Dehydration Kinetics and Thermochemistry of Selected Hydrous Phases, and Simulated Gas Release Pattern in Carbonaceous Chondrites

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Abstract

As part of our continued program of study on the volatile bearing phases and volatile resource potential of carbonaceous chondrite, we report results of our experimental studies on the dehydration kinetics of talc as a function of temperature and grain size (50 to 0.5 μm), equilibrium dehydration boundary of talc to 40 kbars, calorimetric study of enthalpy of formation of both natural and synthetic talc as a function of grain size, and preliminary results on the dehydration kinetics of epsomite. In addition, we have carried out theoretical calculation on the gas release pattern of Murchison meteorite, which is a C2(CM) carbonaceous chondrite.

The kinetic study of talc leads to a dehydration rate constant for 40-50 μm size fraction of $k = 3.23(10^4)\exp(-Q/RT)$ min^{-1} with the activation energy $Q = 376$ (± 20) kJ/mole. The dehydration rate was found to increase somewhat with decreasing grain size. The enthalpy of formation of talc from elements was measured to be - 5896(10) kJ/mol. There was no measurable effect of grain size on the enthalpy beyond the limits of precision of the calorimetric studies. Also the calorimetric enthalpy of both synthetic and natural talc was found to be essentially the same, within the precision of measurements, although the natural talc had a slightly larger field of stability in our phase equilibrium studies. The high pressure experimental data the dehydration equilibrium of talc (talc = enstatite + coesite + H_2O) is in strong disagreement with that calculated from the available thermochemical data, which were constrained to fit the low pressure experimental results. The calculated gas release pattern of Murchison meteorite were in reasonable agreement with that determined by stepwise heating in a gas chromatograph by Hashimoto et al. (1979).
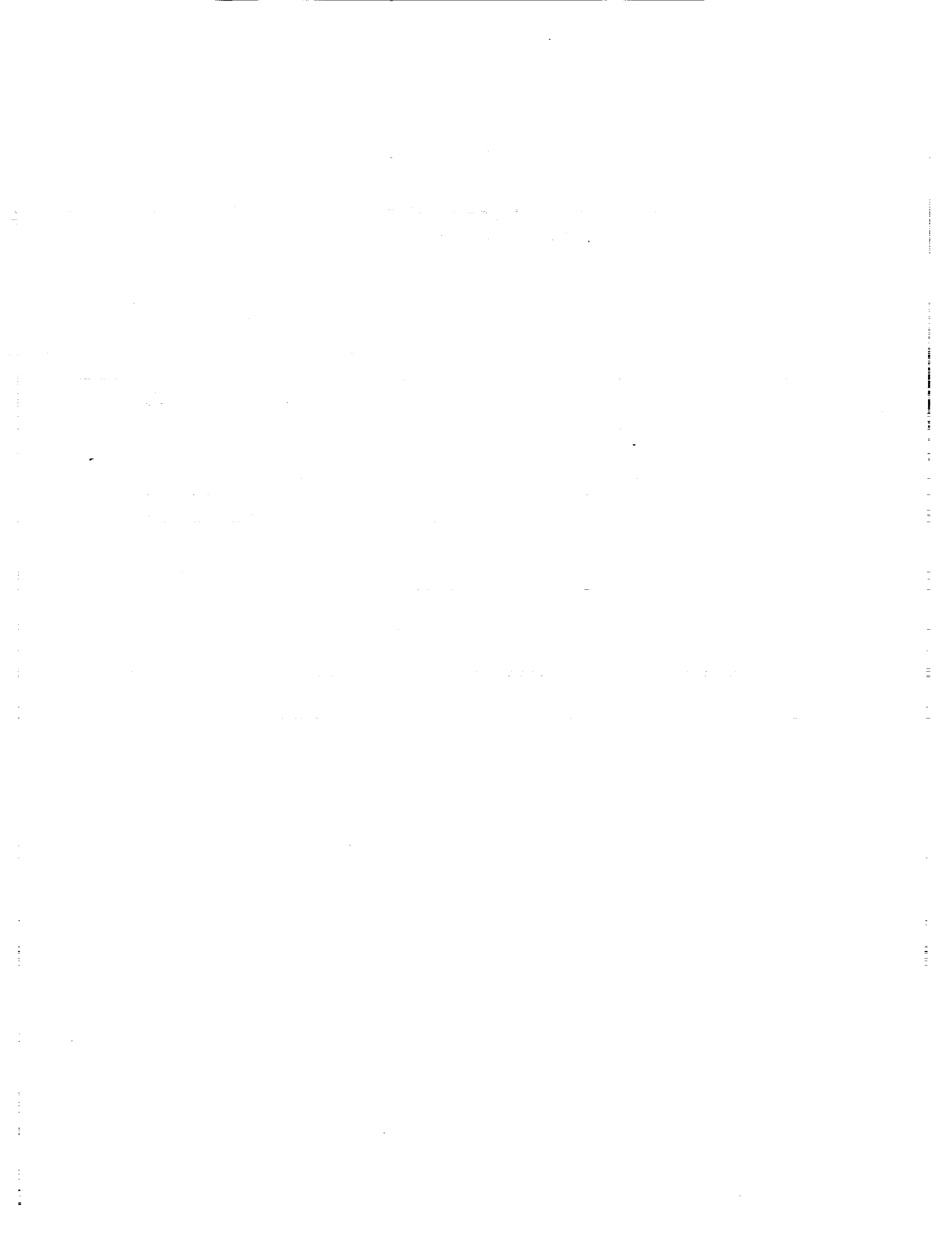
Introduction

