

Endothermic Decompositions of Inorganic Monocrystalline Thin Plates. II. Displacement Rate Modulation of the Reaction Front

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Copper sulfate pentahydrate dehydration into trihydrate was investigated using monocrystalline platelets with (110) crystallographic orientation. Temperature and pressure conditions were selected so as to obtain elliptical trihydrate domains. The study deals with the evolution, vs time, of elliptical domain dimensions and the evolution, vs water vapor pressure, of the D/d ratio of ellipse axes and on the other hand of the interface displacement rate along a given direction. The phenomena observed are not basically different from those yielded by the overall kinetic study of the solid sample. Their magnitude, however, is modulated depending on displacement direction. The results are analyzed within the scope of our study of endothermic decomposition of solids.

Introduction

Much scientific work has been devoted to the endothermic decomposition of crystallized solids where a gas is removed from the initial arrangement. This work was carried out in parallel to the development of the heterogeneous kinetics of solid-gas reactions.

Within this scope, most of the research related to the study of reaction rate undertaken to know the reaction mechanism, concerns the kinetic study of the whole system, e.g., the weight loss of the whole sample is followed vs time. From the progress curves the global kinetic characteristics of the reaction are deduced.

As it is not possible, however, to define directly the actual phenomena at reaction field level from those data, a number of so-called local measurements were made. Numerous papers have already studied, most often by means of microscopic observations,

the shape of the domains, where the solid is transformed, and their development rate as well (1-8).

Now, the results obtained for the same transformation and related to the overall rate of the reaction and the displacement rate of the reaction front, hence resulting from local measurements, do not always seem consistent but sometimes are even contradictory. Thus few interpretations take both types of data into account. In fact the present study, the results of which are set out below, was carried out to know whether such a correlation exists. In addition this study should allow one to put in evidence the features induced by the solid anisotropy upon the reaction rate.

For this purpose the reaction selected was the conversion of copper sulfate pentahydrate into trihydrate for three main reasons, i.e., because pentahydrate monocrystals are easily obtained, because we noted that earlier studies, although numerous and

dealing with both overall (9–13) and local aspects (1, 2, 6, 7), had not been carried out sufficiently in parallel to allow the interpretation of the kinetic features collected in both cases, and finally because we have already investigated systematically the kinetics of this transformation (14). We determined an interesting characteristic about the $v(P)_T$ pressure laws, the curves of which show the well-known Smith–Topley effect in dehydrations.

After studying the shape of the trihydrate domains occurring over the surface of cut, crystalline platelets of pentahydrate during decomposition (15) we continued doing research on this point and present below the features of local kinetics, i.e., the displacement rate of the reaction front which is precisely the outline of these domains. Then in the subsequent discussion we will compare the overall and local kinetic characteristics especially with respect to pressure laws and we will try to draw from this analysis information about the reaction mechanism.

I. Materials and Procedure

In an earlier paper (16) we have shown that the domains of copper sulfate trihydrate occurring over the surface of cut, pentahydrate platelets are elliptical, when the decomposition of the initial salt occurs under given conditions of water vapor pressure and temperature. The shape of these domains is characterized by the D/d ratio of half-axes. We have shown that this ratio value is closely related to the crystallographic orientation (hkl) of the platelet, which enabled us to find out a reaction ellipsoid (16).

For the present study platelets obtained by cutting pentahydrate monocrystals in parallel to the index natural face $M(110)$ were used (17). According to the usual procedure the polished sample (20–25 mg) was put out of equilibrium by fixing a given value for each constraint in the reactor: water vapor pressure and temperature. Domain

visualization was achieved using binocular glasses equipped with a photographing device. Measurements of domain development vs time were made after magnifying the pictures obtained at different times.

II. Experimental Results

II.1. Evolution vs Time of the Size of an Elliptical Domain

Figure 1 shows, at a pressure of 4.5 mm Hg and a temperature of 62°C, the variation in length, vs time, of each main axis D and d of the ellipse and also that of some intermediate directions. Time zero corresponds to when the eye can see, on the enlarged picture, the decomposition domain, i.e., about 0.1 mm.

