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DEHYDRATION KINETICS OF TALC AT 1 BAR

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Abstract

We present experimental results on the dehydration kinetics of talc, which is likely to be a major potential resource for water and hydrogen in carbonaceous chondrites. The rate of dehydration of an essentially pure Mg-end member natural talc, $(\text{Mg}_{.99}\text{Fe}_{.01})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, was studied by measuring in situ weight change under isothermal condition at 1 bar as a function of time in the temperature range 775-985°C. The grain size of the starting material was 0.7-1 micron. It was found that the data up to 50-60% dehydration can be fitted by an equation of the form $\alpha = \exp(-Kt^n)$, where α is the weight fraction of talc remaining, K is a rate constant and n is a numerical constant for a given temperature. For any set of isothermal data, there is a major change in the value of n for larger dehydration. For up to ~ 50% dehydration, all rate constants can be described by an Arrhenius relation with an activation energy of 432 (± 30) kJ/mol; n has a nearly constant value of 0.54 between 775 and 875°C, but increases almost linearly according to $n = -10.77 + 0.012T(^{\circ}\text{C})$ at $T \geq 875^{\circ}\text{C}$.

Introduction

Carbonaceous chondrites are usually believed to be the primary constituents of near-Earth asteroids and Phobos and Deimos, and are potential resources of fuels that may be exploited for future planetary missions. The most volatile-rich members of this class of meteorite are known as C1 (or CI) and C2 (or CM) classes. Our group has been involved in an integrated study on the thermodynamics and kinetics of reactions of the volatile-bearing phases that are likely to be present in carbonaceous chondrites. The results will provide important constraints on fundamental aspects concerning nature, abundance, and time scale of formation of volatile-bearing phases in the solar nebula, and the practical problem of the feasibility of extraction of volatiles for fuels from carbonaceous chondrites.

In collaboration with Dr. Surendra Saxena (Professor of Geochemistry at the Brooklyn College, City University of New York, and Uppsala University, Sweden), we have been engaged in deriving and systematizing a set of internally consistent thermochemical data for the minerals that could form within the range of bulk compositions displayed by carbonaceous chondrites, and computer calculations of equilibrium phase relations, along with modal abundance and composition of the phases through the minimization of Gibbs free energy. Although this is an on-going project, subject to revisions and refinements with the improvement and expansion of thermochemical data

base, the results of the calculations carried out so far suggest that talc, $(\text{Mg,Fe})_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, and antigorite, $(\text{Mg,Fe})_{48}\text{Si}_{34}\text{O}_{85}(\text{H})_{62}$, with or without magnesite, $(\text{Mg,Fe})\text{CO}_3$, are likely to be the major volatile-bearing inorganic phases in the C1 and C2 carbonaceous chondrites (Ganguly and Saxena, 1989).

Having identified the most likely mineralogical source of volatiles in the carbonaceous chondrites, we have begun a program of systematic kinetic study of devolatilization reactions, along with our on-going research on thermochemical properties and phase equilibrium calculations. The results will provide the framework for the most energy efficient Engineering designs for the extraction volatiles.

From considerations of the structural properties of phyllosilicates (e.g Bailey, 1988, Evans and Guggenheim, 1988), it is clear that on the average, the hydroxyl groups are more strongly bonded in talc than in antigorite. This is reflected in their relative thermal stabilities. Consequently, the dehydration kinetics of talc is expected to be significantly slower than that of antigorite. During the course of the current funding cycle (March, 1990- February, 1991), we have begun and made significant progress in understanding the dehydration kinetics of talc, as reported below. Work is currently in progress to evaluate the effect of surface area and Fe/Mg ratio on the reaction kinetics, and the mechanism of dehydration reaction.

Experimental Methods

The dehydration kinetics of talc has been determined by monitoring the in situ weight change of a natural talc as a function of temperature and time at 1 bar pressure. A schematic of a **Thermogravimetry Apparatus** constructed for this purpose is shown in Fig. 1.

The sample is suspended in an alumina crucible inside a vertical furnace, which has about 2" hot spot of constant temperature near the center. The temperature distribution has been determined by shifting the position of thermocouple along the length of the furnace. The temperature of the sample is monitored by a thermocouple placed very close to the alumina crucible. The bottom of the furnace is closed by a plexiglass so that the position of the sample and the thermocouple can be observed during a run by a mirror, placed underneath the furnace. In order to determine in situ weight change, it is extremely important to ensure that the sample is suspended freely without touching the furnace wall or the thermocouple.

During a run, the suspension of the sample inside the furnace is supported by a needle passing through a small loop in a platinum wire connected to the sample crucible, and resting on a glass tube. The sample weight is determined at desired intervals by connecting the platinum wire to an extension support connected to the pan of an analytical balance through the bottom end. The connection between the analytical balance and the loop in the platinum wire is made by a rigid wire