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 the fundamental aspects concerning nature, abundance, and time scale of formation of volatile-bearing phases in the solar nebula, and the closely related practical problem of the feasibility of extraction of volatiles for fuels from carbonaceous chondrites. Some insight into the latter problem can be gained from the results of step-wise heating experiments of meteorite samples, and analyzing the released gas in an on-line mass spectrometer (e.g. Hashimoto et al., 1979). Our objective is to develop a more general and operationally much simpler approach in which the pattern of volatile release during controlled heating of a meteorite can be depicted into a computer terminal through numerical experiments if one feeds in the data on heating rate, range of temperature of interest and bulk composition of the sample. A preliminary report of this numerical experiment at 1 bar in the temperature range 400 -800°C has been published earlier (Ganguly and Saxena, 1989), in which it is assumed that the equilibrium volatile release is obtained at each heating step. The bulk composition chosen are those corresponding to the average compositions of Orgueil (C1) and Murchison (C2) meteorites. The results of volatile release pattern for Murchison are found to be broadly similar to those of step-wise heating experiments by Hashimoto et al. (1979).

Our on-going project involves determination of thermochemical properties and dehydration kinetics of minerals which are potential components of carbonaceous chondrites, refinement of the numerical experiments by incorporating these data. The latter part of the project has been carried out in collaboration with Professor Surendra Saxena (Brooklyn College, New York and University of Uppsala, Sweden).

The results obtained during the current funding period are reported below.

Dehydration Kinetics of Talc and Epsomite

A) Talc

In our last progress report, we had reported the results of dehydration kinetics of talc in the temperature range 775-985°C. These experiments were carried out at 1 bar pressure, on a 'coarse'

(40-50μ) grain size of natural talc. However, since reaction kinetics are known to depend on grain size (surface area), we have investigated the dehydration kinetics of fine grain separates (1.0 μ and <0.5 μ) of natural as well as synthetic talc (~1.0 μ). The process of separating small grain size fractions is very tedious, involving repeated cycles of spinning in an ultra-centrifuge with a small (<50 mg) mass yield. The thermogravimetric apparatus built in our laboratory requires at least a gram quantity of sample for dehydration kinetic experiments. Also, a maximum amount of 200 mg of talc can be synthesized at a time in laboratory. Because of these constraints, we have carried out the dehydration kinetic experiments on the synthetic and the fine grain separates of natural talc in a micro-thermogravimetric apparatus (SETARAM) in the laboratory of Professor A. Navrotsky, Princeton University. This instrument is capable of detecting weight changes in the nanogram level. In order to check the reliability and consistency of data obtained at the two laboratories, we repeated the dehydration rate measurement at 900°C on the coarse grain natural talc in TGM apparatus at Princeton. As shown in *Figure 1*, the results are in excellent agreement with those obtained in our laboratory.

Over the temperature range of 775-985 °C, the data on the dehydration kinetics of natural talc can be nicely fitted by a second order rate expression:

$$-d\alpha/dt = k\alpha^2, \tag{1.1}$$

or the equivalent integrated form:

$$1/\alpha = 1/\alpha_0 + kt \tag{1.2}$$

where α is the weight fraction of talc remaining at time t. The results at 950°C are illustrated in fig.2. The Arrhenian plot of the rate constant in the range 875-985 °C is shown in *Figure 3*. The least square regression of the data (for 40-50 μm size fraction) yields

$$k = 3.23(10^4)\exp(-Q/RT) \text{ min}^{-1} \tag{2}$$

where the activation energy Q = 376 ($\pm$20) kJ/mol, the error bar representing 1σ uncertainty.

The rate of dehydration for the smaller grain sizes are found to be faster than the coarser fractions (*Figure 4*). However, there is no significant difference in rates between the 1.0μ and <0.5μ size fractions of natural talc. This may be the result of clustering of the small grains due to high electrostatic surface charging. It is also possible that the difference between the dehydration rates of talc for the above size fractions is too small to be detectible. It may, however, be noted that in

contrast to these data, Gregg and Razouk (1949) found a maximum around 150- 180 μ size fraction in the rate of dehydration of Brucite as function of grain size.