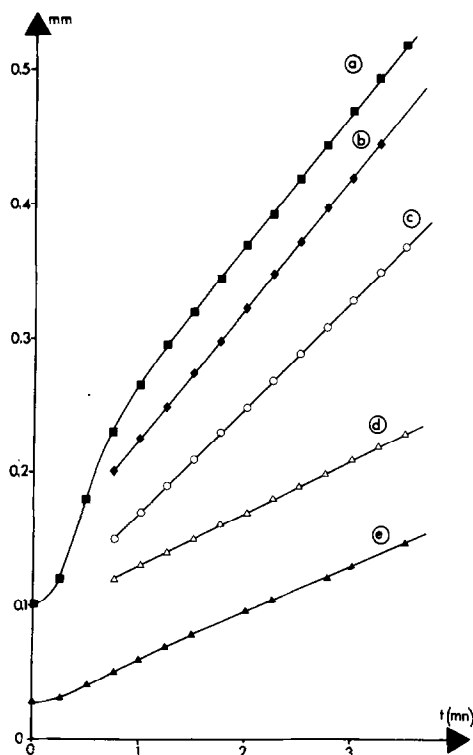


FIG. 1. Variation, vs time, of the D and d axes of an ellipse and of some intermediate directions making an angle θ with D ($T = 62^\circ\text{C}$, $P = 4.5$ mm Hg). (a) Along D ; (b) $\theta = 15^\circ$; (c) $\theta = 30^\circ$; (d) $\theta = 45^\circ$; (e) along d .

We notice that for a short period, less than 1 min, the displacement rate in a given direction first increases, then slows down, and finally becomes constant. These observations concern isolated ellipses. The linearity of the displacement vs time remains so long as the domain development is not disturbed by the approach of another ellipse or by the platelet edge.

This study takes into account the specific evolution in the early stages of the reaction in that the information about the size of an ellipse or the displacement rate of the reaction front always concerns the linear part of the above-mentioned curve.

II.2. Evolution, vs Pressure, of the D/d Ratio of Ellipses Developing at Constant Temperature

A series of experiments similar to the previous series is repeated at the same temperature but under water vapor pressures which are farther and farther away from equilibrium pressure; the variation of the D/d ratio is deduced.

The curves in Fig. 2 were plotted for three temperatures, 50, 57, and 62°C. A large number of measurements was made for each couple of values of pressure and temperature and for several platelets derived from the same or different crystals. Despite this the experimental plots are only slightly dispersed except for pressure noted P^* which is located in the pressure area where the domains are no longer elliptical (15) but are stick shaped as shown in Figs. 3a and b. Figures 3c and d correspond to ellipses observed in either part beyond this pressure range.

Unexpected as it may be, the profile of each curve is the same: when pressure decreases, the D/d ratio increases, reaches a maximum, and then decreases.

The experimental study had to be limited to a pressure range comprised between a few scores and a fraction of Torr. In the first case the rate becomes too slow for observations to be carried out. Under low pressures the