Thermogravimetry Apparatus

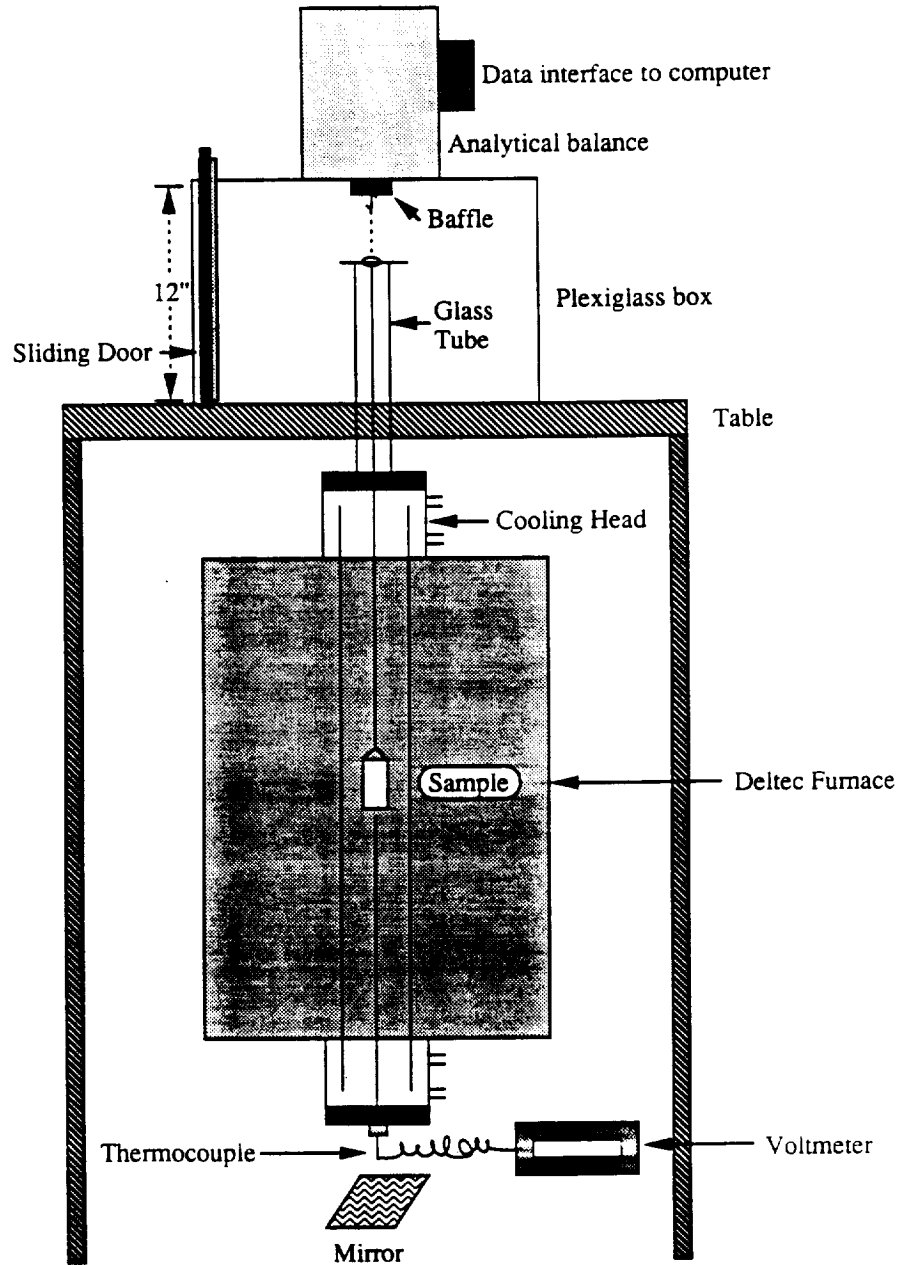


Fig. 1: Schematic of the apparatus designed for the measurement of in situ weight change as a function of temperature and time. The plexiglass box (supporting the balance) has a sliding door to permit access to the suspension assembly. The base of the analytical balance is fitted with a baffle to prevent disturbance of the weighing pan (supporting the suspension hook) by thermal current rising from the furnace.

of controlled length and removing the supporting needle such that the position of the sample inside the furnace is not disturbed. The output from the weight transducer in the balance is taken directly to a computer through an interface attached to the balance. The weight of the sample is then recorded in the computer by averaging over a short time interval, 90-120 seconds, after the initial fluctuations resulting from the attachment of the sample to the balance have stabilized. Typically it needs about 2-3 minutes to stabilize these fluctuations, after which there is a small fluctuation (± 0.0001 gm), which is an intrinsic property of the balance.

We initially kept the sample suspended directly from the analytical balance so that the weight change can be monitored continuously as a function of time. However, this method has to be finally abandoned owing to the creep of the weight transducer, usually in runs greater than half-hour. The creep effect was discovered by monitoring the weight of a sample directly on the pan of the balance in the usual manner as a function of time, and ensuring that there is no disturbance through air circulation. The creep effect is illustrated in Fig. 2 by comparing the weight monitored continuously as a function of time with that determined by the method described above at essentially the same temperature.

The thermal current rising from inside the hot furnace causes another perturbation (Fig. 3) to the determination of weight change of a sample suspended inside the furnace. Fig. 3a shows the fluctuations of the weight of a crucible measured as a function of time. The fluctuations are usually in the range of ± 0.0005 gm. In this example, the creep effect was fortuitously quite small. Fig. 3b shows how the measured weight of a sample oscillates as the furnace is repeatedly heated and cooled. The effect of the thermal current was greatly minimized by putting a baffle at the bottom of the balance, with a small hole to allow free passage of the suspension attachment. The effect of putting the baffle is shown in Fig. 4. In this case, the weight of the sample was monitored at 1 minute interval using the arrangement illustrated in Fig. 1. The initial induction period is about 2 minutes, after which the system achieves a stable state with intermittent fluctuations of ± 0.0001 gm.