Figure 5 shows the difference in dehydration rates between the natural and synthetic talcs, indicating a difference in their energetic properties. This is also reflected in our phase equilibrium studies on the dehydration of talc, which showed the natural talc to have a slightly higher field of stability than synthetic talc (see section on Equilibrium Dehydration of Talc).

In order to quantitatively specify the thermochemical property of both natural and synthetic talc along with its dependence on grain size, we undertook a study (in collaboration with Professor A. Navrotsky and Dr. P.Burnley of Princeton University) of the heat of formation of talc by drop solution calorimetry. Unfortunately, the experimental uncertainty was too large to resolve the small difference in the energetic properties of these materials. The heat of solution of three different size fractions, $>1\mu$, 1.0μ and $<0.5\mu$, as well as of the synthetic talc were found to be essentially the same (502 $\pm$10 Kj/mol). Using previously reported solution enthalpies for quartz, periclase and brucite, we derived a heat of formation from the elements for talc ΔH_f = -5896 ($\pm$10) kJ/mol. This is in close agreement with those obtained by evaluation of phase equilibria data. This work has been submitted as a paper for the Fall Meeting of the American Geophysical Union (AGU), San Francisco, Dec. 7-11, 1992 (See Appendix I).

X-ray powder diffraction studies of the products of dehydration kinetic experiments of talc did not show any x-ray reflection of the products of dehydration, which is likely to be result of their extremely fine grain size. However, in order to formulate the kinetic rate law and mechanism, it is essential to know the products of a reaction. We have, thus, conducted Transmission Electron Microscopy (TEM) studies (in collaboration with Dr. S. Supapan, Material Science Department, University of Arizona) of the starting materials and the dehydration run products. The electron diffraction pattern suggests the breakdown products of talc to be enstatite and quartz. Further work is in progress to characterize these materials unambiguously.

Equilibrium Dehydration of Talc at High Pressure

In order to test the internal consistency of the thermochemical properties of talc and its dehydration products, including water, we have carried out precise experimental determination of the equilibrium boundary of talc (Talc = Enstatite + Quartz(Coesite) + H_2O) upto 40 kbar pressure (this part of the project was only partially supported by the NASA grant). The synthetic talc was found to have a

slightly smaller thermal stability than the natural talc, indicating a higher free energy of the synthetic talc compared to the natural talc. More significantly, the experimentally determined equilibrium is in strong disagreement with that calculated from the available thermodynamic data indicating that the thermodynamic data of one or more phases is in need for significant revision. The results of this study have been submitted as a paper for AGU Fall Meeting, San Francisco, Dec. 7-11, 1992 (see Appendix II).

B) Epsomite

The earlier work of Ganguly & Saxena (1989) on the calculation of modal abundance of minerals in C2 bulk composition has been expanded by incorporating the thermochemical properties of minerals that have been available recently. The major hydrous mineral phases predicted by these calculations are epsomite, talc and brucite. Since the equilibrium dehydration temperature of epsomite at 1 bar is significantly lower (<160°C) than that of talc (375°C), the investigation of epsomite as a possible source of easily extractable volatile is needed.

Figure 6 shows α vs time for epsomite dehydration at 160°C. This work was carried out by Rajib Ganguly as part of his undergraduate chemistry honors project at the University of Arizona (Chem 105 H) with the P.I. as his mentor. There are three other known hydrates of magnesium sulfate in addition to brucite ($MgSO_4.Nh_2O$, $n=7$ for brucite, $n=6$, 4 or 1 for hexa-, tetra- and mono hydrate respectively). It is necessary to determine the phase equilibria in this system before one can determine the dehydration kinetics of epsomite. Work is currently under progress to constrain the thermochemical properties of these phases.

Calculation of Volatile Release Pattern of Murchison Meteorite

Using our internally consistent thermochemical database, we have performed, in collaboration with Professor Surendra K. Saxena of the Uppsala University, Sweden, theoretical calculations on the gas release pattern of Murchison meteorite, which is a C2(CM) carbonaceous chondrite. The calculation was performed by the minimization of Gibbs free energy, constrained to the bulk composition of this meteorite. The results are illustrated in Figure 7, and compared with those of step-wise heating of a sample of Murchison meteorite and gas chromatographic analysis of the released volatiles by Hashimoto et al. (1979). There is good agreement between the overall pattern, except that in the experimental studies, the gases were released at somewhat higher temperatures than those calculated from the minimization of Gibbs free energy. This may be due to kinetic problem (the extent of overstepping depends on the rate of heating). In contrast to the theoretical calculation, however, the release of water did not begin until 500K in the experimental studies. This is definitely due to the fact that the sample of meteorite was washed in water before heating, which resulted in the loss of epsomite which is a water soluble hydrous phase with very low dehydration temperature.