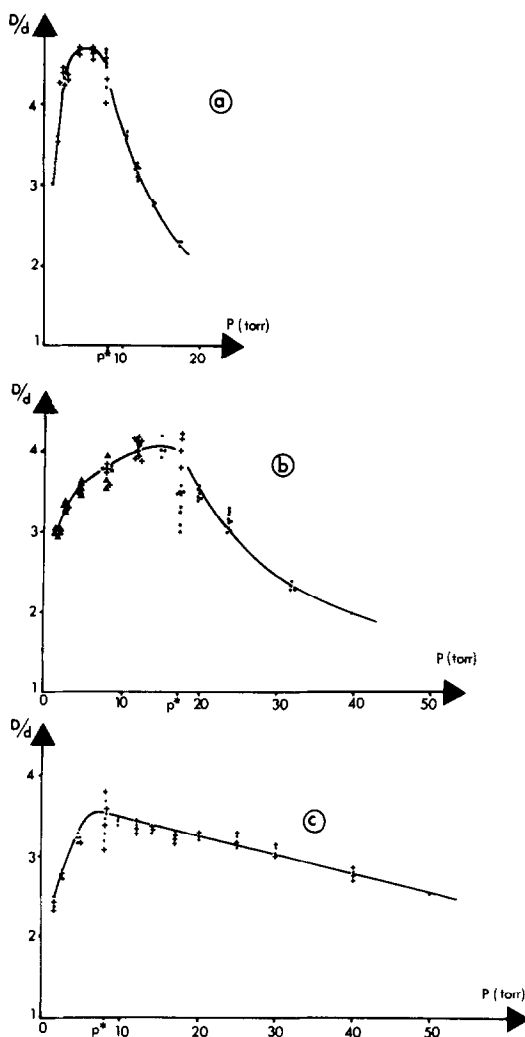


FIG. 2. Variation of the D/d ratio of ellipses vs pressure, at various temperatures. (a) $T = 50^\circ\text{C}$ (equilibrium pressure $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{O}_g$) = 44 Torr; (b) $T = 57^\circ\text{C}$ (equilibrium pressure $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{O}_g$) = 60 Torr; (c) $T = 62^\circ\text{C}$ (equilibrium pressure $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{O}_g$) = 82 Torr.

experiments can no longer be effected either because the solid transformed is not trihydrate but monohydrate or because of a deformation in the ellipses as already reported by Garner (2) and more recently by Lyakhov *et al.* (7) with occurrence of secondary growth directions.

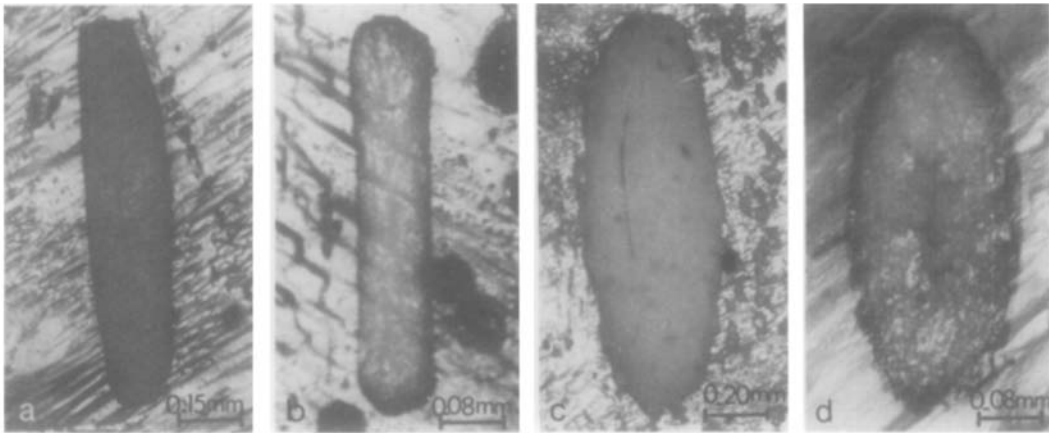


FIG. 3. Morphology of dehydrated domains at $T = 57^{\circ}\text{C}$. (a) $P = 16.0$ mm Hg; (b) $P = 17.5$ mm Hg; (c) $P = 1.6$ mm Hg; (d) $P = 31.8$ mm Hg.

The D/d ratio is equal to the ratio of the displacement rates v_D/v_d of the domain outline along the perpendicular directions of the main axes. Following these observations the study was carried out by determining the displacement rate in each separately.

II.3. Evolution, vs Pressure, of the Interface Displacement Rate along a Given Direction

Experiments were carried out to obtain the pressure law corresponding to a domain development along a given direction, i.e., the $v(P)_T$ curves. The reason is that the latter have a particular profile, a point which has been recalled in the introduction, when the overall rate of the system evolution is measured; thus it is of interest to know whether this pressure law is locally found again, i.e., if the displacement rate along a given direction of the transformed domain outline follows a law of the same type.

As already mentioned the displacement rate of the interface becomes rapidly constant vs time and this occurs whatever the development direction of the domain. This rate is measured separately for direction D and the perpendicular d from the slope of the progress curves such as those in Fig. 1.

Curves (a) and (b) in Fig. 4 are the $v(P)_T$ curves plotted for each direction D and d .

For each a decrease in a certain pressure range is noticed. This characteristic of the pressure law, known as Smith–Topley effect, to our knowledge, has never been reported in the case of the displacement of a transformed domain over the surface of a monocrystal.

In Figs. 5a and b are listed the results obtained for three temperatures. It should be noticed that the higher the temperature the stronger the effect, which is easily integrated in the phenomenology of the Smith–Topley effect (14). These figures also contain the curves obtained by Lyakhov *et al.* (7) at 45°C . Each is normally included within the network plotted. Working with only one temperature these authors concluded that the development rate of the elliptical domains was independent of the pressure value when it was less than 10 Torr. Our results show that this conclusion is not valid.