In each run, the furnace was first preheated to the desired temperature, and the sample was then suspended near the top of the furnace at about 250°C (which is about 140°C below the equilibrium dehydration temperature at 1 bar) for at least 24 hours to drive off absorbed water. The weight change of the sample was monitored as function of time to ensure complete removal of absorbed water. The sample was then lowered to the hot spot of the furnace, and its weight monitored at desired intervals, as discussed above. Before each weighing, the balance was calibrated using a computer controlled internal calibration, and the calibration was cross checked by weighing a certified weight on the pan of the balance. Because the maximum possible weight change (due to complete dehydration) was 4.5% of the initial weight, and there was about ± 0.0001

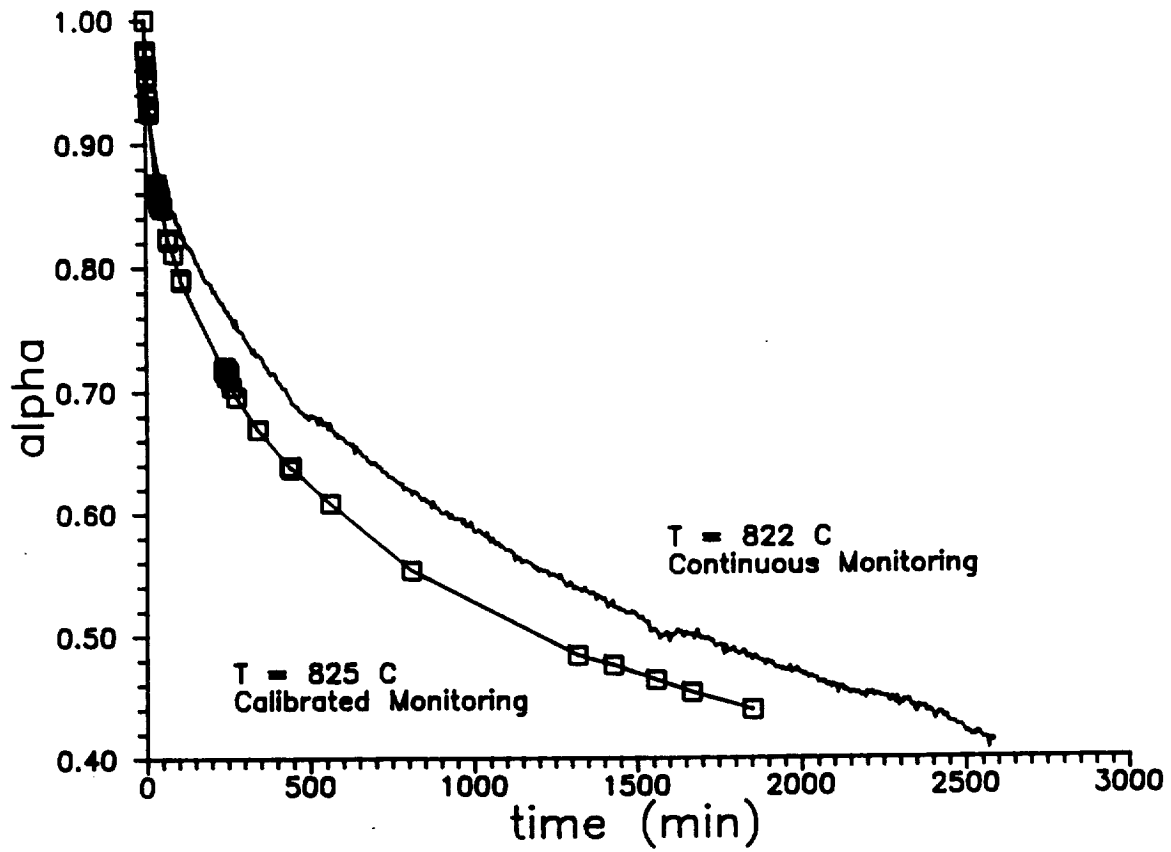


Fig. 2: Comparison of weight change of talc monitored continuously (through a data interface linking the output from a weight transducer to a computer) with that determined after calibrating the balance at discrete intervals. α is the weight fraction talc remaining as defined by eqn. (1).

