Thermochimica Acta, 214 (1993) 59–66
Elsevier Science Publishers B.V., Amsterdam

Reversible dehydration in Sinya sepiolite

S.Berglund

Chemistry Department, University of Dar es Salaam, Tanzania
and (present address)
University College of Sundsvall-Harnosand,
P.O. Box 860, S-851 24 SUNDSVALL, Sweden

Abstract

Water loss in Sinya sepiolite (meerschaum) was studied in the range 300-1200 K, primarily by TG. Fully reversible dehydration was found up to 500 K; several overlapping weight loss processes were seen but not resolved. Above 590 K, there were three further weight loss steps, partly or wholly irreversible.

Dehydration was studied in vacuum at 303, 313, 323 and 333 K. After a rapid initial phase, the kinetics were first order, rate constant $k_{dehyd} = 5.62*10^8 \exp(-57.8*10^3/8.314T)$ min^{-1}.

Rehydration at p_{H2O}= 2.64 kPa was also studied. Over a major part of the composition range, the kinetics were first order with respect to the sample composition, rate constant $k_{hyd} = 1.87*10^4 \exp(-35.9*10^3/8.314T)$ min^{-1}.

1. INTRODUCTION

Sepiolite is a layer silicate; a rock form is also known as "meerschaum". It is essentially a hydrated magnesium silicate. magnesium ions periodically link neighbouring "infinite" silicate layers, creating sandwich-like ribbons. Hydroxyl and (at the ribbon edges) "structural" water is added as needed for octahedral coordination around the magnesium; the ribbons surround channels which may contain loosely bound "zeolitic" water [1, 2]. Zeolitic water is introduced by monolayer adsorption followed by capillary condensation [3]; two crystallographically non-equivalent types of structural water have been distinguished [4, 5]. Apart from the water content, the composition varies mostly because of substitution of magnesium with other cations. The structure makes sepiolite a useful adsorbent, catalyst and catalyst carrier.

Commercially exploitable sepiolite deposits are not common. One of the most extensive is in Tanzania, at Sinya, 2°43'S and 37°03'E, that is, to the northwest of Mount Kilimanjaro, it comprises both meerschaum and sepiolitic clay [6]. The Sinya deposit has been mined for meerschaum for handicraft objects but is only a potential source of technical grade sepiolite. The details of the adsorption and desorption behaviour of Sinya sepiolite are therefore of some practical interest, and in particular, the kinetics of reversible processes

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This paper was presented at the 13th Nordic Symposium on Thermal Analysis and Calorimetry, Stockholm, Sweden, 9–11 June 1992

Sepiolite loses water on heating; the total weight loss is of the order of 20%, corresponding to total loss of hydrogen in the form of water. In air at atmospheric pressure, water is lost in three main steps [7-8], the first below 523 K, the second at 523-923 K (in two sub-steps) and the third at 1023-1123 K. Infrared observations [5, 9-14] have revealed a number of distinct types of OH groups; on this basis, the main steps have been interpreted as loss of surface adsorbed and zeolitic water, structural water, and hydroxyl, respectively

Loss of structural water causes channel collapse, with drastic loss of surface area [8, 15-16]. Complete dehydration irreversibly transforms sepiolite to enstatite.

In a temperature programmed desorption study, the first dehydration step kinetics were found to be first order [17]. Various types of kinetics have been reported for the following steps [12, 17-18]. The first two dehydration steps are generally considered reversible, wholly or in part, but sepiolite rehydration kinetics have not been studied.

2. EXPERIMENTAL

Sinya meerschaum was provided by the Geology Department of the University of Dar es Salaam (sample no. MP464)· a massive, whitish piece, with no visible inhomogeneity.

Electron microscopy was performed using a JEOL U-3 instrument with a Link Systems 360-II energy dispersive X-ray spectrometer (EDS). X-ray powder diffraction patterns were obtained by means of a 40.16 mm Guinier-Hagg camera, using monochromatized 0.154060 nm radiation. Infrared spectrometry was done on Nujol mulls using a Pye Unicam SP300 instrument.

Thermogravimetry was done on 0.1 g samples using a Linseis L81 thermobalance. Non-isothermal TG-DTA was carried out in flowing air saturated with water at 295K (water vapour partial pressure 2.64 kPa, referred to as "moist air" below). For isothermal observations, the thermobalance was equipped with an adapter which permitted alternate exposure to vacuum and the vapour pressure of a small quantity of water maintained at 295 K. Rehydration/dehydration curves were obtained at 303, 313, 323, and 333 K.

