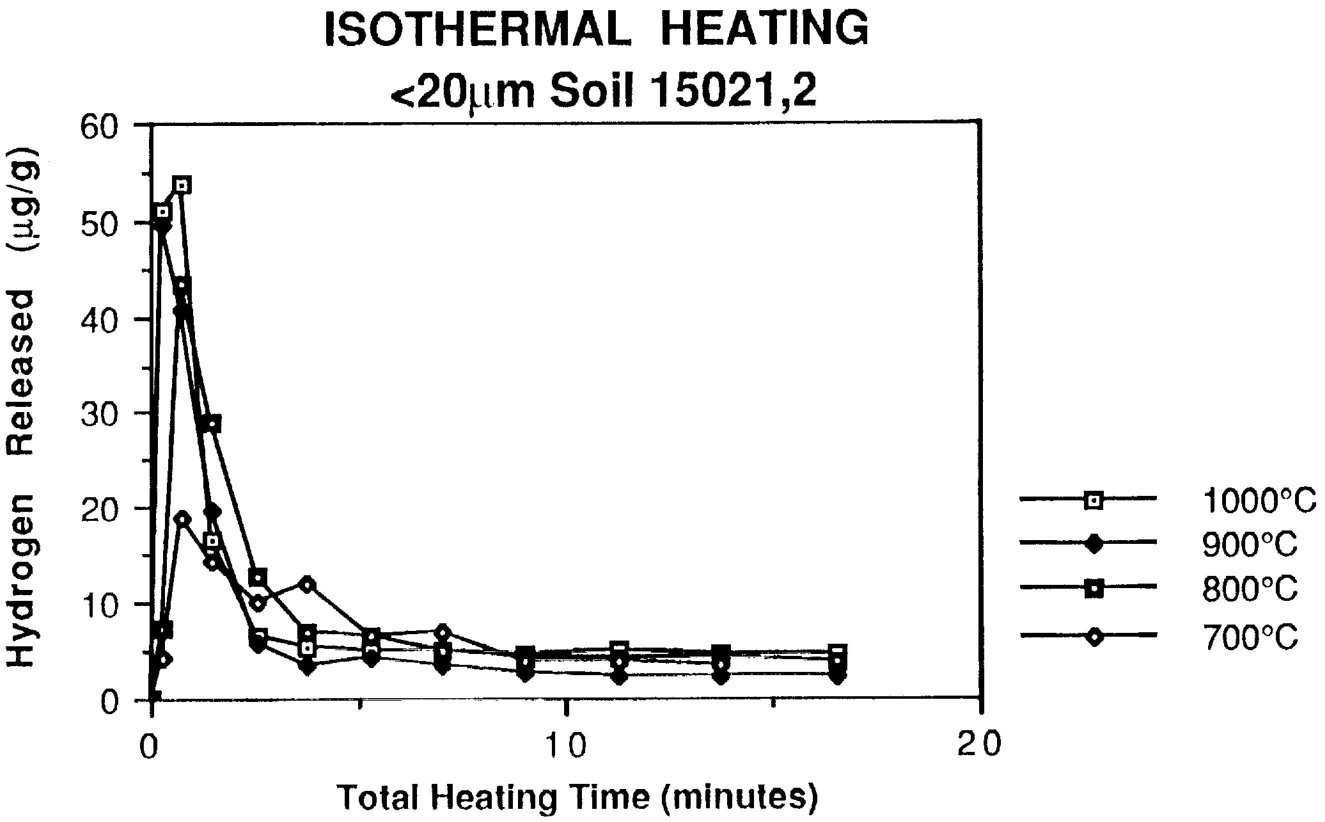
ISOTHERMAL HEATING
<20μm Soil 15021,2
Hydrogen Released (μg/g)
60
50
40
30
20
10
0
0
10
20
Total Heating Time (minutes)
1000°C
900°C
800°C
700°C