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Appendix I

Heat of Formation of Synthetic and Natural Talc by Drop Solution Calorimetry: a Test of a New Technique

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High Temperature solution calorimetry represents one of the few tools we have to directly measure the energetics of synthetic high pressure phases. Due to the instability of many of these compounds at calorimeter temperature, drop solution calorimetry is the preferred technique. Samples are either pressed into pellets or enclosed in platinum or solvent glass capsules and dropped into the calorimeter at room temperature. Synthetic high pressure phases with a Mg:Si ratio > 1 present additional challenges. Pellets with a high Mg content tend not to dissolve rapidly in the solvent, leading to excessive experimental duration and unacceptable levels of uncertainty. Similarly, if the heat effect due to the capsule is much larger than that of the sample the quality of the measurement is degraded. To overcome these problems, we have developed a new ultra light (~ 10 mg) quartz glass capsule. These capsules make only a small contribution to the heat effect measured, dissolving rapidly and exposing the powder within to solvent from all sides. We demonstrate the feasibility of this technique with talc.

We measured the heat of drop solution in molten lead borate of natural samples of talc $(Mg_{0.99}Fe_{0.01})3Si_4O_{10}(OH)_2$ using both pellets and ultra light quartz glass capsules. The measured enthalpy of 502 (8) kJ/mol using quartz glass capsules compares well with the value of 495 (5) kJ/mol using pellets; thus demonstrating that this will be a useful technique for size limited samples. We also investigated the effect of particle size using grain size sorted samples of natural talc. Enthalpies for >1 μm, 1 μm and <0.5 μm natural talc samples as well as the synthetic talc were identical to within the limits of the uncertainty (~10 kJ/mol). Using previously reported solution enthalpies for quartz, periclase and brucite, we derive a heat of formation from the elements at 295 K for talc of ΔH_f = -5896 (10) kJ/mol. This value is in close agreement with those obtained by evaluation of phase equilibria data (cf. Hemingway, 1991).

Appendix II

High Pressure Phase Equilibria in the System MgO-SiO$_2$-H$_2$O: Quartz-Coesite Revisited and Dehydration of Talc

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We have investigated the quartz-coesite transition between 500 - 1100°C and the dehydration equilibrium talc = 3 enstatite + quartz/coesite + H$_2$O up to 40 kb. The P-T slope of the quartz-coesite equilibrium is $\approx$ 7 bar/°C, which is in essential agreement with that determined by Bohlen and Boettcher (1982)[1], but disagrees with that of Mirwald and Massonne (1975)[2]. However, the position of the equilibrium is about 1.2 -1.7 kb higher than that determined by Bohlen and Boettcher. All experiments were carried out in Piston-cylinder apparatus with 0.5 or 0.75" inner diameter carbide cores and pressure cells with CsCl outer bushing. The friction characteristic of the pressure medium was determined by continuous (computer) monitoring of the piston-displacement as a function of time at a fixed nominal pressure and analysis of hystereses loops of nominal pressure vs. piston displacement at several run temperatures. Work is in progress to measure melting temperature by in situ DTA to further check the friction behavior of the pressure cell.

The P-T slope of the dehydration equilibrium of talc changes sign ~ 30 kb, which is in sharp contrast to the prediction from the available thermodynamic properties of the phases. The latter leads to a negative dP/dT slope ~ 10-15 kb. The discrepancy between the measured and predicted equilibrium temperatures at 40 kb is at least 120°C. Work is currently in progress to identify the problem with the thermodynamic data. Our data also extend the field of stability of the 10 Å phase to at least 820°C at 38 kbars.