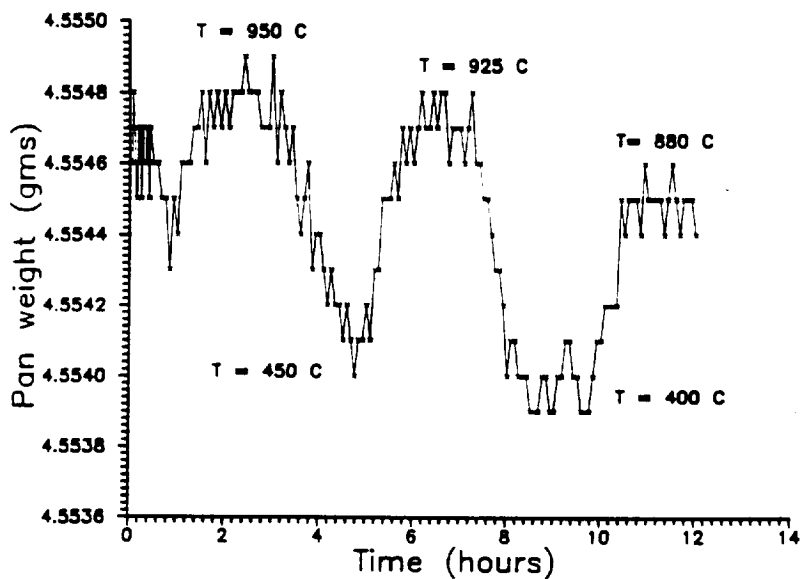
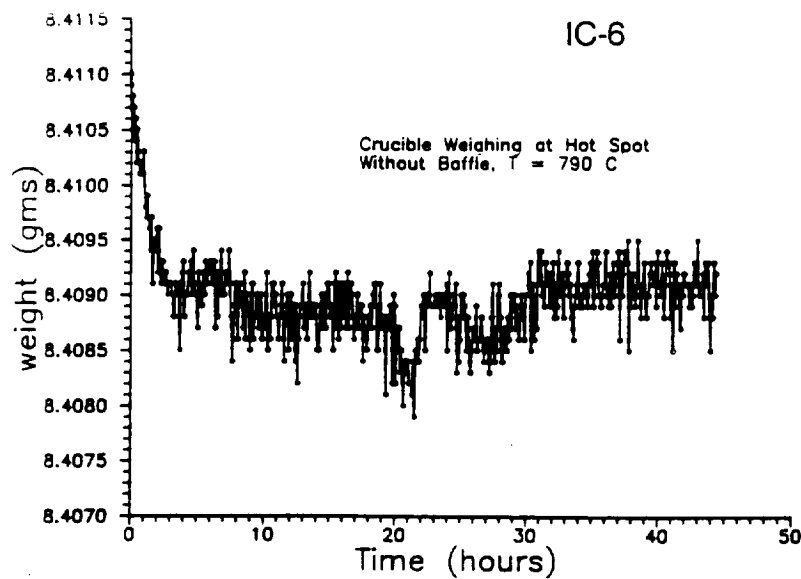


Fig. 3: Effect of thermal current on the measurement of the weight of a sample crucible suspended inside a furnace, as illustrated in Fig. 1. No baffle was used at the base of the balance. (a) Fluctuations in the measured weight of the crucible held at a constant temperature of 790°C inside the furnace. (b) Change in the measured weight of the crucible as the temperature inside the furnace is raised and lowered, as shown in the figure.

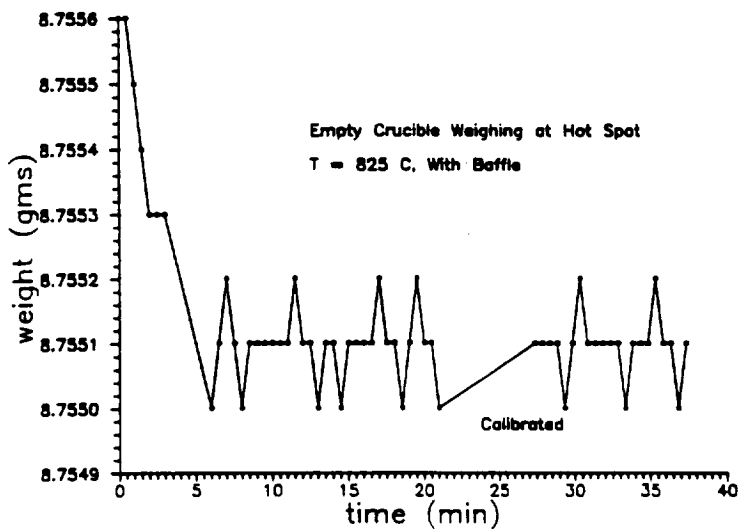


Fig. 4: The effect of introducing a baffle at the base of the balance (Fig. 1) on the measurement of the weight of a sample crucible.

gm statistical fluctuation of the weight recorded by the balance, it was necessary to use a sufficiently large amount of sample so that the statistical fluctuations were small compared to the recorded weight changes. Typically about a gram quantity of sample was used in each run.

Starting Material

The starting material was made of 0.7-1.0 micron grain size separates obtained by coring a block of talc with a diamond coring tool. It was thought that crushing may introduce too many defects that might enhance the dehydration kinetics. The X-ray diffractogram of the material did not show any other phase. However, a few grains of tremolite was detected in the electron microprobe analysis. The average of several spot analysis in the microprobe yields the following composition of the natural talc used in this study: $Mg_{(0.99}Fe_{0.01})_3Si_4O_{10}(OH)$.

Experimental Results and Theoretical Analysis

The weight change of talc as a function of time was measured at 775, 825, 875, 925, 975, 985°C. Selected run data are illustrated in Fig. 5 a-b. Here α is the weight fraction of talc remaining at time t, i.e.

$$\alpha = \frac{W_t - W_{\infty}}{W_0 - W_{\infty}} \quad (1)$$

where $W(t)$ is the weight of the sample at time t, and W_0 and W_{∞} are the sample weights at $t=0$ and $t = \infty$. W_{∞} , thus, corresponds to the weight of the sample after complete dehydration. The theoretical weight loss of the sample after complete dehydration is 4.5%. W_{∞} was also checked experimentally by making a very long run at 985°C, which is shown in Fig. 6. The weight after 49 hours is within 1.2% of the theoretical weight after complete dehydration. Thus, the theoretical value of W_{∞} was accepted in calculating α from eqn. (1). In each run, W_0 was taken to be the measured weight of the sample after it was introduced into the hot spot of the furnace, allowing about 3 minutes time for the stabilization of the system. This induction time was subtracted from the total time of the run.