Figure 3b

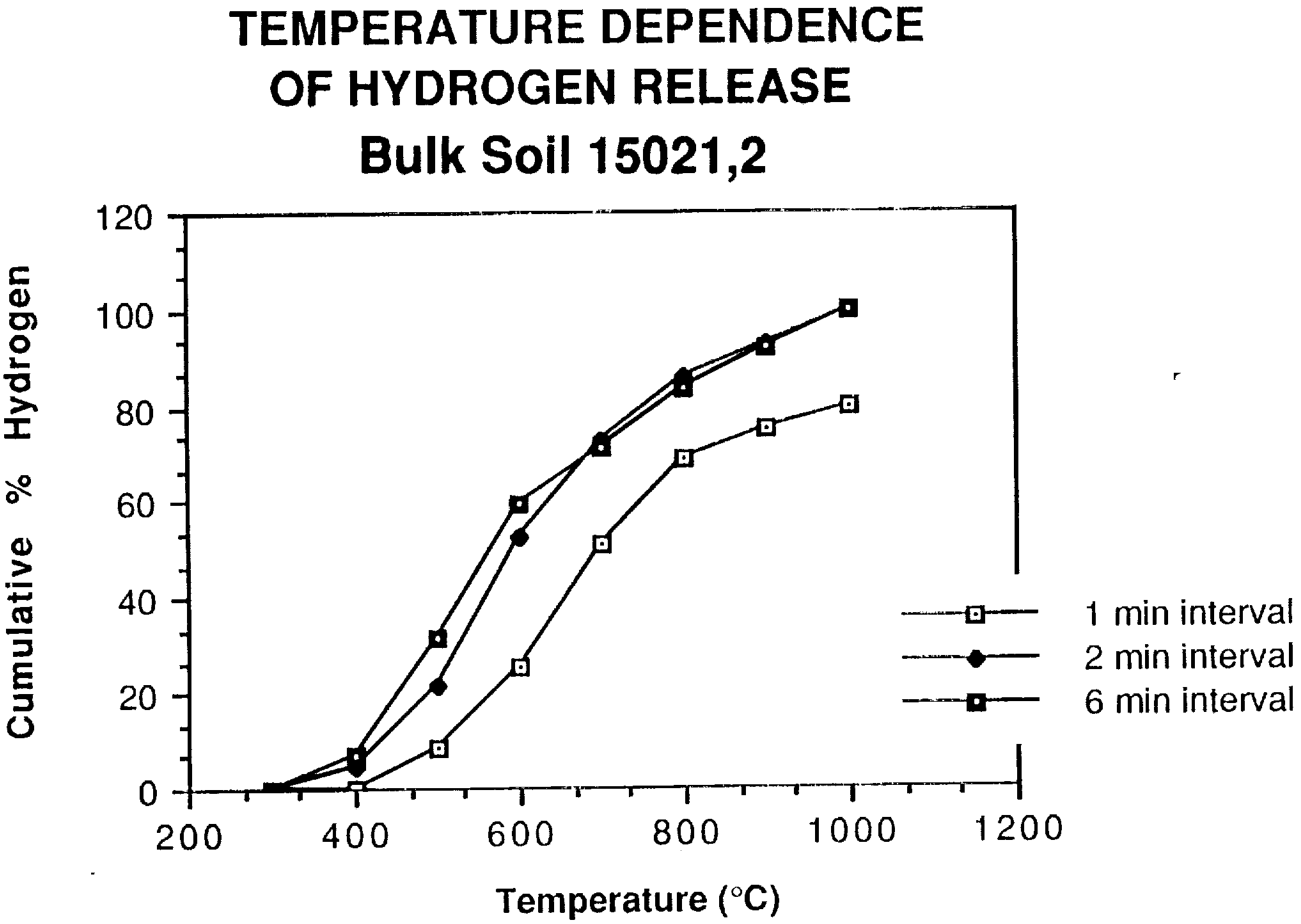

Figure 4. Temperature Dependence of Hydrogen Release for Different Heating Intervals for Bulk Soil 15021,2.

