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The Preparation and Thermal Decomposition of the Carbonates of Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc*

by

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ABSTRACT

The preparation and thermal decomposition of the carbonates of the lighter lanthanons, La through Gd, were described at the 1963 Third Rare Earth Conference in Clearwater, Florida. This paper presents the results of the extension of those studies to the heavier lanthanons, and yttrium and scandium.

The hydrated carbonates were prepared by precipitation from a homogeneous aqueous solution by thermal decomposition of the corresponding trichloroacetates as previously described. In all cases except for scandium and lutetium, the ratio of carbonate to oxide was 2.93 or greater, the ratio of water to oxide was between 2.1 and 2.3, and the compounds were isostructural with $Nd_2(CO_3)_3 \cdot 2H_2O$. For lutetium, the compound had corresponding ratios of 2.99 and 5.2 and the structure was different from the others. For scandium, the compound with the highest carbonate content had a ratio of carbonate to oxide of 2.25. The thermal decomposition studies were done on the dicarbonate, $Sc_2O(CO_3)_2 \cdot 4H_2O$.

The thermal decomposition of these compounds was studied with a recording vacuum thermobalance in vacuum, carbon dioxide, and water vapor. Except for lutetium and scandium the decomposition proceeded by the steps $M_2(CO_3)_3 \cdot xH_2O \rightarrow M_2(CO_3)_3 \rightarrow$ intermediate $\rightarrow M_2O_3$ as shown by corresponding plateaus in the pyrolysis curves. The intermediate was the dioxymonocarbonate for terbium and dysprosium. For Ho through Yb and for Y the intermediate contained less carbonate than the dioxymonocarbonate. No intermediate carbonate was detected for lutetium. The plateau for the intermediate was shorter for the higher atomic number elements. The temperature of decomposition of the normal carbonates under 500 mm pressure of carbon dioxide was about 500°C with no marked trend with atomic number. For the intermediate there was a definite trend toward lower decomposition temperatures at higher atomic numbers except for ytterbium, which was out of place. Yttrium carbonate was similar to holmium and erbium carbonates in its behavior.

Introduction - This paper is a continuation of the work described at the Third Rare Earth Conference on the preparation and thermal decomposition of the carbonates of the lighter lanthanons, La through Gd (1). Here results are reported for the carbonates of the heavier lanthanons, Tb through Lu plus yttrium and scandium.

Compound Preparation - The normal sesquicarbonates were prepared by precipitation from homogeneous solution of the corresponding trichloroacetates under carbon dioxide pressure as previously described (1). In the case of scandium, even at carbon dioxide pressures as high as 800 psig and temperatures as low as 67°C it was not possible to obtain the sesquicarbonate, and the product was intermediate between the sesquicarbonate and the monoxydicarbonate. The pyrolysis experiments for scandium carbonate were done on the monoxydicarbonate.

As was done previously (1), the carbonates were analyzed by conventional combustion analysis for carbon and hydrogen and ignition of the final oxide to constant weight in oxygen at 1000°C. The results are shown in Table I. Differences of 0.02 or 0.03 from the theoretical 3.00 for the CO_2/R_2O_3 ratio are not considered significant. By this criterion, Dy, Er, Yb, and Y carbonates show a slight but significant deficiency of carbonate. Scandium forms the monoxydicarbonate.

The hydrated carbonates were examined by X-ray diffraction. The dihydrates were found to be isostructural with $Nd_2(CO_3)_3 \cdot 2H_2O$. The lutetium carbonate gave a new pattern.

Thermal Decomposition - The thermal decomposition of these carbonates was studied at a rate of temperature rise of 36°/hour in vacuum, in water vapor, and in carbon dioxide with a recording vacuum thermobalance (2). The resulting curves are shown in Figures 1-9. Except for scandium and lutetium, which will be discussed separately below, they are very similar to the analogous curves obtained for the thermal decomposition of the lighter lanthanon carbonates. In vacuum there is an initial loss of weight leading to a more or less well-defined plateau at a weight loss corresponding approximately to the anhydrous normal carbonate. In water vapor there is no evidence for any intermediate hydrates between the dihydrate and the anhydrous carbonate.

In carbon dioxide decomposition of the anhydrous carbonates proceeds through at least one intermediate stage. The approximate compositions of these intermediate stages are shown in Table II. These portions of the pyrolysis curves are shown on an expanded scale in Figure 10. In general, as the atomic weight increases the following things are observed: a) the slope of the curve at the fastest rate of decomposition of the normal carbonate decreases, b) the temperature in this region increases, c) the carbon dioxide content of the intermediate phase (2nd intermediate phase for Dy) decreases, and d) the temperature of decomposition of the intermediate phase decreases, except for Yb, which is above Tm.

Yttrium carbonate is very similar to holmium and erbium carbonates, as would be expected from other similarities between yttrium and these elements.

Lutetium carbonate differs from the other members of the series in several respects. It forms a hydrate with about 5 waters of hydration instead of 2, and there are slight breaks in the curve for decomposition in water vapor at compositions of about 3.2 and 2.5 waters of hydration, respectively. The pyrolysis curve in carbon dioxide does not show any intermediate phase between the normal carbonate and the oxide.

The pyrolysis curves for scandium carbonate are for a composition which is nominally the monoxydicarbonate with 4 waters of hydration. The interpretation of these curves is obscure.

In all cases the oxide formed by thermal decomposition of the carbonate in vacuum, water vapor, or carbon dioxide was the sesquioxide, even for terbium.

Some of the hydrated carbonates have been examined optically and found to be anisotropic.

Samples of the anhydrous carbonates and of the materials at the various plateaus will be taken and examined by X-rays and by optical microscopy. The results will be reported at the meeting.