To analyze the experimental data, we begin by assuming that the dehydration of talc is controlled by a nucleation and growth law of the form

$$\alpha = \exp(-Kt^n) \quad (2)$$

where K is a rate constant. In an earlier study, Ward (1975) was able to fit the dehydration of talc with $n = 1$. The eqn. (2) can be linearized to the following form.

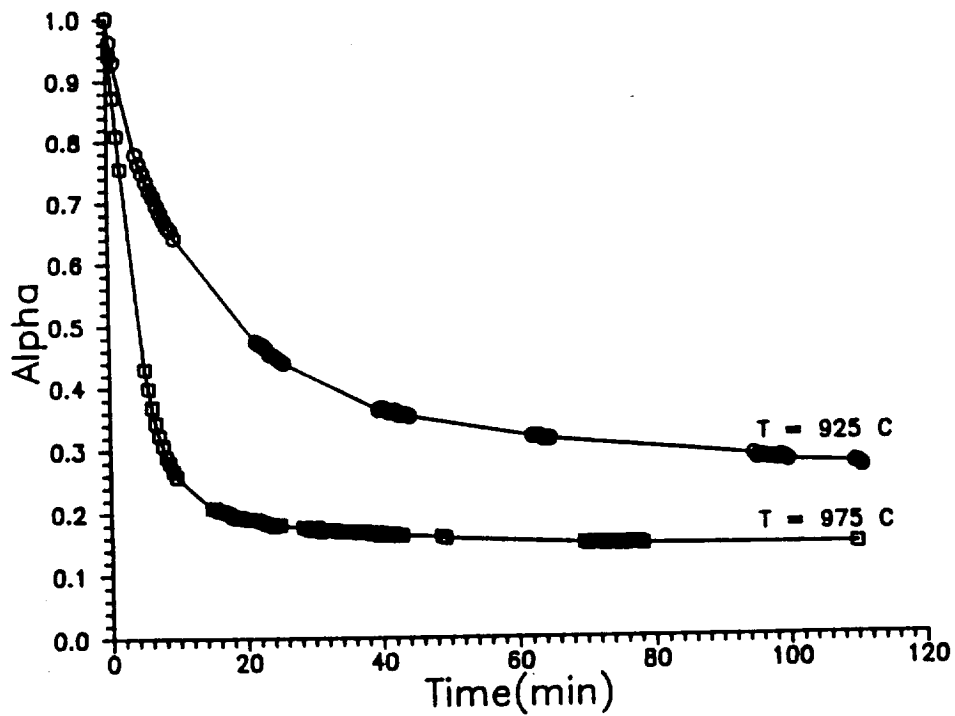
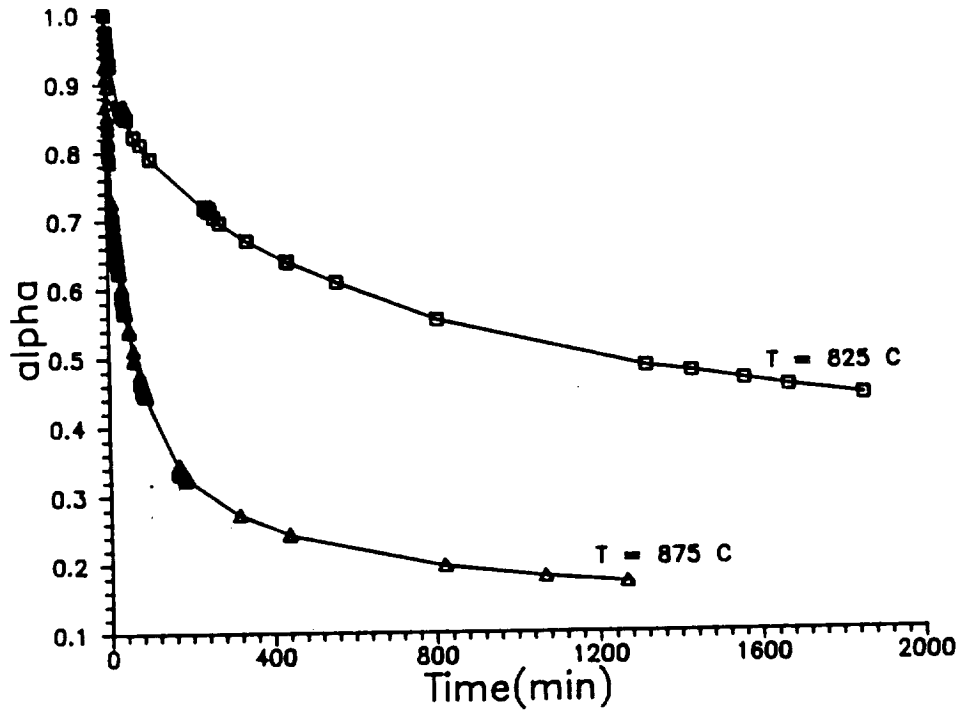


Fig. 5: Selected examples of the change in the weight of talc as function of time, as measured at discrete intervals. The balance was calibrated before each measurement, and the effect of thermal current was essentially eliminated by putting a baffle at the base of the balance (Fig. 1).