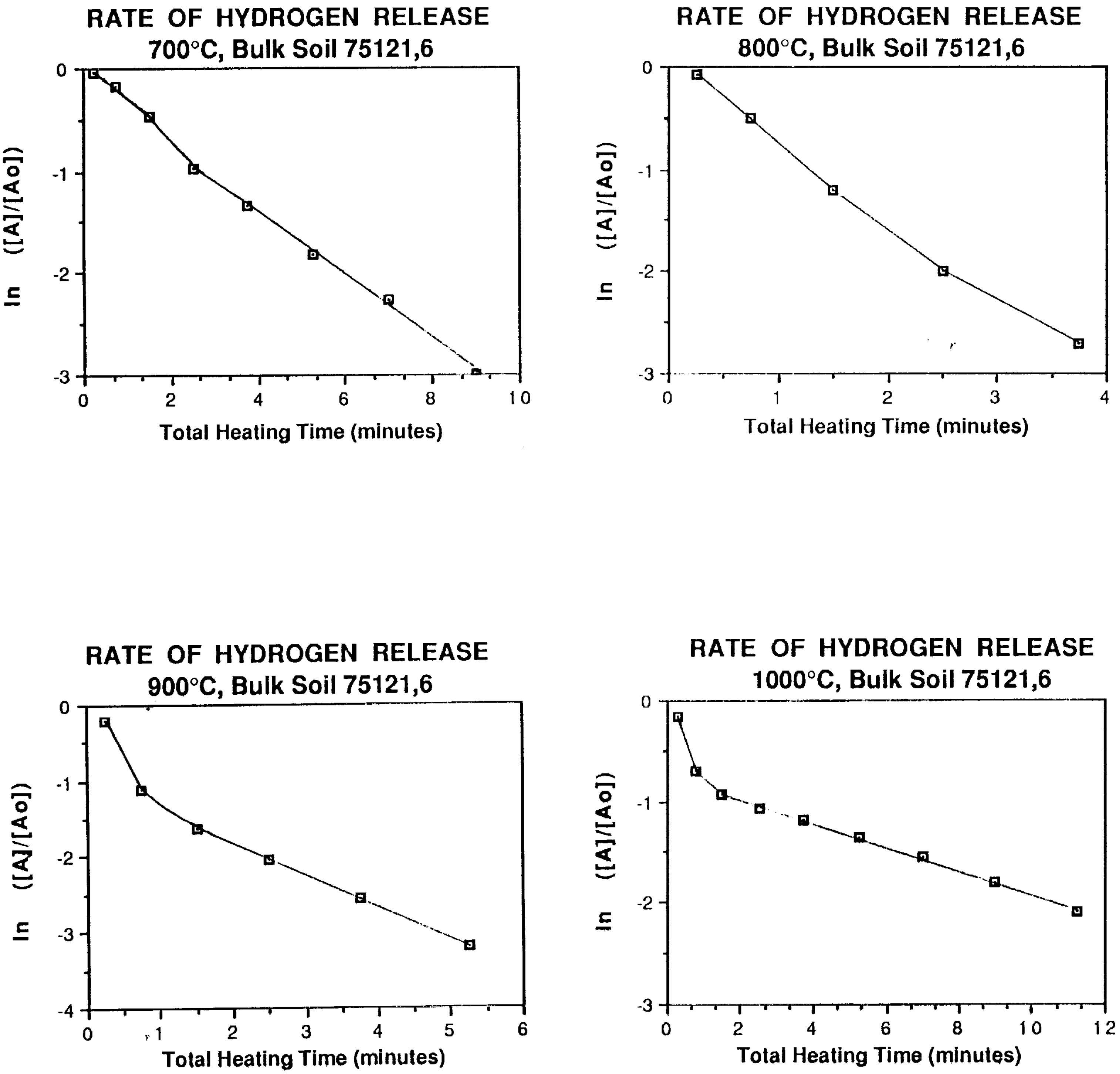

Figure 5. Graphs Showing the Kinetics of Hydrogen Release for Bulk Soil 75121,6.