Discussion - The preparation and thermal decomposition of the carbonates of the heavy lanthanons and of yttrium and scandium have been studied by Strouth (3). She used the trichloroacetate method of preparation for all of them except scandium, which was prepared by repeated washing of the ammonium scandium double carbonate. The preparations were carried out at atmospheric pressure and resulted in the normal sesquicarbonates for yttrium and terbium and in the monoxydicarbonates for dypsrosium, holmium, erbium, thulium, ytterbium, lutetium, and scandium. For the normal carbonates of yttrium and terbium she found the 15-hydrate and tri-hydrate, respectively. She found by differential thermal analysis that the normal carbonates decomposed according to

$$M_2(CO_3)_3 \rightarrow M_2O(CO_3)_2 \rightarrow M_2O_2CO_3 \rightarrow M_2O_3 \; .$$

Although she did not isolate the dioxymonocarbonates of Dy, Ho and Er, she did report the isolation of this compound for Y, Tb, Tm, Yb, and Lu.

Wendlandt and George (4) have also reported work on the preparation and thermal decomposition of several rare earth carbonates, but the report gives very few details of their work.

Yttrium carbonate has been studied by Domingues, Wilfong, and Furlong (5). They reported $Y_2(CO_3)_3 \cdot 3H_2O$ as their starting material, and they found evidence for both the oxydicarbonate and the dioxymonocarbonate intermediate compositions.

In the work reported in this paper the ability to prepare the normal sesquicarbonates of all of the rare earths by the technique described herein has been demonstrated. The dioxymonocarbonate of Tb and Dy was observed and isolated, but this was not so for the succeeding heavy lanthanons, Y, and Sc. Only decomposition products intermediate between the dioxymonocarbonate and the oxide were observed for Ho, Er, Tm, Yb, and Y; however, higher CO_2 pressures conceivably would produce the dioxymonocarbonates of these elements. No monoxydicarbonate was observed except with Sc, for which it was the starting material.

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BIBLIOGRAPHY

1. Head, E. L., and Holley, C. E., Jr., Rare Earth Research, 3, 1963, in press.
2. Head, E. L., and Holley, C. E., Jr., Los Alamos Scientific Laboratory Report LA-2691 (1962).
3. Sr. M. Clarus Strouth, Thermal Decomposition of Yttrium, Scandium, and Heavy Lanthanon Oxalates and Carbonates. Thesis, Michigan State University, 1962, Univ. Microfilm (Ann Arbor, Mich.), Order No. 62-3192.
4. Wendlandt, W. W., and George, T. D., Texas J. Sci., 13, 316 (1961).
5. Domingues, L. P., Wilfong, R. L., and Furlong, L. R., Bur. Mines Rept., Invest. 6029 (1962).

Table I

Analysis of Rare Earth Carbonates Used in Pyrolysis Experiments

Element	CO_2/R_2O_3	H_2O/R_2O_3
Tb*	2.97	2.1
Dy	2.95	2.3
Ho	2.98	2.1
Er	2.96	2.2
Tm	2.99	2.1
Yb	2.96	2.2
Lu	2.99	5.2
Y	2.93	2.1
Sc	2.04	4.0

*For terbium the oxide was determined by difference.

Table II

Intermediate Solid Phases in Decomposition of Rare Earth Carbonates in Carbon Dioxide (500 mm)

Element	1st Stage	2nd Stage
Tb	$Tb_2O_{2.02}(CO_3)_{0.98}$	
Dy	$Dy_2O_{1.98}(CO_3)_{1.02}$	$Dy_2O_{2.06}(CO_3)_{0.94}$
Ho	$Ho_2O_{2.11}(CO_3)_{0.89}$	
Er	$Er_2O_{2.12}(CO_3)_{0.88}$	
Tm	$Tm_2O_{2.18}(CO_3)_{0.82}$	
Yb	$Yb_2O_{2.48}(CO_3)_{0.52}$	