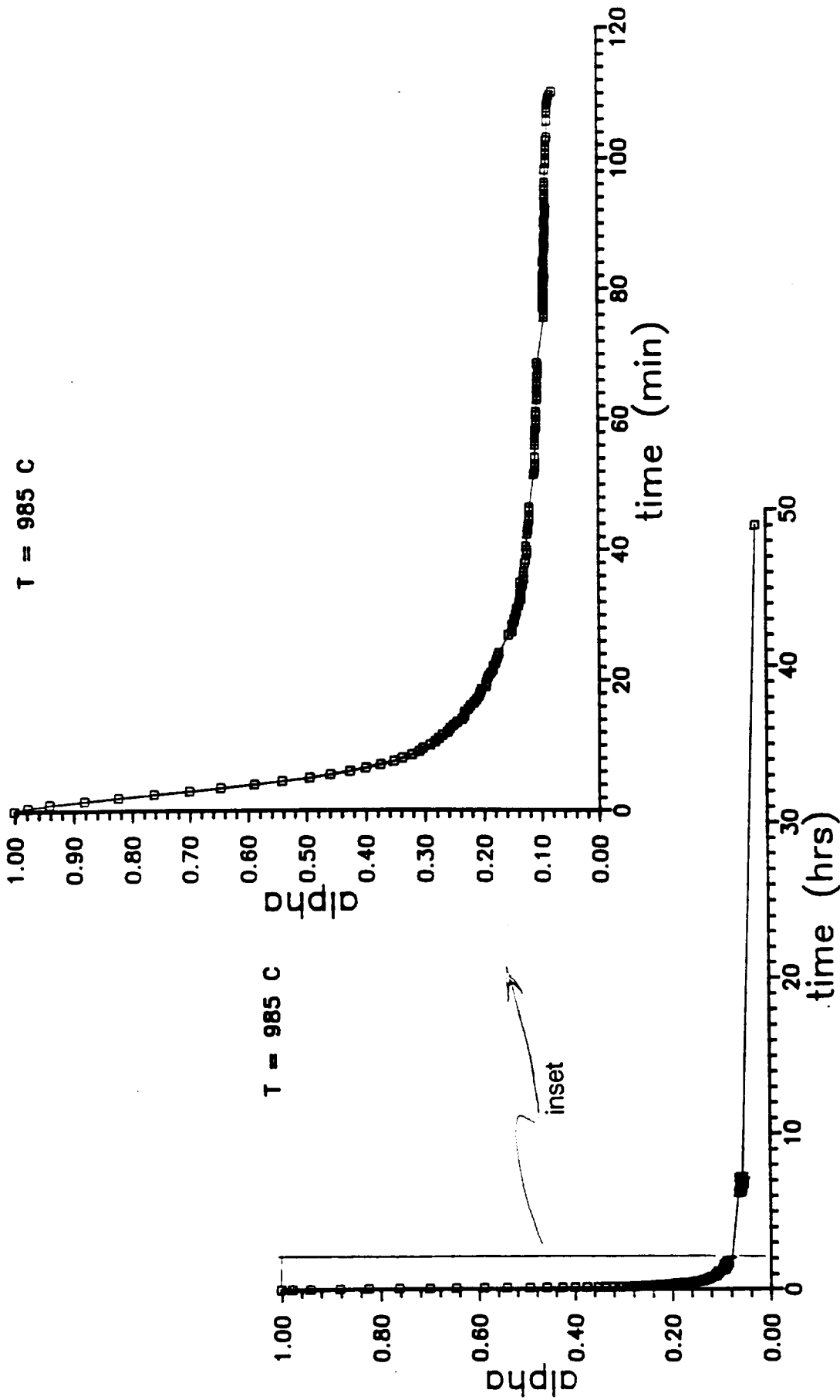


Fig. 6: A long run (49 hrs) at 985°C to determine the weight loss after complete dehydration (i.e. W_{α}) of the natural talc used in the experimental studies. The weight of talc remaining at the end of the run is only 1.2% less than the theoretical limit, calculated from the chemical formula.

$$\ln(-\ln\alpha) = n\ln K + n(\ln t) \quad (3)$$

Fig. 7 shows a typical isothermal plot of $\ln(-\ln\alpha)$ vs. $\ln t$. It is clear that eqn. (3) can describe the experimental data only up to 60 % dehydration. The change of slope typically takes place in the range of 50-60% dehydration.

If we restrict ourselves to dehydration up to the above linear range, then the dehydration rate can be described as function of temperature and time according to eqn. (2) with

$$K = 3.906(10^{21})\exp(-Q/(R^*T)) \text{ min}^{-1} \quad (4.1)$$

where the activation energy $Q = 432 (\pm 20)$ kJ/ mol. The value of n remains essentially constant at ~ 0.54 between 775 and 875°C, but increases almost linearly according to

$$n = -10.77 + 0.0122T(^{\circ}\text{C}) \quad (4.2)$$

The Arrhenian relation of the rate constant is illustrated in Fig. 8. The results are also compared with those of Ward (1975). The rate constants for the two sets of data agree within an order of magnitude at $T \leq 875^{\circ}\text{C}$, but there is strong disagreement at higher temperature. The results of Ward (1975) are suggestive of a change of dehydration mechanism around 875°C, which is in contrast to our results.

