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Thermal transformations of vaterite and calcite [1]

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Abstract

The polymorphic transition and the thermal decomposition of vaterite are characterized. The effect of the morphology of the parent vaterite upon the polymorphic transition as well as upon the decomposition of pseudomorphous ex-vaterite, i.e. "spherulitic" calcite, is presented. It is shown for the first time that vaterite can be decomposed into calcium oxide and carbon dioxide before being transformed into calcite. The nature of the evaluated kinetic parameters and derived mechanistic interpretations are discussed.

INTRODUCTION

Calcium carbonate in its three polymorphic modifications calcite, aragonite and vaterite represents one of the most important inorganic materials with respect to the global carbon cycle (it is noteworthy that calcium carbonate is probably the most important sink for the immobilization of CO_2 during the generation of the present atmosphere) as well as with respect to the development of the present human civilization in terms of the production of motars and concrete [1–4].

Of the three modifications, calcite is thermodynamically the most stable, followed by aragonite and then vaterite which is the least stable. The structural frameworks of the modifications can be described as follows [5, 6]: in calcite Ca^{2+} adopts a slightly distorted CaO_6 octahedral coordination, in vaterite a heavily distorted cube-like CaO_8 coordination and in aragonite a CaO_9 coordination. The Ca^{2+} coordination polyhedra as well as the corresponding Ca–O distances for calcite and vaterite are displayed in

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[1] Dedicated to Hans Georg Wiedemann.

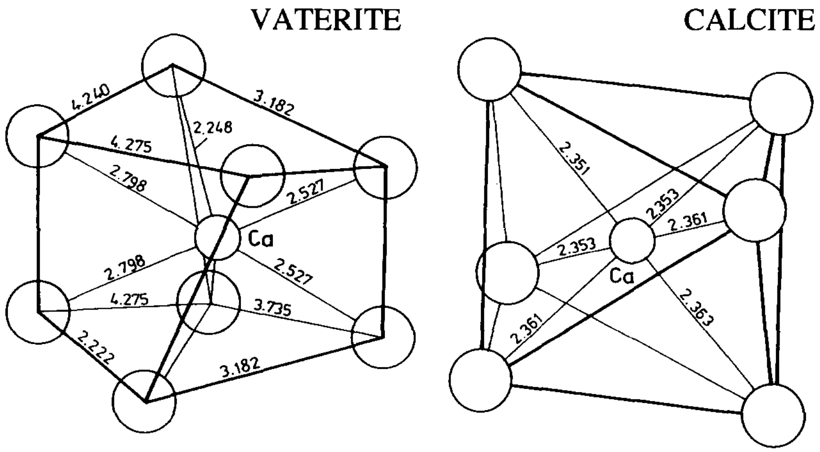

Fig. 1. Coordination polyhedra and Ca–O bond lengths in calcite and vaterite.

Fig. 1. They were calculated using the program ORTEP [7]. In this paper we focus on the modifications vaterite and calcite. In Fig. 2 the fundamental differences between the corresponding structural frameworks are shown schematically: in vaterite, the plane on which the planar CO$_3^{2-}$ ions are arranged is parallel to the *c* axis, whereas in calcite it is perpendicular to the *c* axis.

The thermochemical reactivities of vaterite and calcite exhibit distinctly divergent features. Whereas the thermal stability of calcite is very high,