Figure Captions

Fig. 1 Terbium Carbonate, $Tb_2(CO_3)_3\cdot 2.1H_2O$

Fig. 2 Dysprosium Carbonate, $Dy_2(CO_3)_3\cdot 2.3H_2O$

Fig. 3 Holmium Carbonate, $Ho_2(CO_3)_3\cdot 2.1H_2O$

Fig. 4 Erbium Carbonate, $Er_2(CO_3)_3\cdot 2.2H_2O$

Fig. 5 Thulium Carbonate, $Tm_2(CO_3)_3\cdot 2.1H_2O$

Fig. 6 Ytterbium Carbonate, $Yb2(CO_3)_3\cdot 2.2H_2O$

Fig. 7 Lutetium Carbonate, $Lu_2(CO_3)_3\cdot 5.2H_2O$

Fig. 8 Yttrium Carbonate, $Y_2(CO_3)_3\cdot 2.1H_2O$

Fig. 9 Scandium Carbonate, $Sc_2O(CO_3)_2\cdot 4H_2O$

Fig. 10 Thermal Decomposition of Rare Earth Carbonates in ~500 mm Carbon Dioxide

Fig. 1 Terbium Carbonate, $Tb_2(CO_3)_3 \cdot 2.1\ H_2O$

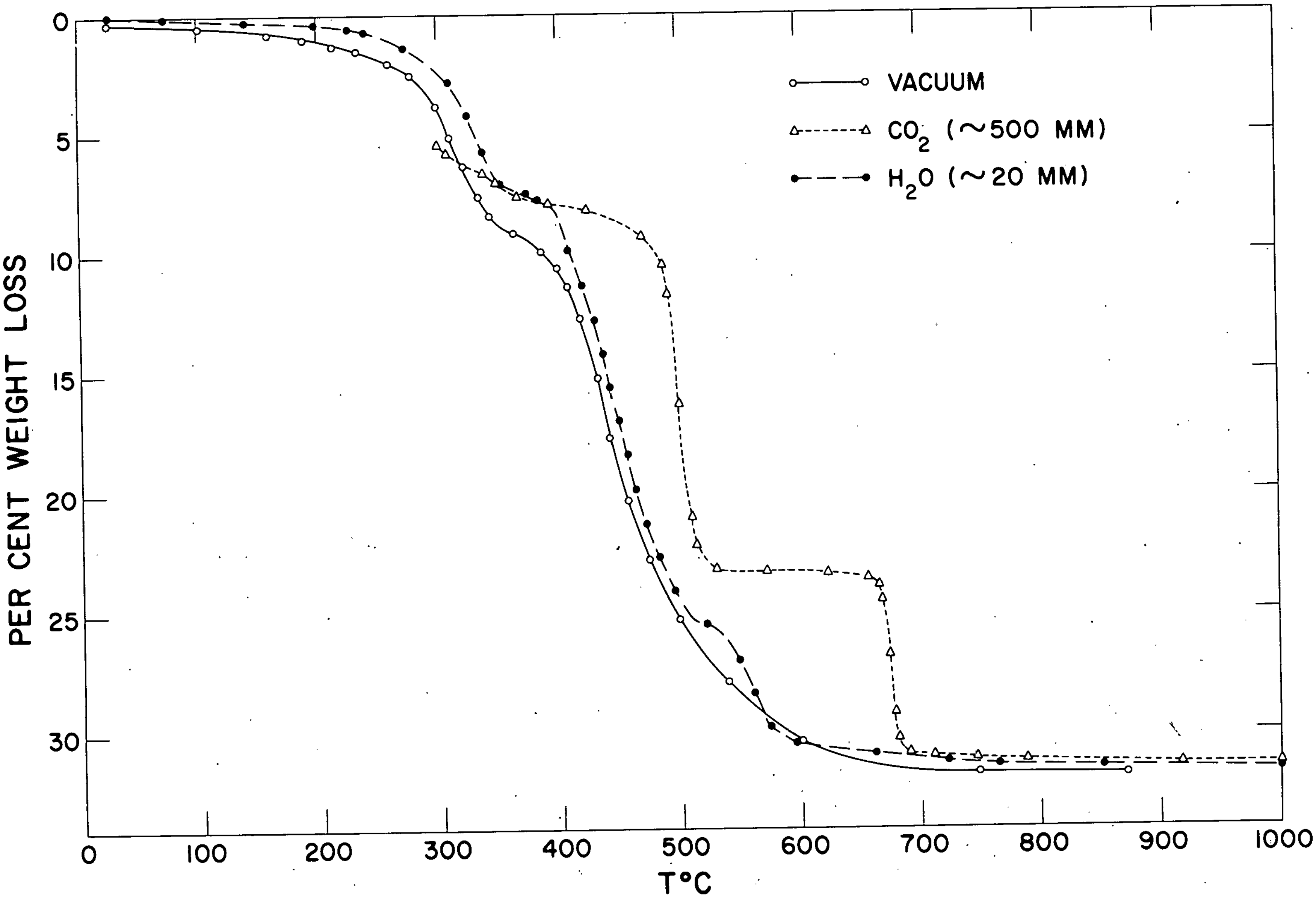

Fig. 2 Dysprosium Carbonate, $Dy_2(CO_3)_3 \cdot 2.3\ H_2O$

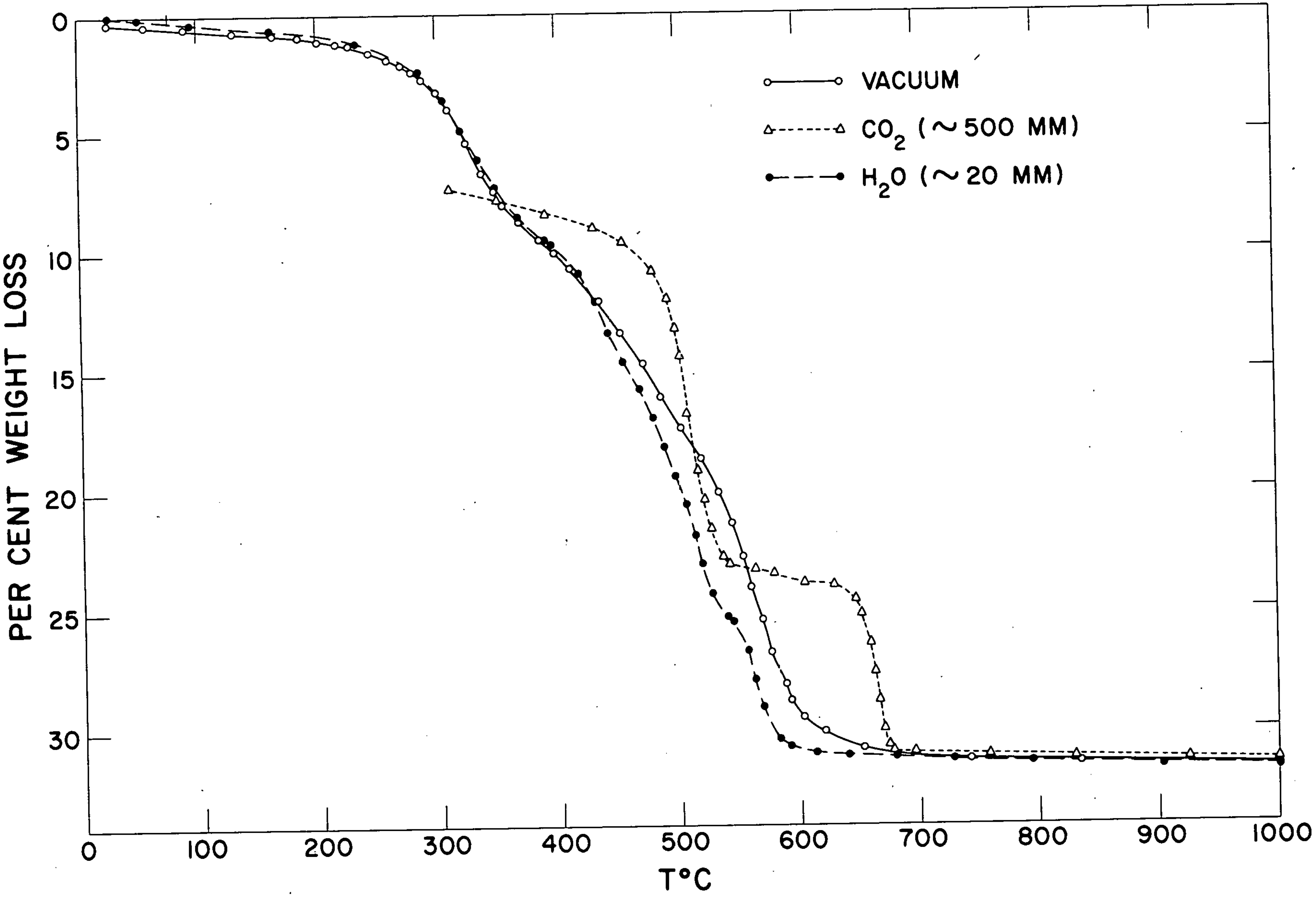