III. Discussion

Two main results related to the kinetic features of the displacement of the transformed domain outline may be drawn: on the one hand the progress curve profile and the

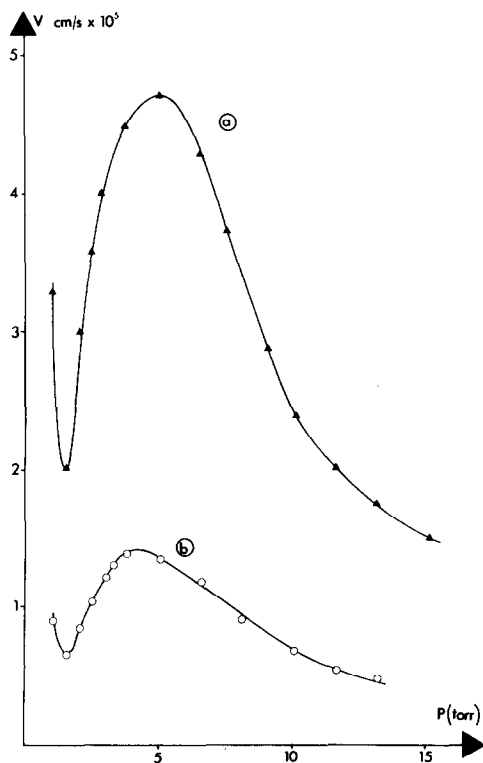


FIG. 4. Variation of the displacement rate of dehydrated domains vs pressure at $T = 57^\circ\text{C}$. (a) Along D ; (b) along d .

pressure law; on the other their change as a function of the orientation chosen on the platelet.

These results will be compared to those of the overall evolution of various systems submitted to the same constraints each yielding an endothermic transformation with release of a gas from the condensed phase. Conclusions on the reaction mechanism will be drawn. First, to clarify this discussion, it is useful to give information on the morphological features of a transformed domain. It is derived from rather recent studies carried out in our laboratory which have led to the knowledge of the rearrangement mode of the crystal stacking during a decomposition (18).

III.1. Nature of Transformed Domains

The interface, the kinetics of which was studied, separates the monocrystalline

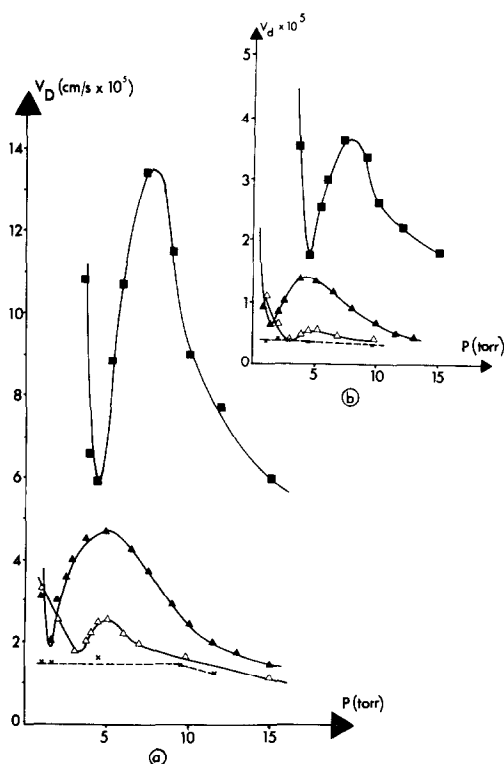


FIG. 5. Curves $V(P)_T$ obtained for various temperatures. (a) Along D ; (b) along d . X---X, curves and results obtained at 45°C , reported by Lyakhov *et al.* (7); open triangles, 50°C ; filled triangles, 57°C ; filled squares, 62°C .

matrix from the transformed domain which has become polycrystalline because of decomposition. This interface moves through the matrix by local repetition, around the domain outline, of the sequence water removal and restacking. The new stacking is built up at the expense of the initial arrangement, which has become lacunar with the help of cooperative movements that require no displacement of atoms longer than the crystal lattice. When the gas is removed and when the edifice is rearranged, mechanical stresses relax, which brings about the division of matter into crystallites, each of which is a coherence domain. Depending on circumstances, these crystallites are more or less oriented with one another. The interface between each crystallite

and the gas no longer moves once it has occurred through division.