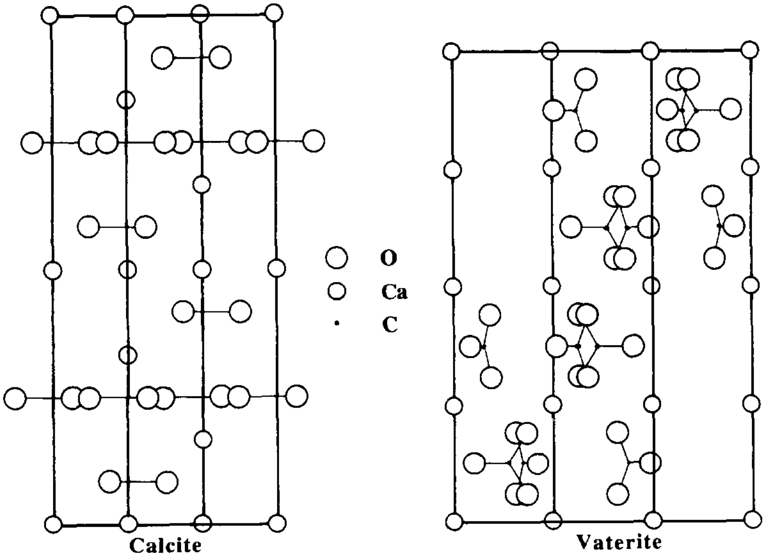

Fig. 2. Schematic representation of the structural frameworks of calcite and vaterite.

vaterite is much more reactive, i.e. it transforms into calcite at relatively low temperatures. Vaterite is also the most important phase for biomineralization processes [8]. It was first described as μ-$CaCO_3$ by Vater [9, 10] some 90 years ago, but it remains only a poorly characterized (bio-)mineral [11-16]. Details of its paragenesis are unknown. Vaterite is easily transformed in aqueous solution into stable calcite at room temperature, a phenomenon which is not observed in the case of aragonite.

In this study the thermochemical reactivity of vaterite is investigated. This includes not only the transformation into calcite but also considers factors such as morphology of the parent material as well as experimental conditions determining the kinetic and mechanistic course of the general process expressed by the equation

$$CaCO_3 \leftrightarrows CaO + CO_2$$

EXPERIMENTAL

Preparation of vaterite

The preparation of pure vaterite is very difficult: during the precipitation from aqueous Ca^{2+} solutions not only the temperature, the concentrations of the reactants and pH, but also parameters such as type of counter ion present, duration of precipitation or intensity of the mixing procedure decide upon the formation of pure vaterite or the co-precipitation of the other modifications [17-19]. According to Kamhi [20] the temperature influences the number of carbonate oxygen atoms coordinating the Ca^{2+} during the precipitation and thus the type of modification being formed. At temperatures of 300 K or lower, the predominant phase formed is calcite with a six-fold oxygen coordination. At slightly higher temperatures, i.e. 300-360 K, the thermal "vibrations" favour a higher oxygen coordination and vaterite adopting a CaO_8 coordination forms. At even higher temperatures, i.e. above 360 K, precipitation leads to the formation of aragonite with a CaO_9 coordination. Studies on the precipitation conditions have confirmed that at high pH values pure vaterite (1-2% calcite) can be obtained from diluted aqueous solutions (0.1 M) of calcium chloride and ammonium carbonate [17, 18].

Thermoanalytical measurements

The thermochemical reactivity of the calcium carbonate samples has been investigated using a Mettler DTA 2000 C and a Perkin-Elmer DSC-2 as well as a Netzsch STA 409 instrument. The determination of kinetic parameters of the studied processes was performed using a method described in detail elsewhere [21, 22].

Structural investigations

Powder X-ray diffractometry was carried out using a Siemens D-5000 unit using Cu Kα radiation. Measurements were performed in a step mode with a step size of 0.01° per 0.3 s in the range $20° \leq 2\theta \leq 90°$. Temperature dependent experiments were performed on a Guinier–Lenné camera (Cu Kα radiation).

Morphological studies

For morphological studies a scanning electron microscope (SEM) Stereoscan SI (Cambridge Instruments) was used.

RESULTS AND DISCUSSION

Phenomenological findings

Vaterite prepared according to the above procedure was used in all the studies described here. Figure 3 presents a diffractogram of this material. It