1) *J. Geophys. Res., 87*, 7073-7078
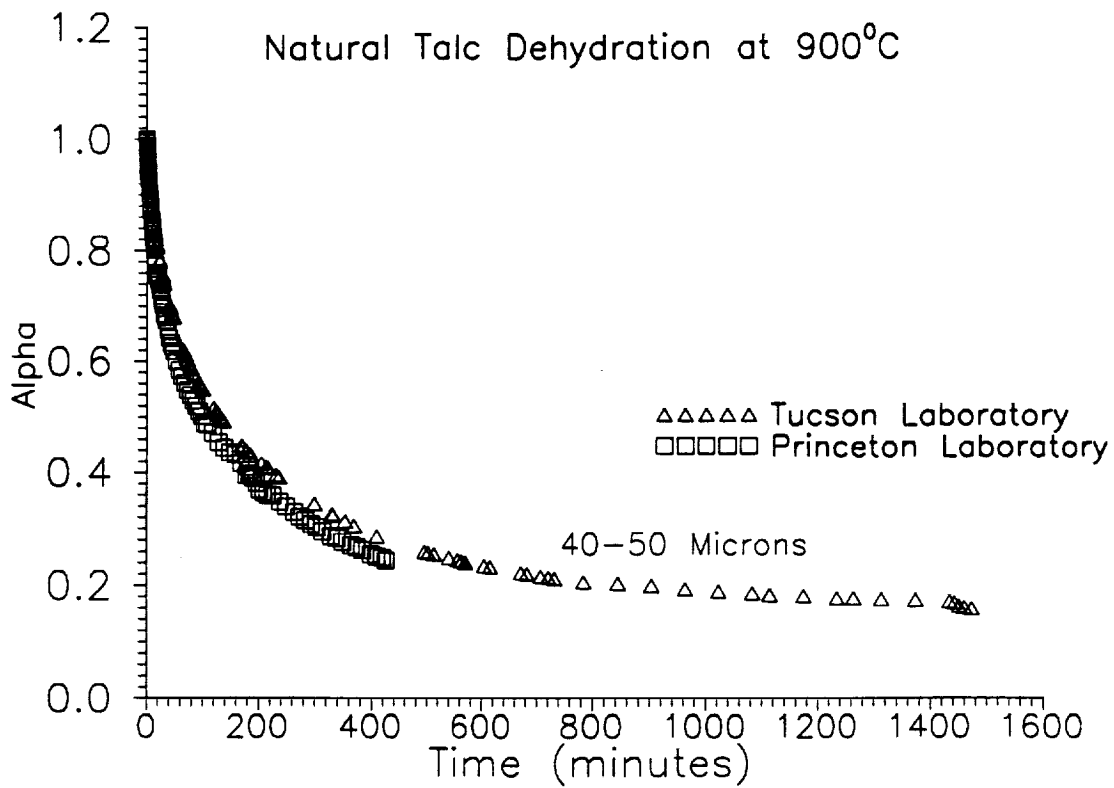2) *J. Geophys. Res., 85*, 6983-6990