This series of events cannot be confused with that prevailing in nucleus growth. Indeed, what we observe is the reaction front displacement where the processes resulting in crystallite formation occur: gas removal and restacking according to a mode which may be likened to a shear transformation. The rate of such a transformation being usually very high, we may wonder from the kinetic point of view if water removal is not the determining process. The following discussion enables us to answer this question.

III.2. Progress Curve and Pressure Law

The progress curve is the basic datum of any kinetic study. From its profile, for various constraint values, are deduced the pressure and temperature laws characterizing the evolution of the system. The discussion will be focused, here, exclusively on the information concerning the progress curve profile and the pressure law.

III. 2. 1. Four examples of interface endothermic evolution. As announced in the introduction the purpose of this paper is to compare the kinetic features yielded by a local observation of the evolution of solid-gas systems with those of an overall study. The experimental results of the first part of the comparison being described they must now be put into the more general context. Thus three typical examples of interface endothermic evolution, taken from our results already published elsewhere, will be compared with that of the present paper. The whole is illustrated in Fig. 6.

Figure 6a accounts for the evaporation of a liquid with a plane interface (19). For given constraints it is obvious, in this case, that the progress curves will be identical, that the magnitude versus time concerns the overall or local evolution of the system: e.g., the weight loss of the liquid is proportional to the level variation of any point of the interface.

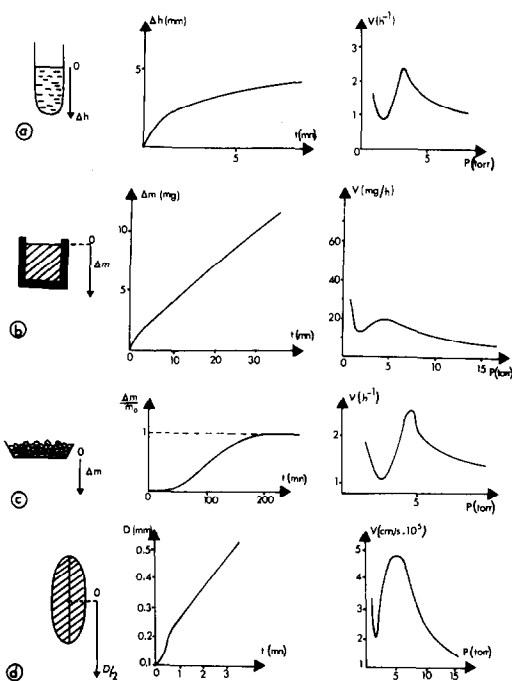


FIG. 6. Four examples of endothermic evolution of interface where a gas is released. (a) Liquid evaporation for a plane interface and a cylindrical sample; (b) dehydration of a monocrystalline cube for a single seeded face; (c) dehydration of a powered sample; (d) dehydration of a monocrystalline plate, reaction front displacement of an elliptical, transformed domain.

The following figures (Figs. 6b, c, and d) relate to the above-mentioned solid-gas system and their triple aspects studied allow one to make two types of comparison: the curves in Fig. 6b relate to a sample conditioned to allow immediate comparison with the evaporation of a liquid column. It is a monocrystalline cube varnished on five faces, the sixth being seeded to allow uniform attack (20).

The curves in Fig. 6c relate to the conventional study of weight loss of a powered sample, i.e., it is basically global. Finally Fig. 6d resumes the results of the present study of the reaction front displacement of an elliptical transformed domain; which means a basically local study.

As the phenomena are quite clear we will first compare the profile of the pressure laws. Then we will comment on the profile of the progress curves requiring more details.

III.2. 2. Common features. The first feature to be noticed, as a common feature of all pressure laws studied, is the Smith–Topley effect. In fact the latter was also found in numerous other reactions (14) and its conditions of occurrence have been established. What is new, here, is that it occurs at the very level of the growth of a very small transformed domain and that its magnitude is modulated according to the crystallographic direction considered.

A common feature also appears for progress curves, i.e., the presence of a linear part in each of them. However, the integral comparison of the curve profiles calls for a comment. Indeed, the variables followed are not the same and the change in the extent of reaction area versus time is not identical in all cases.