Fig. 3 Holmium Carbonate. $Ho_2(CO_3)_3 \cdot 2.1\ H_2O$

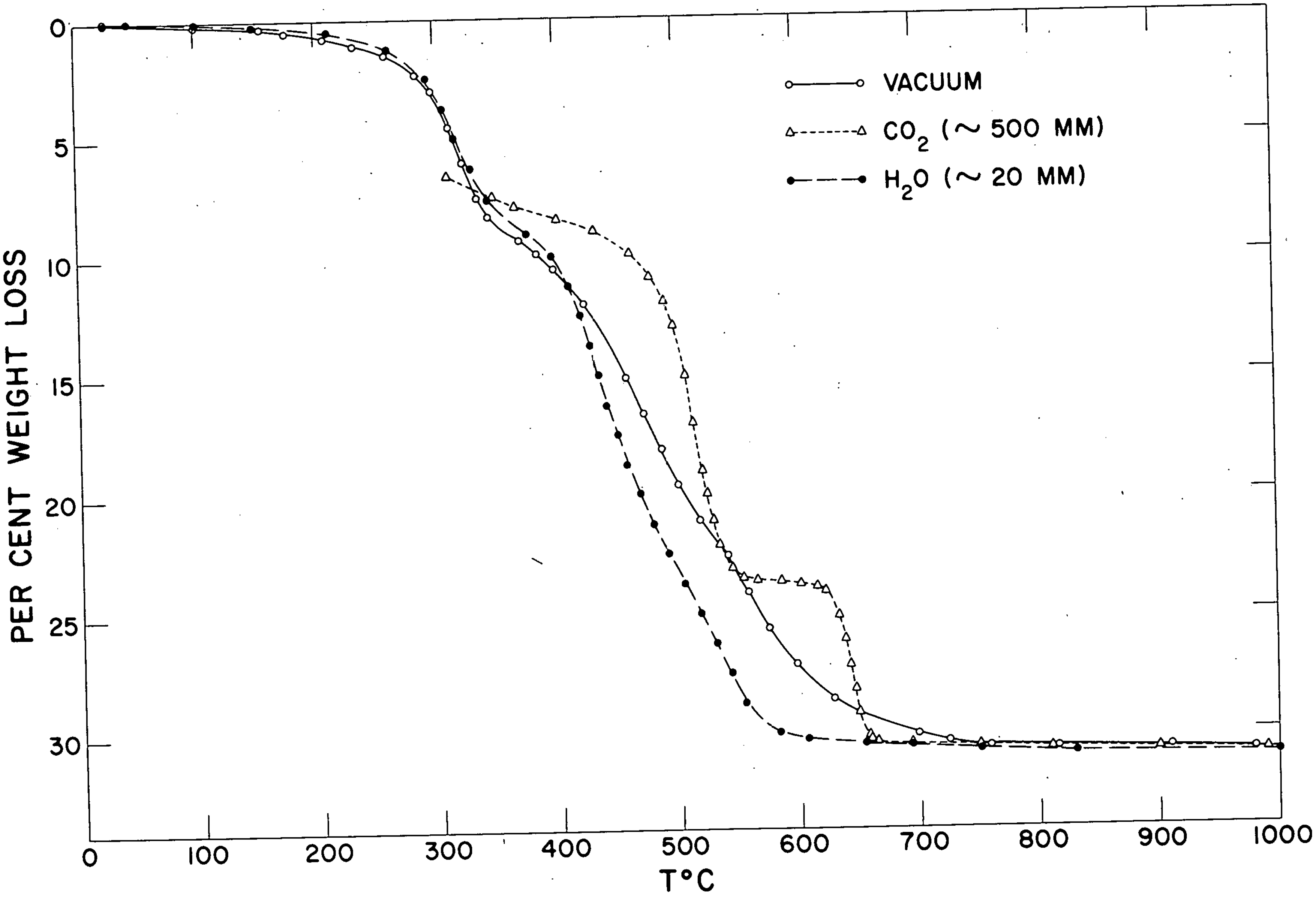

Fig. 4 Erbium Carbonate, $Er_2(CO_3)_3 \cdot 2.2\ H_2O$

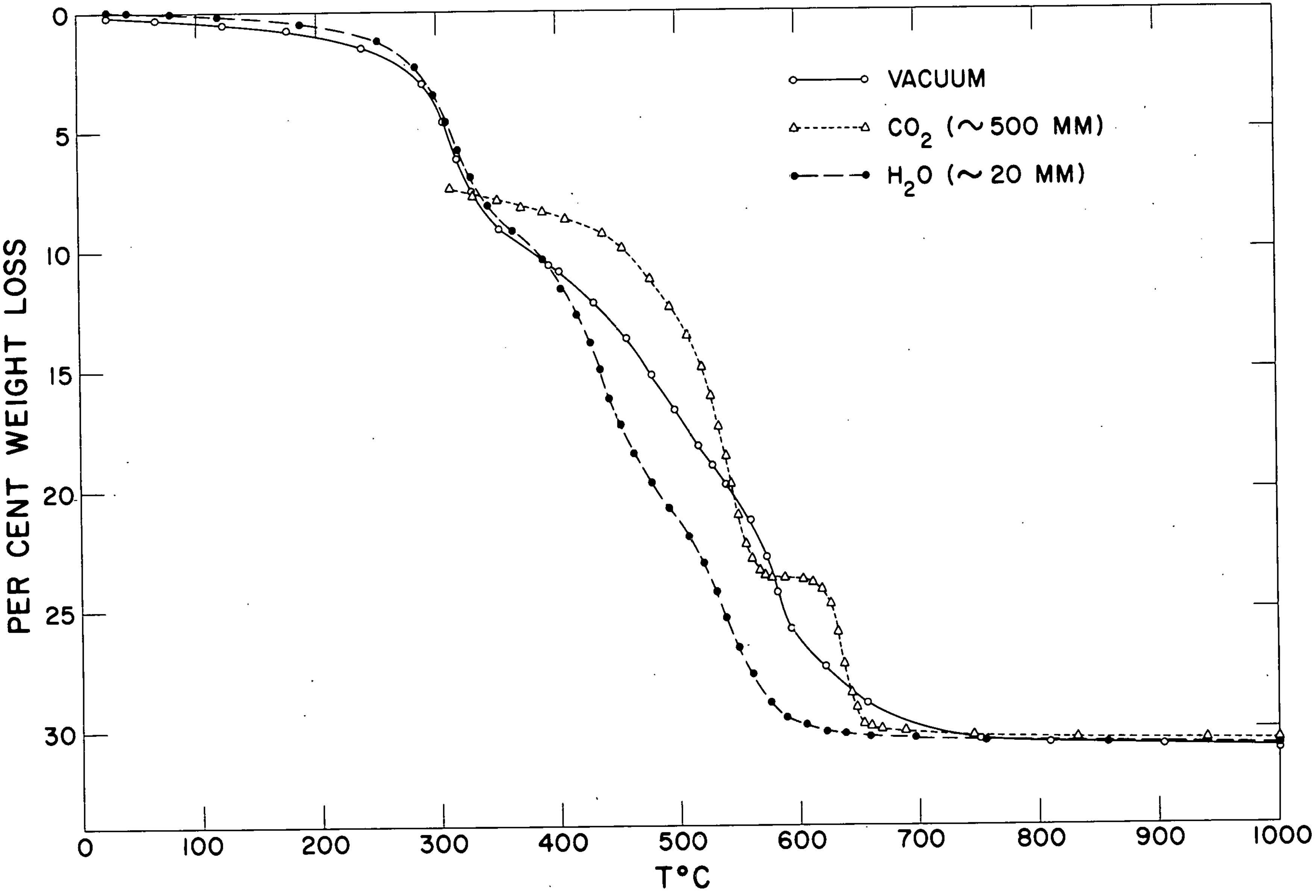

Fig. 5 Thulium Carbonate. $Tm_2(CO_3)_3 \cdot 2.1\ H_2O$