Fig.1: Comparison of dehydration rate measurement of natural talc in our laboratory (Tucson Laboratory) with that measured in the SETARAM micro-thermogravimetric apparatus in Princeton.
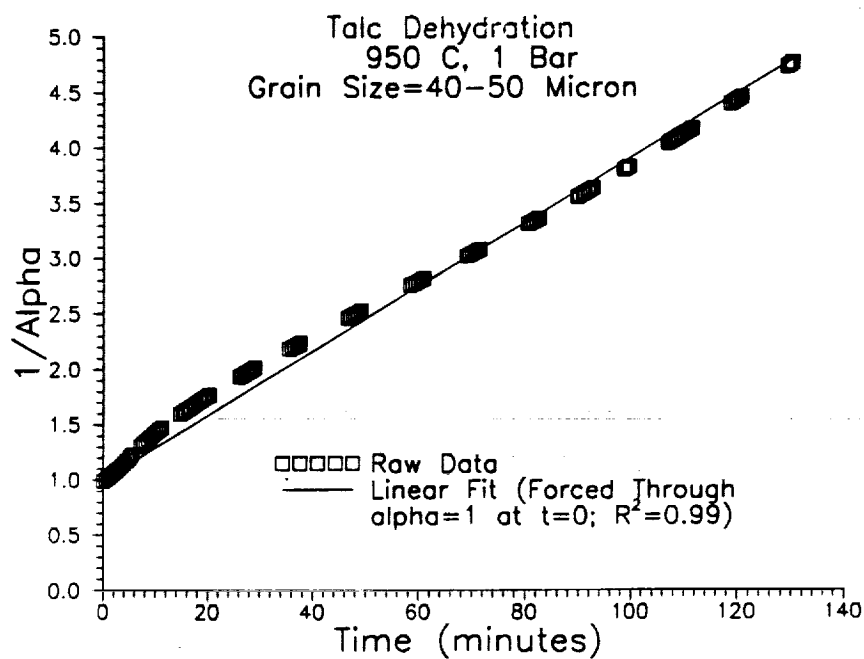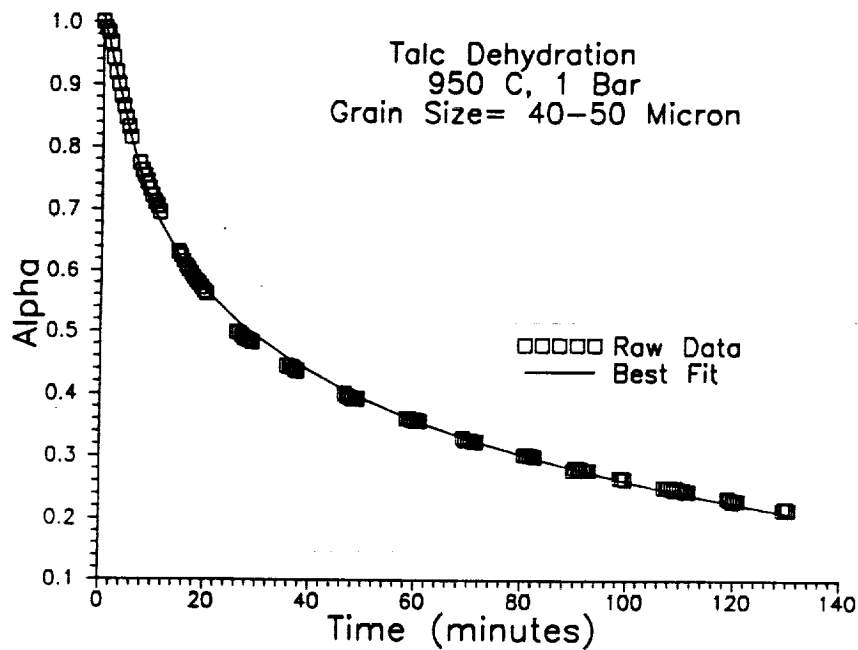
Fig.2: (a) Plot of isothermal dehydration of talc at 950°C, 1 bar. Alpha is the weight fraction of talc remaining at time t. (b) Illustration of the data in terms of $1/\alpha$ vs time. The linear dependence of $1/\alpha$ versus time indicates that the dehydration of talc follows a second order rate law (see text).
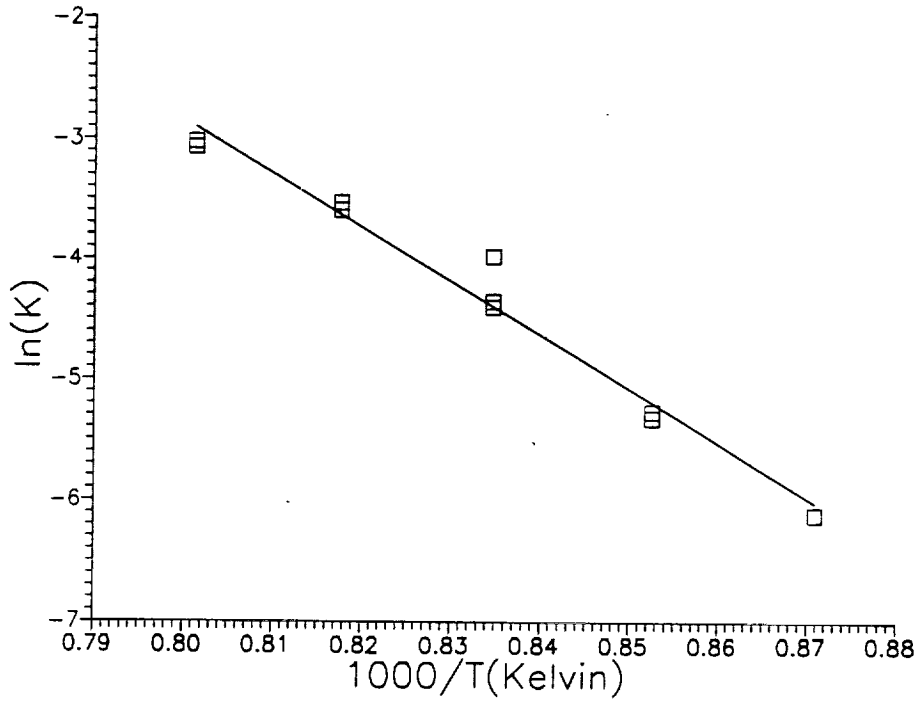
Fig.3: Arrhenian relation of dehydration rate (for 40-50 μm natural talc) constant between 875 and 975°C at 1 bar. The activation energy is 376 kJ/mol.
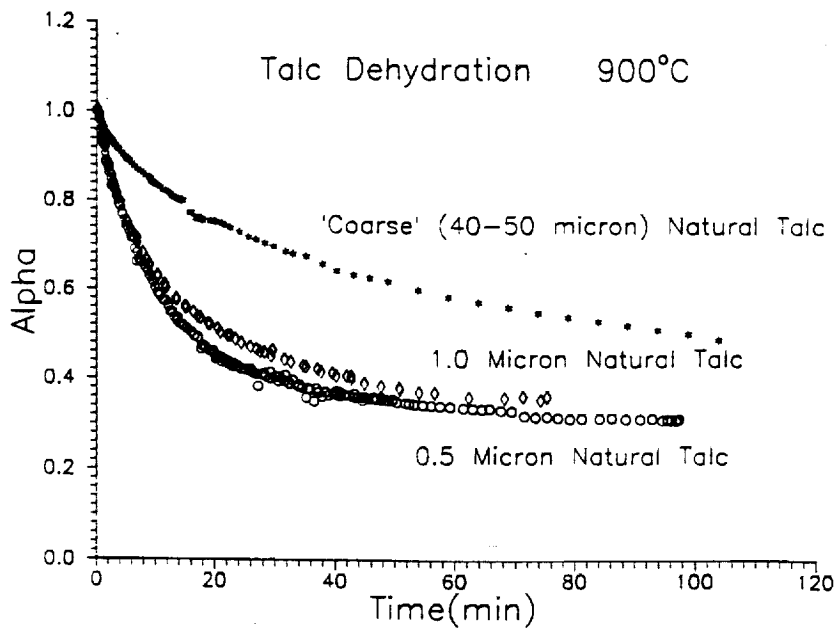