3. PRELIMINARY CHARACTERIZATION

The x-ray powder diffraction pattern of the raw sepiolite was diffuse. A sample heated over night in air at 393 K gave a more distinct version of the same pattern, which was in agreement with previous reports [12]. The observed IR absorption bands agreed with previously reported sepiolite IR data [19]

At 10000x magnification, the sample was seen to consist of randomly packed fibres. (This was the appearance of the sample in vacuum, which may well be relevant in the present case.) Apart from major magnesium and silicon peaks, EDS showed the presence of aluminium (a few % by weight of the magnesium), sulphur and chlorine (both less than 0.1 %), potassium and calcium (both about 0.1 %) and iron (less than 0.05 %).

It was concluded that the Sinya sample was a well-crystallized sepiolite, with a structure and morphology as previously reported, and a low impurity level.

4. RESULTS AND DISCUSSION - THERMOANALYTICAL STUDIES

4.1. Basic thermal behaviour

In preliminary TG observations, no difference could be seen between data obtained for massive (cores, 5 mm diameter) and powdered samples. Therefore, all subsequent TG work was done on powder obtained by filing.

TG and DTG curves for raw sepiolite are given in Figure 1. The general pattern was in agreement with previous observations [7, 8]. However, DTG at low heating rates (Figure 2) revealed fine structure in the range 295 - 410 K, where only a single weight loss step has previously been reported. Evidently, water was desorbed from more than two types of site. In a kinetic context, inter-site water exchange rates may be important.

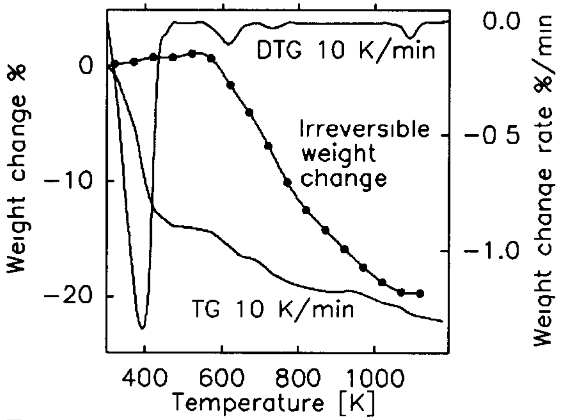

Figure 1.

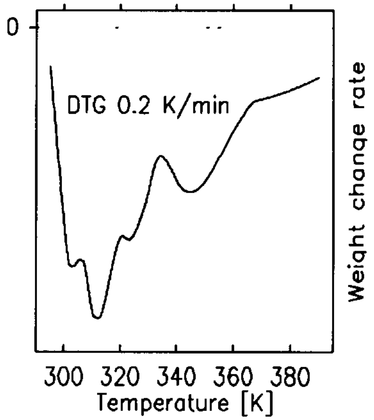

Figure 2.

4.2. Rehydration capacity

Raw samples were heated in moist air from 295 K to various temperatures, equilibrated, then re-equilibrated in moist air at 295 K. The results are given in Table 1 and Figure 1.

Samples heated to less than 570 K gained more weight than they had lost. Dehydration in vacuum caused even greater rehydration capacity enhancement: at 320 K, the ratio of weight gain on rehydration to previous weight loss in vacuum was 1.10. Rehydration capacity thus gained was retained in further loss/gain cycles without further change. Possibly, the water vapour evolved caused mechanical breakup of the fibre aggregates, increasing the adsorption surface. The sudden application of a vacuum would be expected

Table 1
Weight lost on heating to various temperatures in moist air; weight regained on cooling to room temperature (% of original sample weight)

T [K]	Loss	Gain	Irreversible change
320	6.3	6.5	0.2
370	13.7	14.1	0.4
420	14.0	14.6	0.6
470	14.1	14.8	0.7
520	14.8	15.9	1.1
570	17.0	17.1	0.1
620	17.2	17.0	-0.2
670	17.5	13.4	-4.1
720	17.8	10.0	-7.8
770	18.4	9.3	-9.1
820	19.1	6.0	-13.1
870	19.7	5.0	-14.7
920	20.0	4.5	-15.5
970	20.3	3.1	-17.2
1020	20.8	2.0	-18.8
1070	21.6	2.0	-19.4
1120	21.6	1.9	-19.7

to be more efficient in this respect than gradual heating

Above 550 K, reversibility declined, presumably owing to structural degradation. As will be seen from Figure 1, the onset of the decline appeared to be simultaneous with the first structural water loss. However, the decline then continued with no obvious correlation with further weight change.