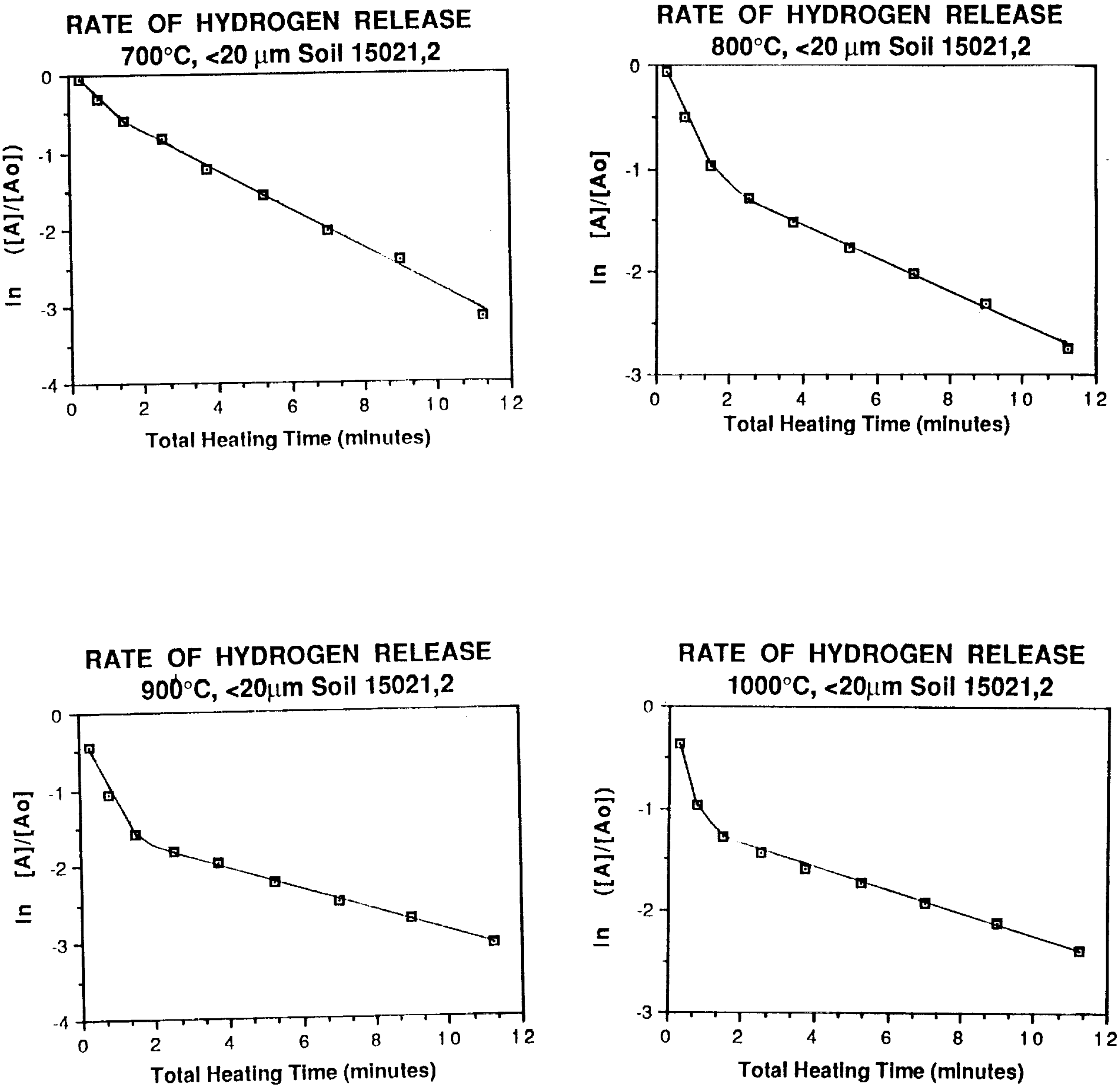

Figure 6. Graphs Showing the Kinetics of Hydrogen Release for <20µm Soil 15021,2.