Fig.4: Plot of isothermal dehydration of talc at 900°C as a function of grain size. The smaller grain size fractions show a faster rate of dehydration than the 'coarser' talc. However there is no significant difference in the dehydration rate between the 1.0 μm and <0.5μm grain sizes.
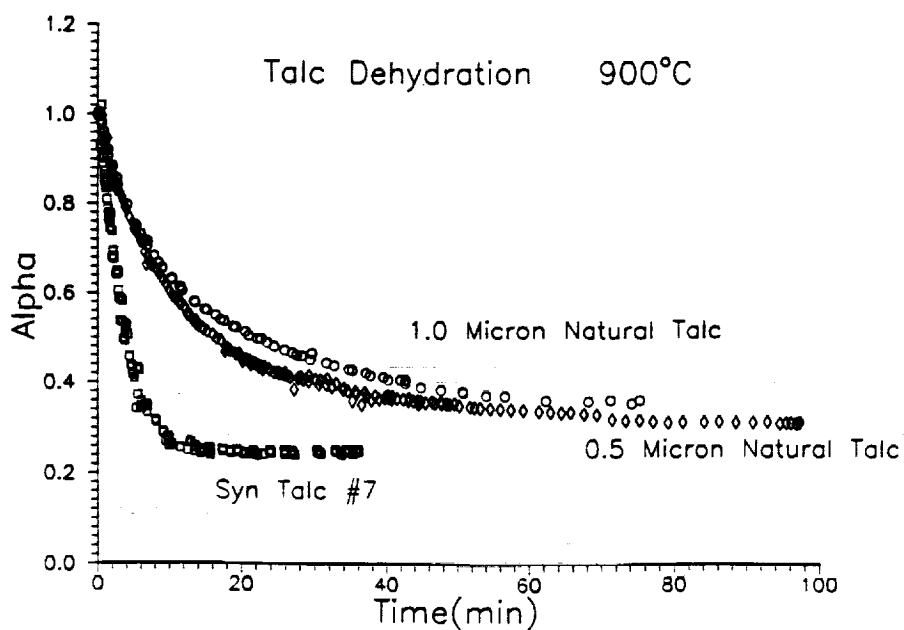
Talc Dehydration   900°C

Fig.5: Difference in rate of dehydration of natural versus synthetic talc. The grain size of the synthetic talc was ~1.0 µm.
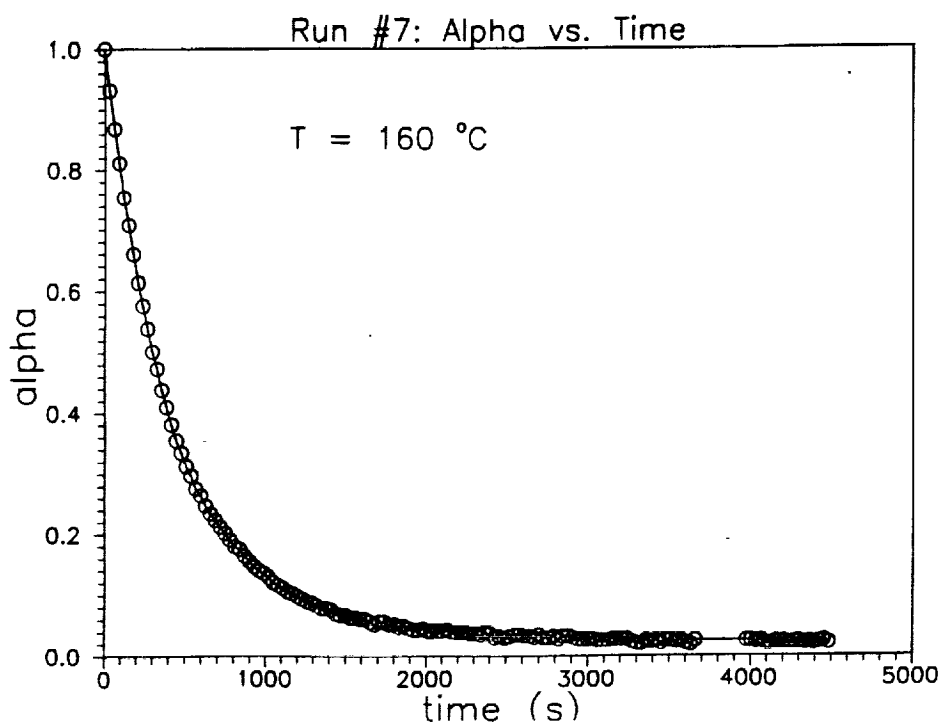
Run #7: Alpha vs. Time