4.3. TG-DTG behaviour of raw and rehydrated samples

TG-DTG data for raw and rehydrated samples displayed the same main features. However, those for raw samples had an irreproducible, "noisy" component particularly apparent in DTG, while curves for material rehydrated after prior heating to 393 K were very reproducible, retaining a fine structure. Therefore, the rest of the TG study was carried out on rehydrated material.

This also had other advantages Sepiolite, unless stored under strictly controlled conditions, contains an ill-defined quantity of surface adsorbed and zeolitic water. On the other hand, dehydration in moist air at 393 K quickly produces a well-defined material in which most of this type of water has been lost whereas structural water and hydroxyl are unaffected. All weight changes were therefore described in terms a "relative excess weight" ε, defined as the difference between the actual weight of the sample and its equilibrium weight in moist air at 393 K, divided by the latter weight.

4.4. Isothermal TG/DTG - rehydration and dehydration

Samples were exposed to vacuum at various temperatures until constant weight was reached. Water vapour (p_{H_2O} = 2.64 kPa) was then introduced. The rehydration rate data thus obtained are given in Figure 3 and Table 2.

The samples were then again exposed to vacuum. The dehydration rate data are given in Figure 4 and Table 3. They cover a smaller excess weight range than the rehydration data. The initial weight loss was very rapid; this was possibly due to loss of capillary condensation water [3]. Initial desorptive cooling made it difficult to obtain rate data at the desired temperatures at high excess weights: at 303 K, the end of the rapid initial phase can be seen.

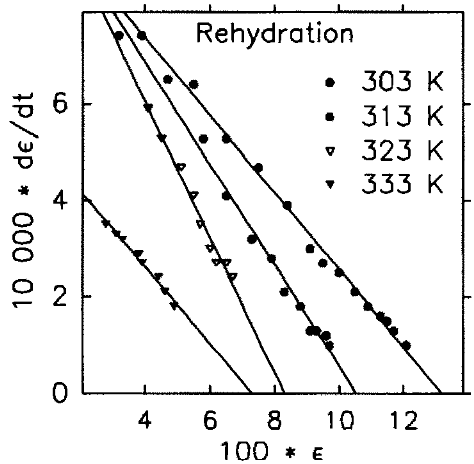

Figure 3.

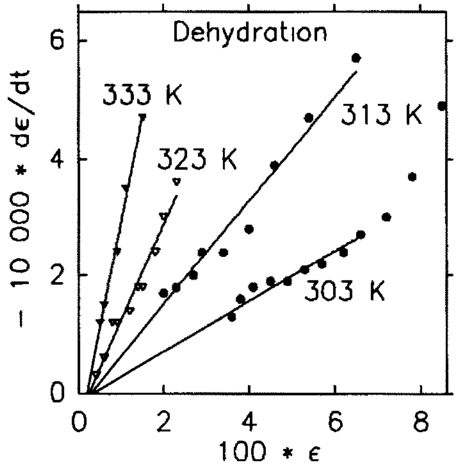

Figure 4.

In addition to simultaneous desorption from and adsorption onto a variety of sites, there was presumably also inter-site exchange. A strict solid-state kinetic evaluation is unrealistic in this case: even assuming some particular form of rate equation, an unrealistic number of parameters would have to be fitted.

However, Figures 3 and 4 give the distinct impression that the actual data do not justify fitting anything but straight rate versus composition lines; extensive computer modelling using a very general curve-fitting program supported this view. It does make sense to assume desorption to be first order with respect to filled adsorption sites and adsorption with respect to vacant ones. (Positive proof of assumptions of this type do, of course, require data collection on a different order of scale with respect to both quality and quantity.)

First order rate constants fitted to the rate data are given in Table 4. The observed rehydration rates were net rates, since there will have been simultaneous dehydration. True rehydration rate constants obtained by adding the corresponding dehydration rate constants are also given in Table 4.