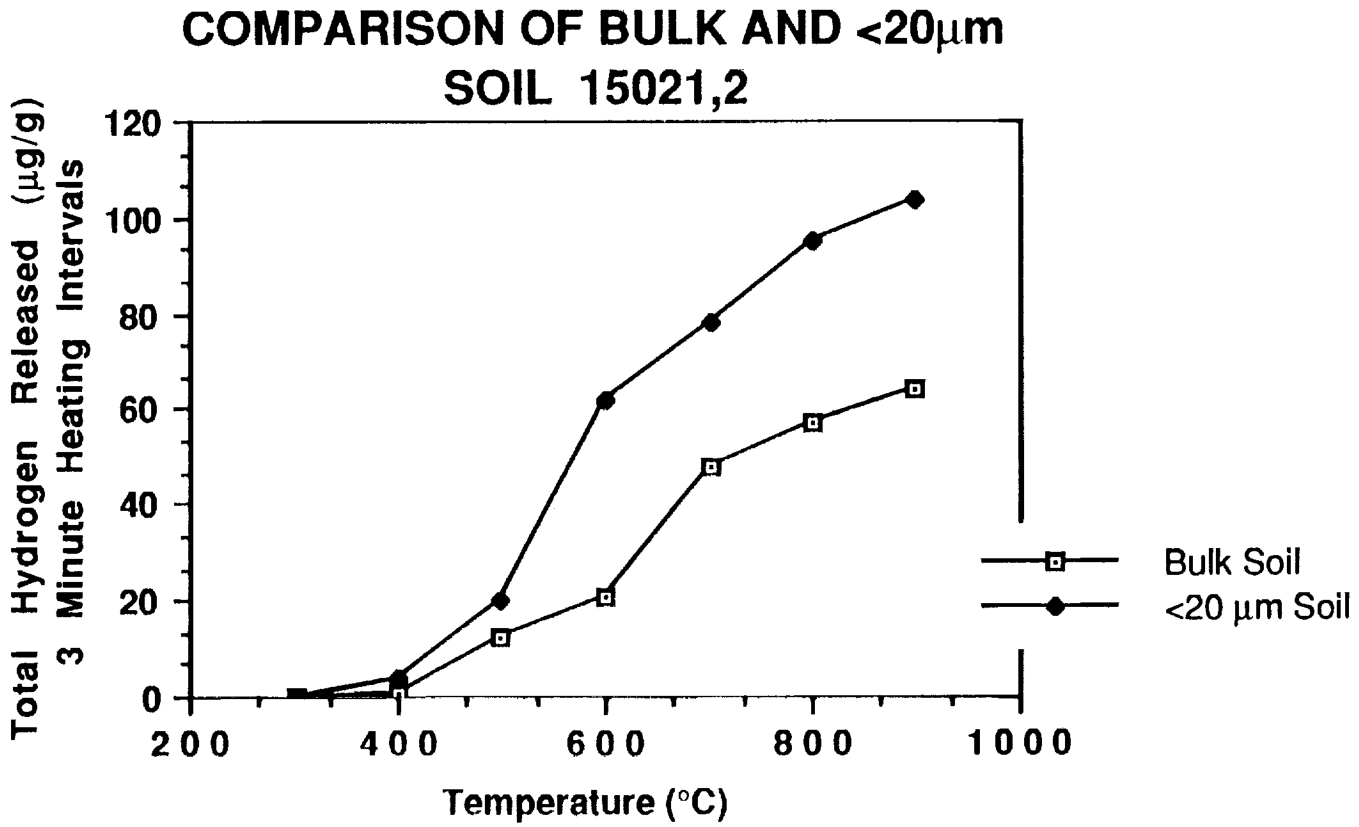

Figure 7. Temperature Dependence of Hydrogen Release for Bulk and <20μm Soil 15021,2.