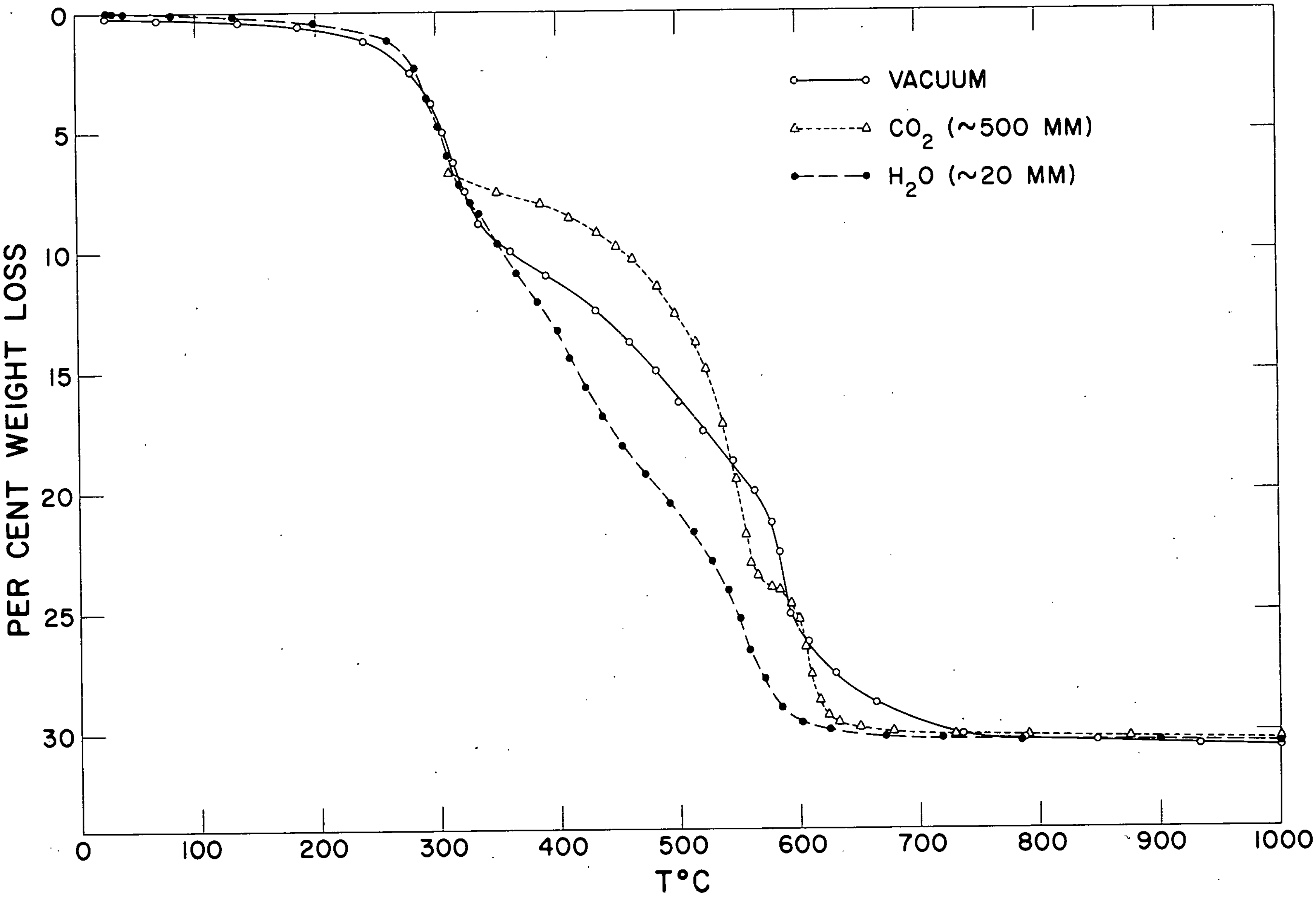

Fig. 6 Ytterbium Carbonate, $Yb_2(CO_3)_3 \cdot 2.2\ H_2O$

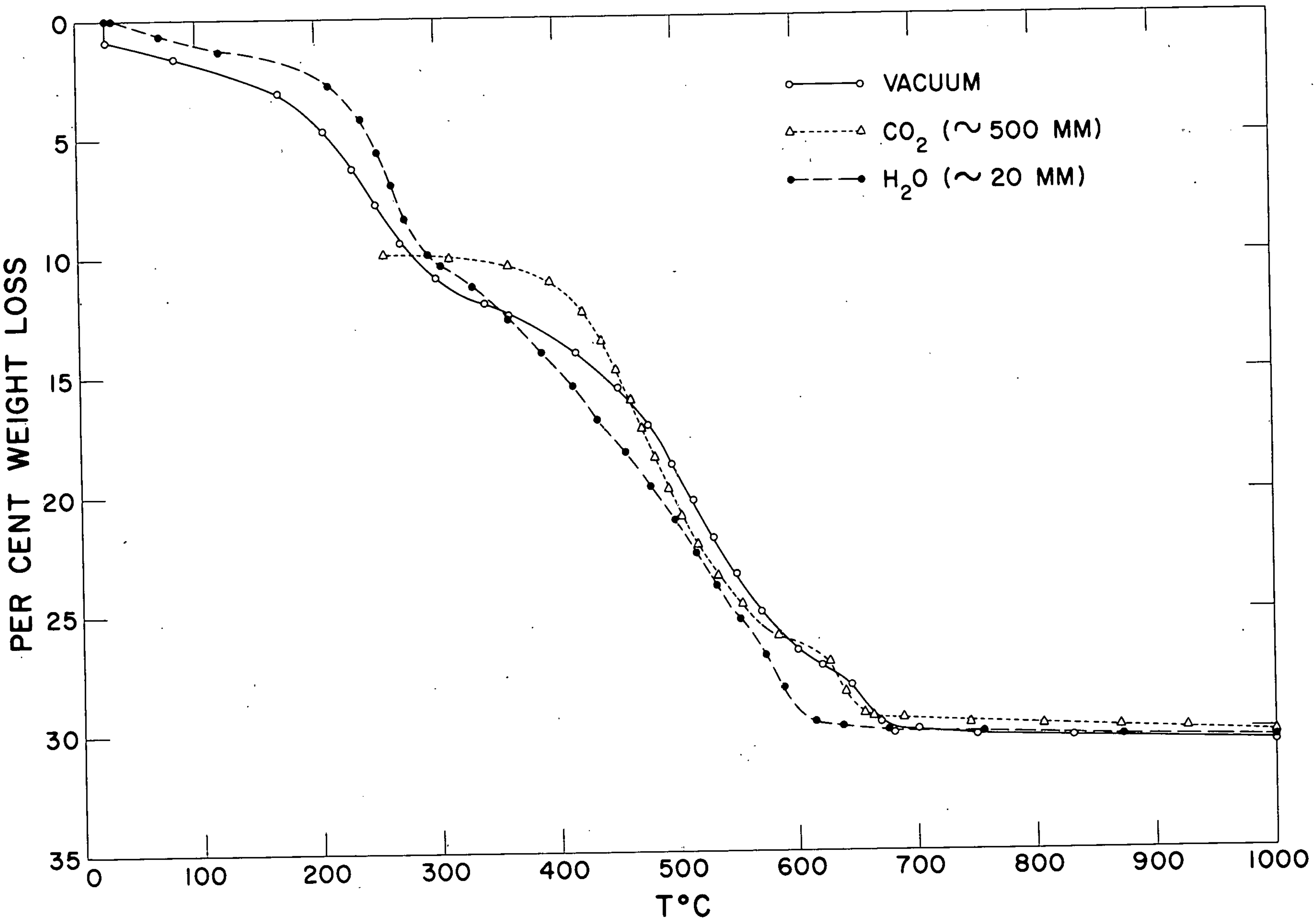

Fig. 7 Lutecium Carbonate, $Lu_2(CO_3)_3 \cdot 5.2\ H_2O$

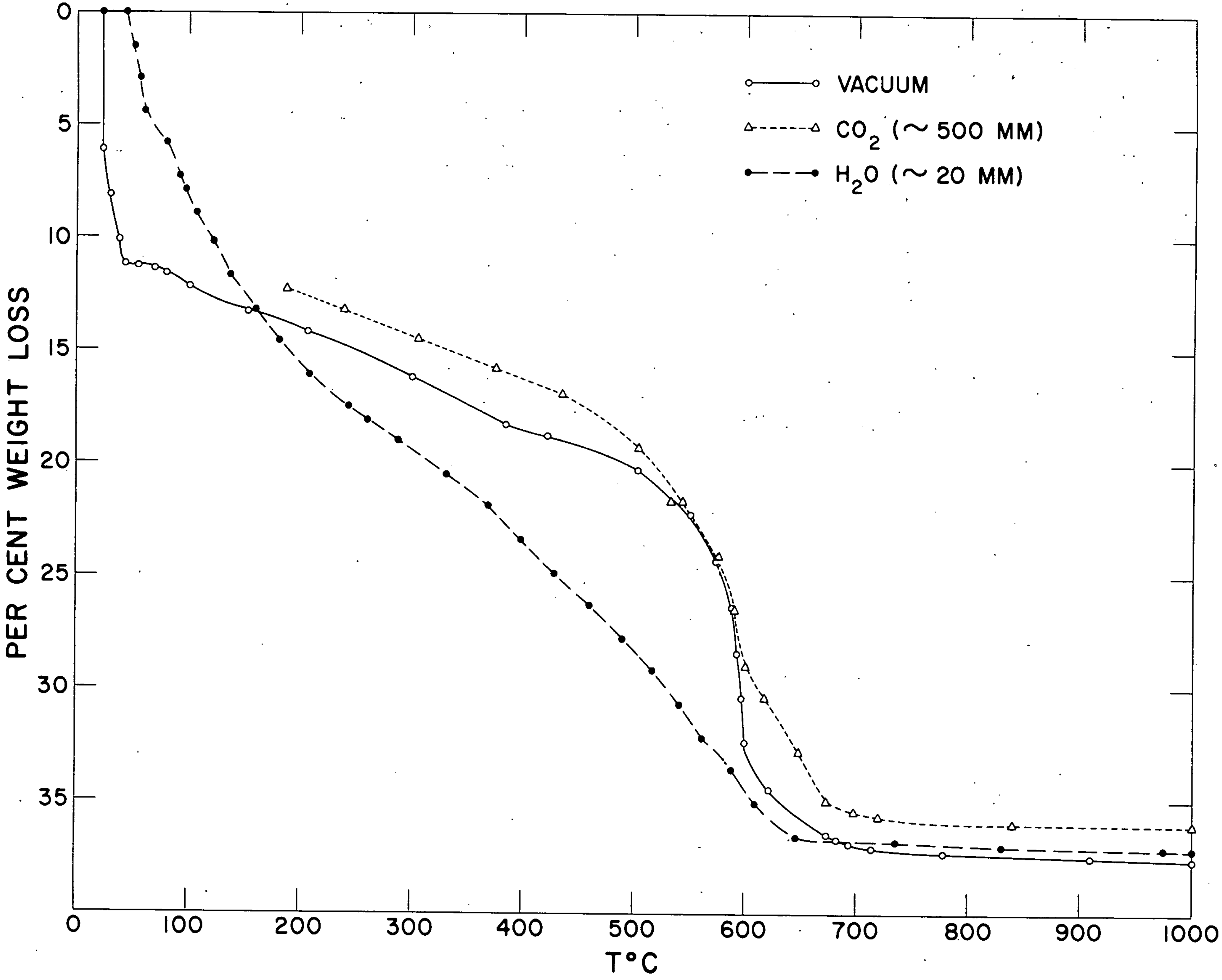