Fig.6: Dehydration of Epsomite at 160°C, 1 bar, as determined by R. Ganguly, as part of an undergraduate Chemistry Honors project.
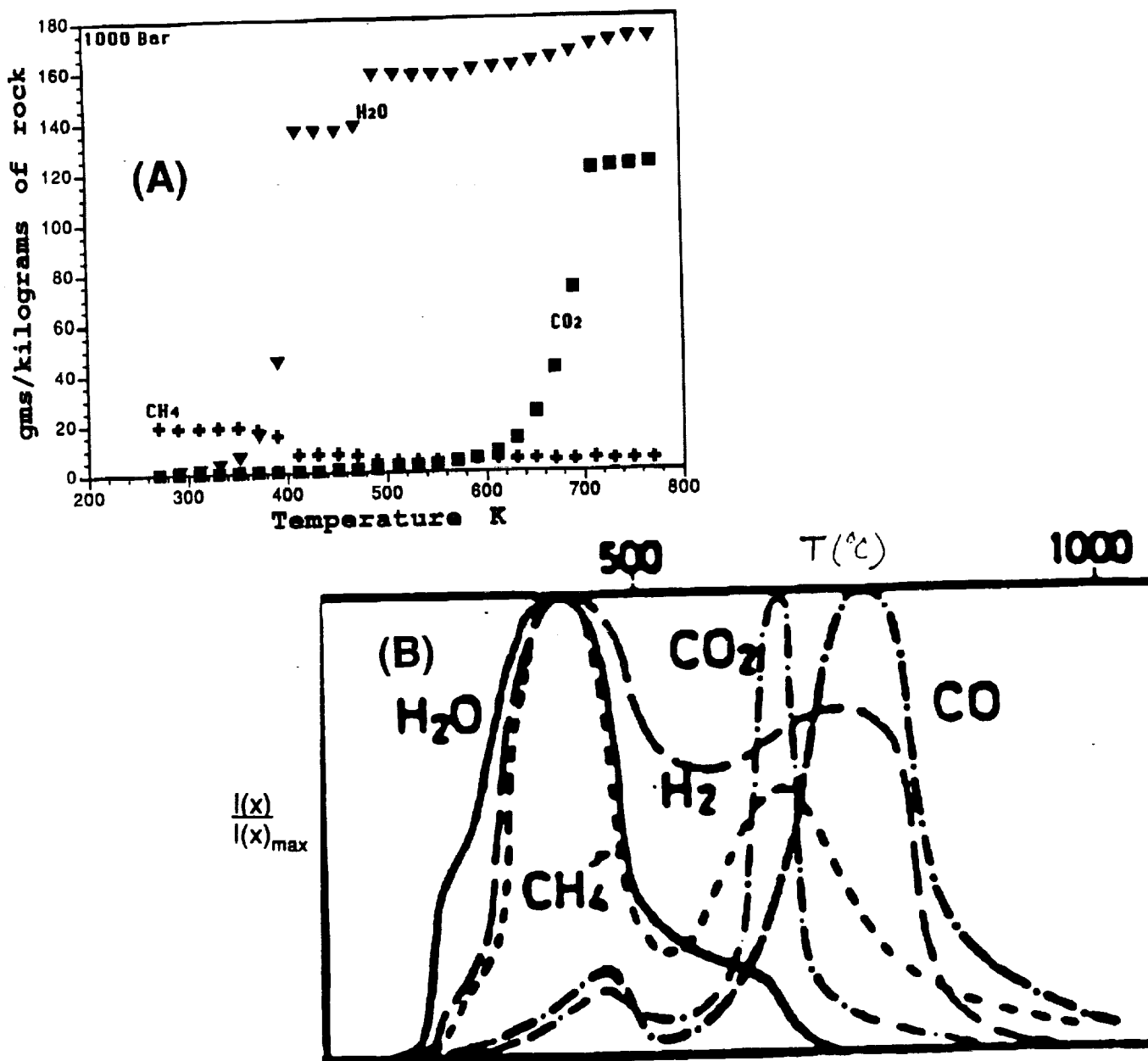
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Fig.7: Comparison of calculated (A: this work) and experimental (B: Hashimoto et al, 1979) gas release pattern of Murchison meteorite. $I(x)/I(x)_{max}$ refers to intensity normalized to the maximum observed intensity of the spike for a specific volatile species in a gas chromatograph. Note that the temperature scales for A and B are degree Celcius and degree Kelvin, respectively. The figures were set to match the temperatures (i.e. 773 K in A matches with 500°C in B).