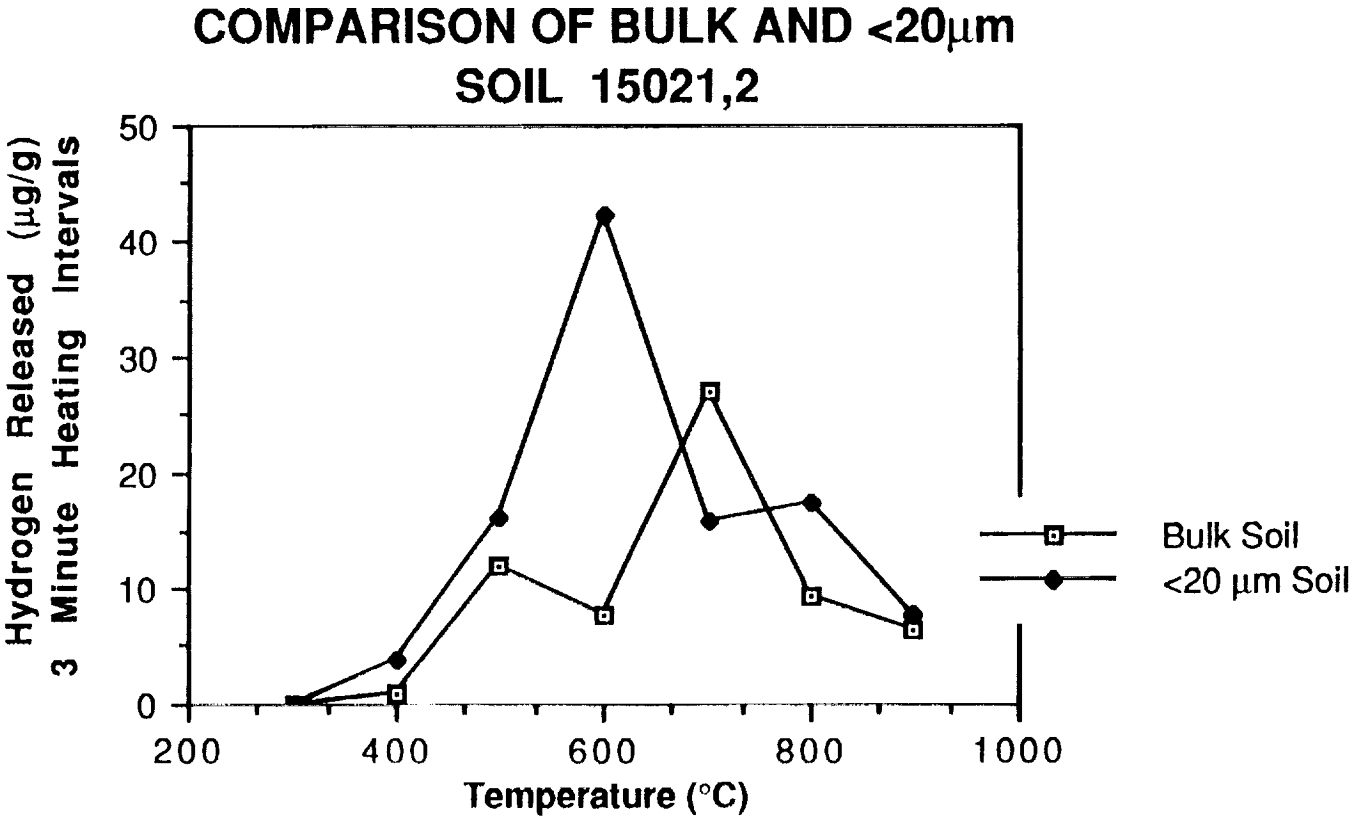

Figure 8. Temperature Dependence of Hydrogen Released per Heating Interval for Bulk and <20µm Soil 15021,2.