Effect of the Dilution of H₂O in the Vapor Phase

Ganguly and Saxena (1990) have presented detailed simulations of equilibrium heating at fixed bulk composition of C1 and C2 chondrites, which show that in the environment of dehydrating talc in carbonaceous chondrites, the concentration of H₂O in the vapor phase will be considerably diluted owing to the presence of other volatile species, primarily H₂, CH₄, CO₂ and CO. Consequently, there may be an enhancement of dehydration kinetics of talc due to the displacement of equilibrium dehydration to lower temperature as a result of dilution of H₂O in the vapor phase. This type of effect is often called the 'thermodynamic effect' on reaction kinetics, which may be calculated as follows.

The net rate of dehydration reaction (R_{net}) represents the difference between the rates of forward (R^*) and backward (R') reactions. It follows from transition state theory (e.g. Lasaga, 1981) that

$$R_{\text{net}} = R^*(1 - \exp(m\Delta G/RT)) \quad (5)$$

where m is constant and ΔG is the Gibbs free energy change of the dehydration reaction at temperature T . Since $R^* = K^*C_{\text{Talc}}$, where K^* is the intrinsic forward rate constant and C_{Talc} is the concentration of talc, it is not affected by the change in the composition of the vapor phase. Consequently, one obtains

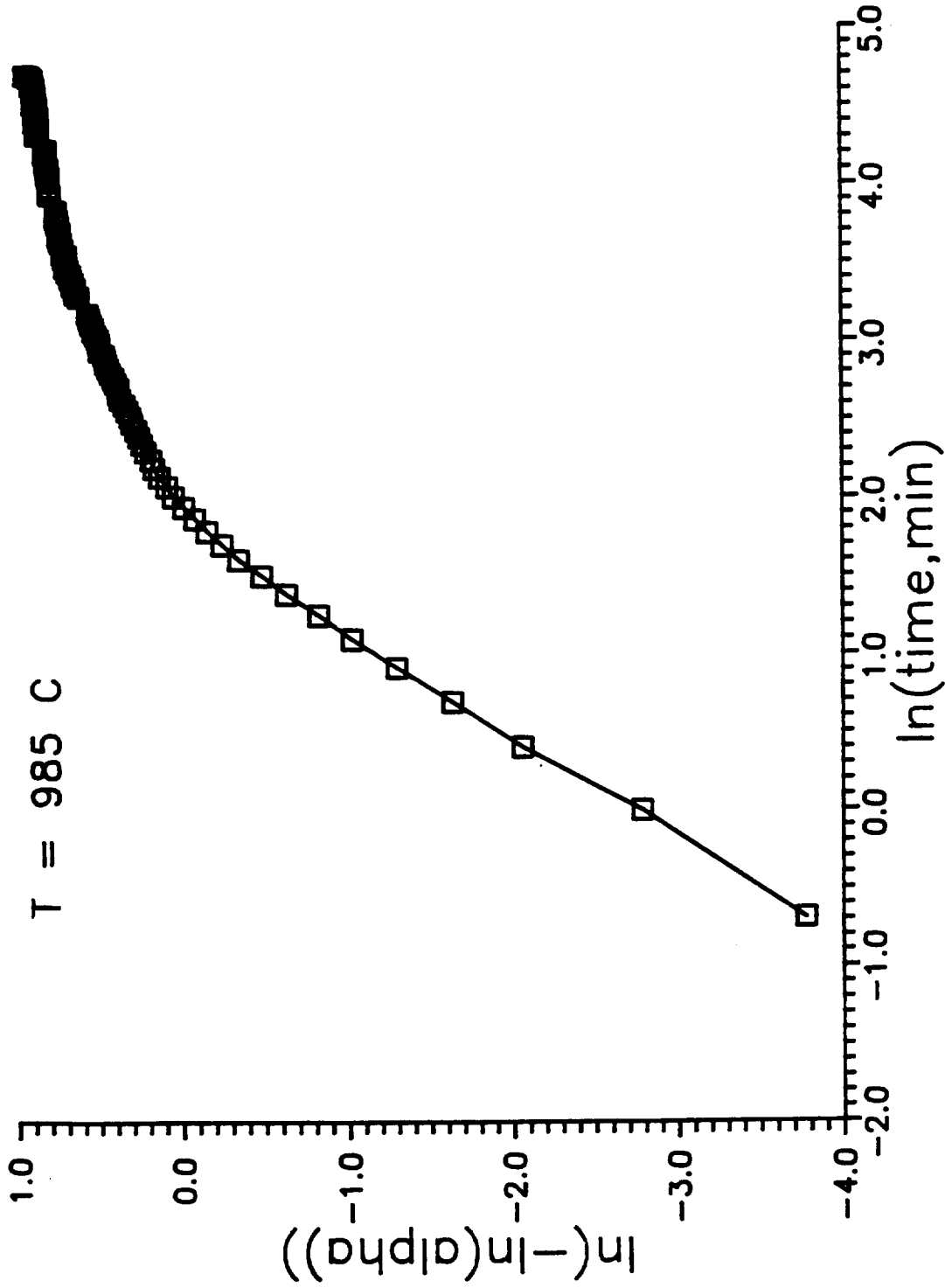


Fig. 7: Plot of isothermal dehydration data in terms of $\ln(-\ln\alpha)$ vs $\ln t$. The relationship should be linear if the dehydration is controlled by nucleation and growth law of the form $\alpha = \exp(-kt^n)$, where n is a constant.