The sigmoidal curve (Fig. 6c), which is different from all others, is only the overall balance of what happens throughout the reaction area. Now, this area changes as the reaction proceeds: it increases, reaches a maximum or makes a step for some time, and then decreases. These considerations, although they are not the only ones to expect, are sufficient to explain the profile of such a curve.

The progress curves in Fig. 6a, b, and d, on the contrary, correspond to a linear variation, whether we consider the interface displacement (Figs. 6a–d) along a given direction or the variation of the weight of a sample with constant interface area. The curves in Figs. 6a and b are perfectly similar. They show that the reaction rate decreases continuously versus time for a relatively short period to become constant until the reaction ends.

This progress curve profile is easy to explain if we consider the temperature evolution of the reaction front versus time.

We have shown, in the case of evaporation (19), that the interface temperature T_i , which at initial time was equal to T_r (the temperature fixed in the reactor) could not remain the same because of the reaction endothermicity. The resulting temperature difference ($T_r - T_i$) increases rapidly with time, then becomes constant when the kinetic working conditions are stationary. Correlatively, the rate decreases and then becomes constant. Various studies in which the temperature of the crystal was measured (20–23) during decomposition justify us in assimilating the interpretation of the progress curves in the case of the liquid–gas and solid–gas interface displacement (Figs. 6a and b).

There remains the case of the progress curve in Fig. 6d. It shows the reaction front displacement of an elliptical domain over the crystal surface along a given direction from the domain formation and a surface site. Using an infrared thermograph (24) has shown the existence of a temperature gradient between the reaction front and the nontransformed crystal surface. The change in this gradient, then its stabilization, as previously, explain the curved part and the linear part of the progress curve. It is, however, noticed that the curved part has a profile which is different from the curves in Figs. 6a and b. This may be assigned to the fact that the reaction develops very slowly in the early stages around a site and on the other hand that the temperature gradient at the solid surface is related to the gas thermal conduction as well as to that of the solid.

Thus this discussion shows that all the progress curves and the derived pressure laws characterized by the Smith–Topley effect are directly related to the occurrence of temperature gradients from the interface.

Using experimental results and a thermodynamic model reported previously (14, 19), we have shown that these effects are kinetic features of the coupling of the interface processes of matter and heat transfer,

coupling whose intensity depends on the disequilibrium conditions of the system in relation with the thermal conductivity of the gaseous atmosphere surrounding the sample and the sample itself.

Finally two major points should be noted.

—First, the fact that the displacement rate of the reaction front along any direction shows the Smith–Topley effect ascertains that this interface phenomenon is general. At any point of the reaction interface the same flows and coupling phenomena occur. The fact that it is also found by global kinetics of sample weight loss shows that the simultaneous repetition at each point of the same local phenomenon brings about the global consequence observed.

—The second remark is about the change in the effect magnitude depending on the crystallographic direction, as a result of the solid anisotropy. The nature of the crystal will generate preferential directions for water removal and will orient the thermal conductivity tensor, and this intervention explains the rate modulation like the Smith–Topley effect modulation with the propagation direction of the interface and hence the variation of the D/d ratio with pressure (Fig. 2), which is the morphological sign (as seen D/d equals v_D/v_a).

Conclusion

As a conclusion, several points should be stressed.

Our having found for the progression of the reaction front in a transformed domain kinetic results closely similar to those for the case of the interface regression during the endothermic evaporation of a liquid allows two major conclusions to be drawn.

(1) Gas removal, i.e., evaporation is the kinetically determining phenomenon in dehydrations. Its correct interpretation requires that one consider matter and heat flows at the reacting interface and their coupling.

The solid is not responsible for these phenomena. It only affects their magnitude according to the propagation direction: a rate and Smith–Topley effect modulation is noted following the crystallographic direction considered.

At this stage of information and taking into account the data about the morphological and structural transformation, a dehydration appears clearly as the succession of an evaporation and a polymorphic transformation.

(2) The similarity in the kinetic features observed on the development of ellipses (dimensions less than 1 mm) as well as on the overall dehydration of a sample followed by thermogravimetry shows that there is no contradiction between the deductions drawn from a local or overall study. The same mechanism model is attained.

The overall result is the sum of identical, local effects directly measurable. This result also shows how insufficient it would be to consider, at the local level, only the chemical processes leaving aside the investigation of transfer processes at the macroscopic sample level.

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