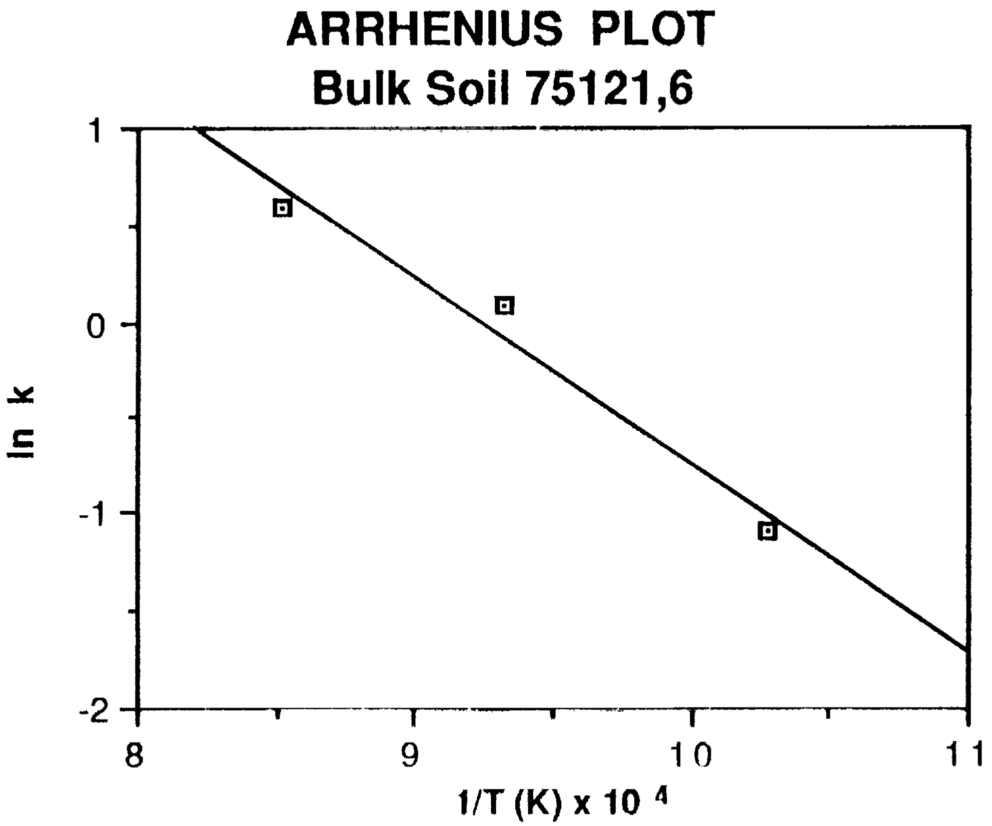

Figure 9. Arrhenius Plot for Bulk Soil 75121,6.

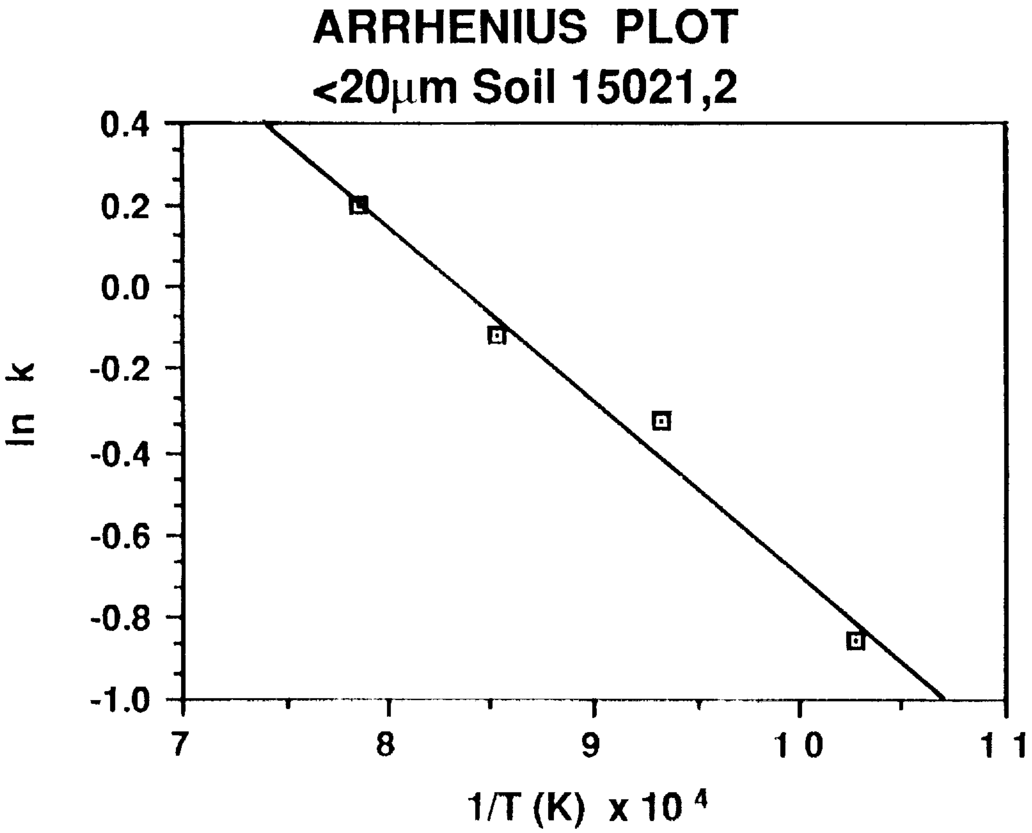

Figure 10. Arrhenius Plot for <20μm Soil 15021,2.