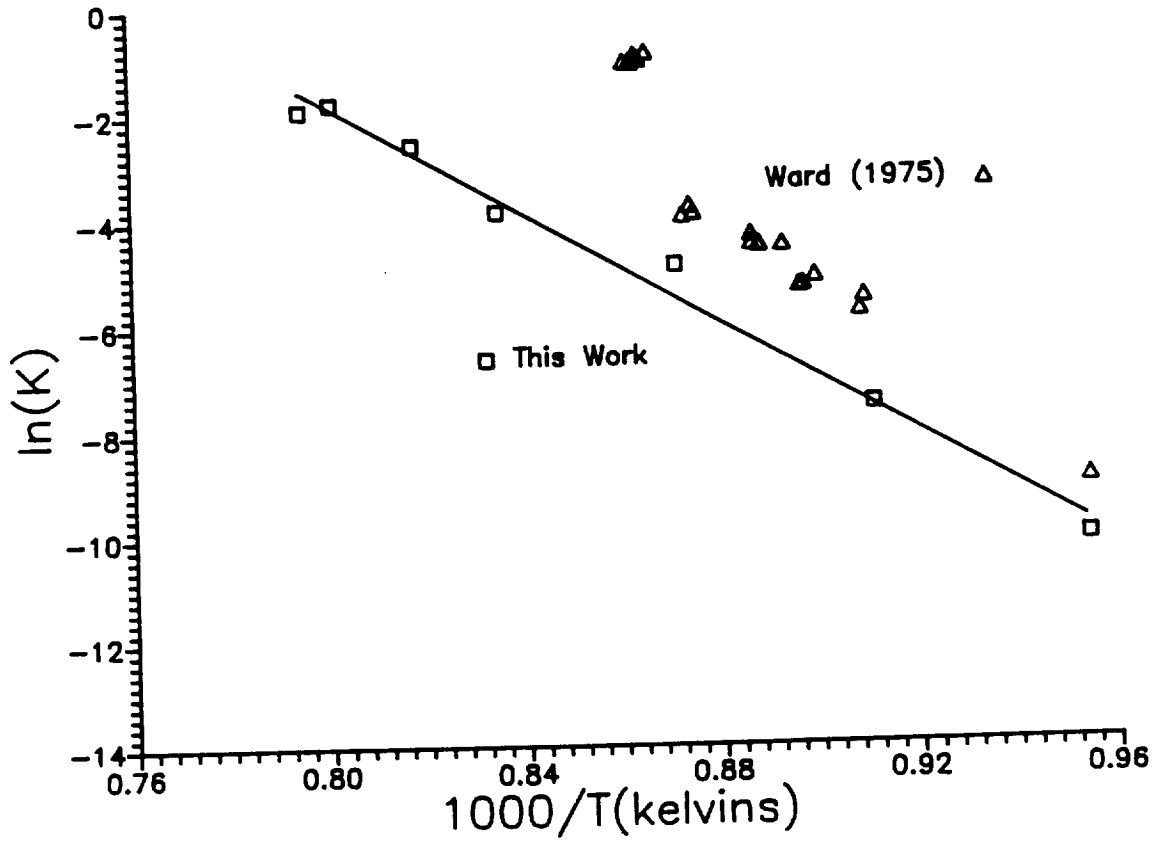


Fig. 8: Arrhenius relation of dehydration rate constant between 775 and 985°C at 1 bar. Squares represent the results of present study, whereas the triangles represent those of Ward (1975). In this work, the rate constant is obtained by fitting experimental data up to 50-60% dehydration (see text for discussion)

$$R_{net}(X) = \frac{1 - e^{m\Delta G(X)/RT}}{1 - e^{m\Delta G^*/RT}} \cdot R_{net}^* \quad (6.1)$$

$$-(A) \times R_{net}^* \quad (6.2)$$

where X stands for the mole fraction of H₂O in the vapor phase, and the superscript * denotes XH₂O = 1.

Work is currently under progress to identify the reaction controlling the dehydration of talc in our experiments. It does not seem to be the simple breakdown of talc to enstatite (MgSiO₃) plus quartz (SiO₂), as suggested in the work of Ward (1975). However, if we assume that the free energy change of the dehydration reaction of talc is comparable to that of the reaction



then we can approximately evaluate the quantity A in eqn. (6), which determines the 'thermodynamic effect' on the dehydration kinetics. The results of our calculation show that at any temperature of practical interest at which $\Delta G^* \ll 0$, the value of A deviates very little from unity as a result of dilution of H₂O in the vapor phase. Thus the thermodynamic effect on dehydration rate of talc is expected to be negligible for the practical purpose of volatile extraction. However, the additional volatile species may have a significant effect on the dehydration kinetics through a change of dehydration mechanism (e.g. Schramke et al., 1987). This problem can only be answered by careful experimental studies.

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II. PRODUCTION OF STRUCTURAL AND REFRACTORY METALS