Fig. 8 Yttrium Carbonate, $Y_2(CO_3)_3 \cdot 2.1\ H_2O$

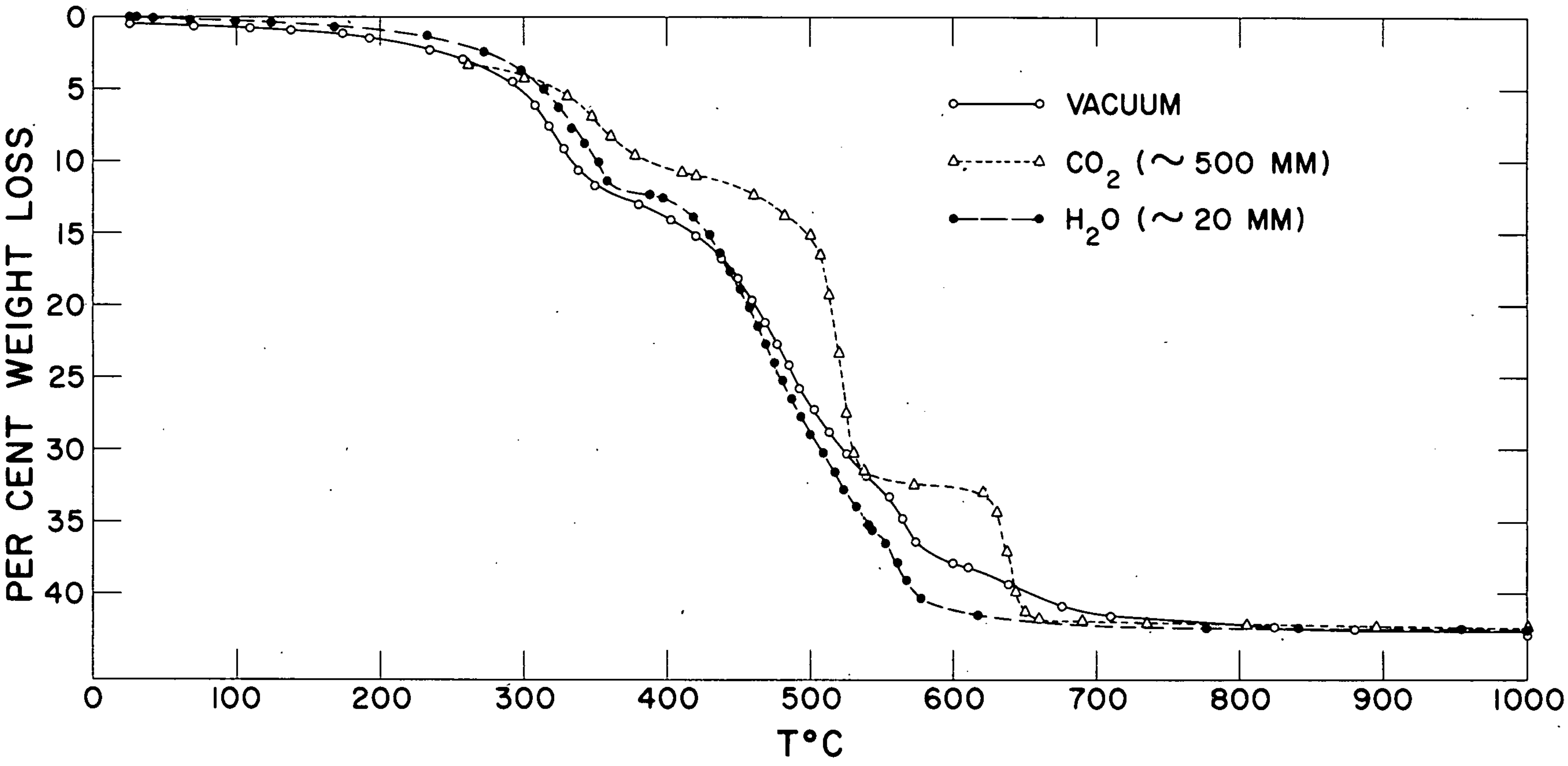

Fig. 9 Scandium Carbonate, $Sc_2O(CO_3)_2 \cdot 4\ H_2O$

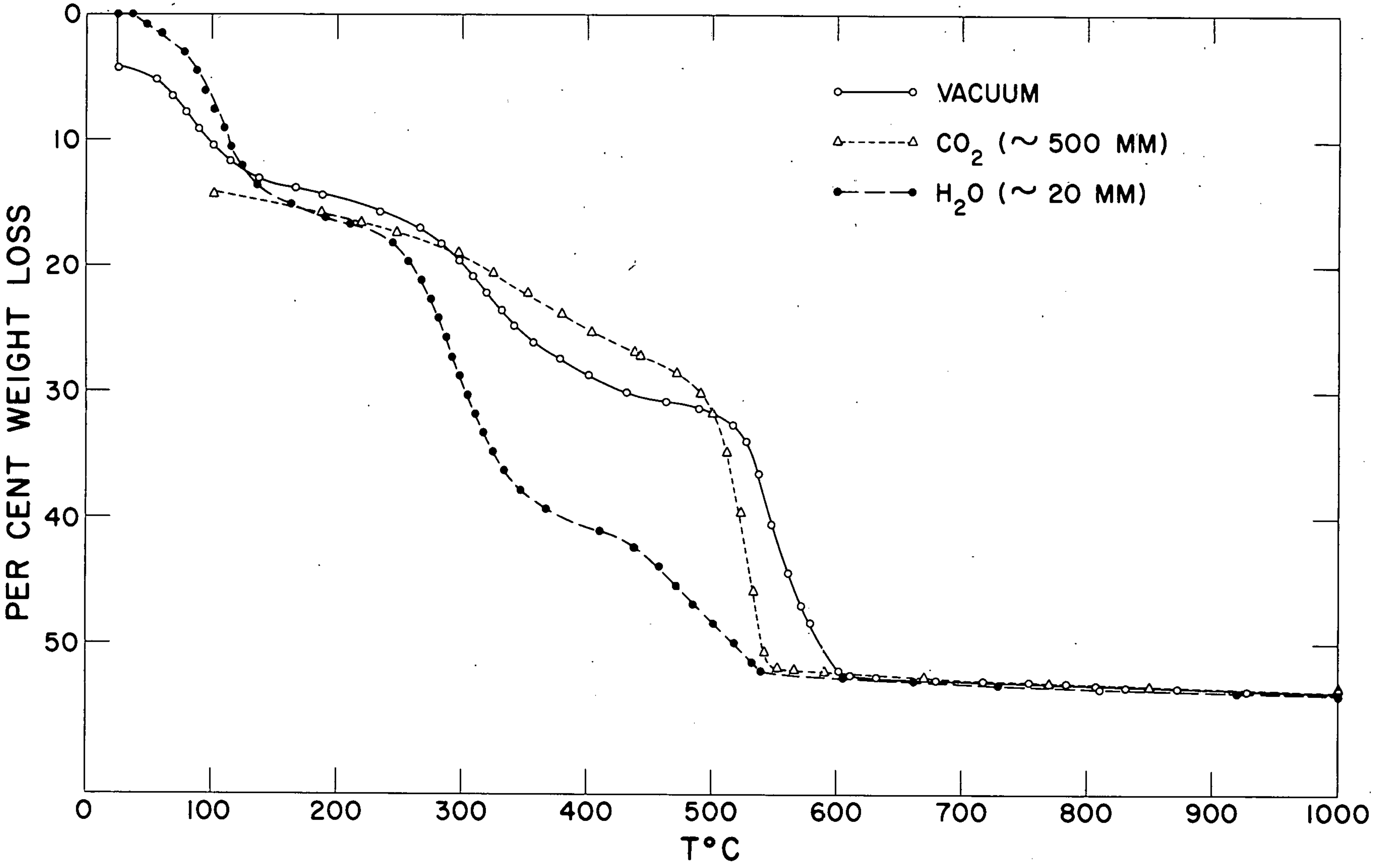

Fig. 10 Thermal Decomposition of Rare Earth Carbonates in ~500 mm Carbon Dioxide