Table 2
Net rate of rehydration in water vapour at 2 64 kPa, at various temperatures. Relative excess weight and rate of change of the same (time unit minutes)

303 K		313 K		333 K		323 K	
100ε	$10^4 d\varepsilon/dt$	100ε	$10^4 d\varepsilon/dt$	100ε	$10^4 d\varepsilon/dt$	100ε	$10^4 d\varepsilon/dt$
3.9	7.4	3.2	7.4	4 1	5.9	2.8	3 5
5.5	6.4	4 7	6 5	4.5	5.3	3.1	3.3
6 5	5.3	5.8	5 3	5.1	4 7	3.3	3.2
7 5	4.7	6.5	4.1	5.5	4.1	3.8	2.9
8.4	3.9	7.3	3.2	5.7	3.5	3.9	2 7
9.1	3.0	7.9	2 8	6 0	3.0	4 4	2 4
9.5	2.7	8.3	2.1	6.2	2.7	4.6	2.1
10.0	2.5	8.8	1.8	6.5	2.7	4.9	1.8
10.5	2 1	9.1	1.3	6.7	2.4		
10.9	1 8	9.3	1 3				
11 3	1.6	9.6	1.2				
11 5	1.5	9 7	1 0				
11.7	1.3						
12.1	1.0						

Table 3
Rate of dehydration in vacuum at various temperatures
Relative excess weight and rate of change of the same (time unit minutes)

303 K		313 K		323 K		333 K	
100ε	$10^4 d\varepsilon/dt$	100ε	$10^4 d\varepsilon/dt$	100ε	$10^4 d\varepsilon/dt$	100ε	$10^4 d\varepsilon/dt$
8.5	-4.9	6.5	-5.7	2.3	-3 6	1.5	-4.7
7.8	-3.7	5.4	-4.7	2.0	-3.0	1.1	-3.5
7.2	-3 0	4.6	-3 9	1.8	-2.4	0.9	-2 4
6.6	-2.7	4.0	-2.8	1.5	-1.8	0.6	-1 5
6.2	-2.4	3.4	-2.4	1.4	-1.8	0 5	-1 2
5.7	-2.2	2.9	-2 4	1.2	-1.4		
5.3	-2.1	2 7	-2 0	0.9	-1 2		
4.9	-1.9	2.3	-1.8	0.8	-1.2		
4.5	-1.9	2.0	-1.7	0.6	-0.6		
4.1	-1.8			0.4	-0.3		
3.8	-1.6						
3.6	-1.3						

Table 4
Dehydration and rehydration rate constants at various temperatures (unit 10^{-2} min^{-1}; 95% confidence ranges)

T [K]	k_{dehyd}	$k_{hyd} - k_{dehyd}$	k_{hyd}
303	0.43 ± 0.02	0.80 ± 0.04	1.23 ± 0.04
313	0.88 ± 0.05	1.05 ± 0.08	1.93 ± 0.09
323	1.63 ± 0.11	1.41 ± 0.19	3.0 ± 0.2
333	3.6 ± 0.2	0.80 ± 0 11	4.4 ± 0.2

The fitted Arrhenius lines (Figure 5) can be expressed as (unit min^{-1})

$$k_{dehyd} = 5.62*10^8 exp(-57.8*10^3/8.314T)$$

$$k_{hyd} = 1.87*10^4 exp(-35.9*10^3/8.314T)$$

For dehydration, an activation energy of "about 9 kcal/mol" has been reported [17]; this is in poor agreement with the present result but may well hold for the rapid initial desorption phase.

The kinetic conclusions reached above presumably apply in the composition ranges where the net adsorption rate behaves linearly: the true desorption and adsorption rates are unlikely to have cancelling nonlinearities.

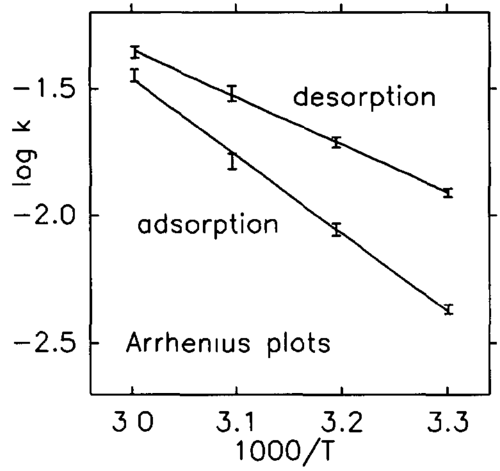

Figure 5

5. ACKNOWLEDGEMENTS

At the University of Dar es Salaam, the experimental TG and IR work was carried out by Mr. S.I.C M Mattu, with practical assistance from Mr. J.N. Nyabuzoki, Mr. H.K. Kabunga and Mr. D. Openshaw.

The Department of Structural, Inorganic and Physical Chemistry of the University of Stockholm provided access to x-ray powder diffraction and electron microscopy facilities; the practical assistance of Mr. Tomasz Niklewski (†) is acknowledged with particular gratitude. Dr. V. Schroder of the University of Trondheim provided literature

This work was supported by the Norwegian Agency for International Development (NORAD)

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