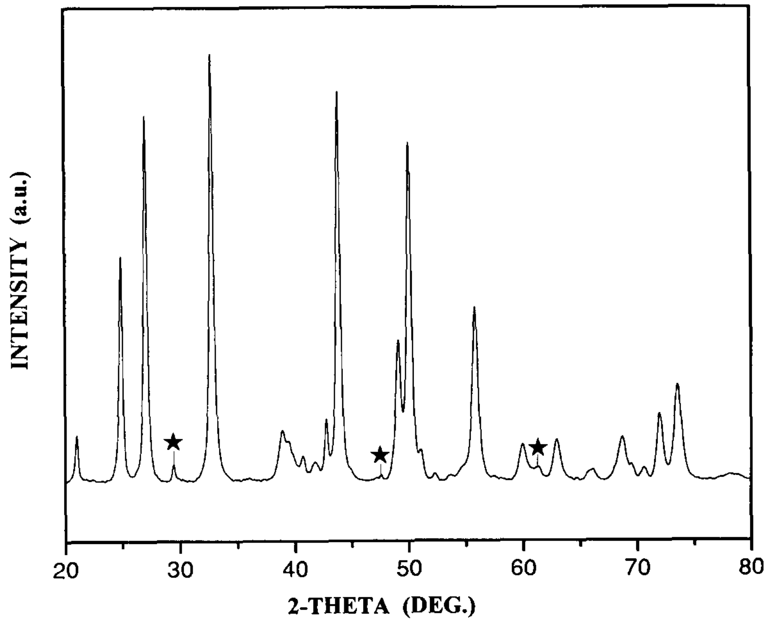

Fig. 3. X-Ray diffractogram of pure vaterite obtained by precipitation at high pH from a highly diluted aqueous $CaCl_2/(NH_4)_2CO_3$ solution. The position of the main calcite reflections (JCPDs file number 5-0586) are marked by stars.

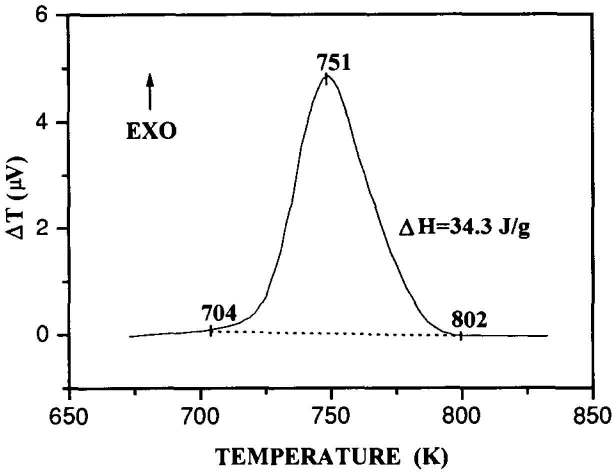

Fig. 4. DTA measurement of the polymorphic transition of vaterite into calcite (heating rate, 10 K min^{-1}; atmosphere, flowing Ar).

clearly confirms that the amount of the by-product formed, i.e. of calcite, is very small (1–2%). The polymorphic transition of vaterite into calcite has been reported in several papers [23–29]. In four of them, kinetic parameters have been determined [26–29]. According to our measurements, determined from experiments performed under non-isothermal conditions, the enthalpy of the polymorphic transition is 34.3 J g^{-1}, i.e. 820 cal mol^{-1} (see Fig. 4). In Fig. 5 the time dependence of the degree of reaction α ($0 \leq \alpha \leq 1$) of the vaterite–calcite transition is presented for several temperatures. From these measurements the following kinetic

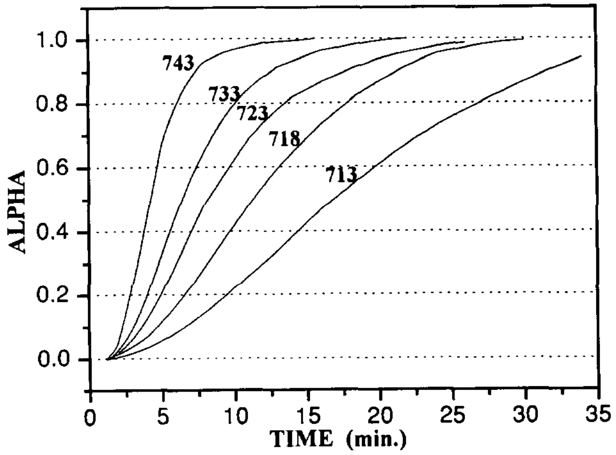

Fig. 5. Reaction degree α vs. reaction time t plots of the polymorphic transition of vaterite to calcite registered at different temperatures (isothermal conditions).

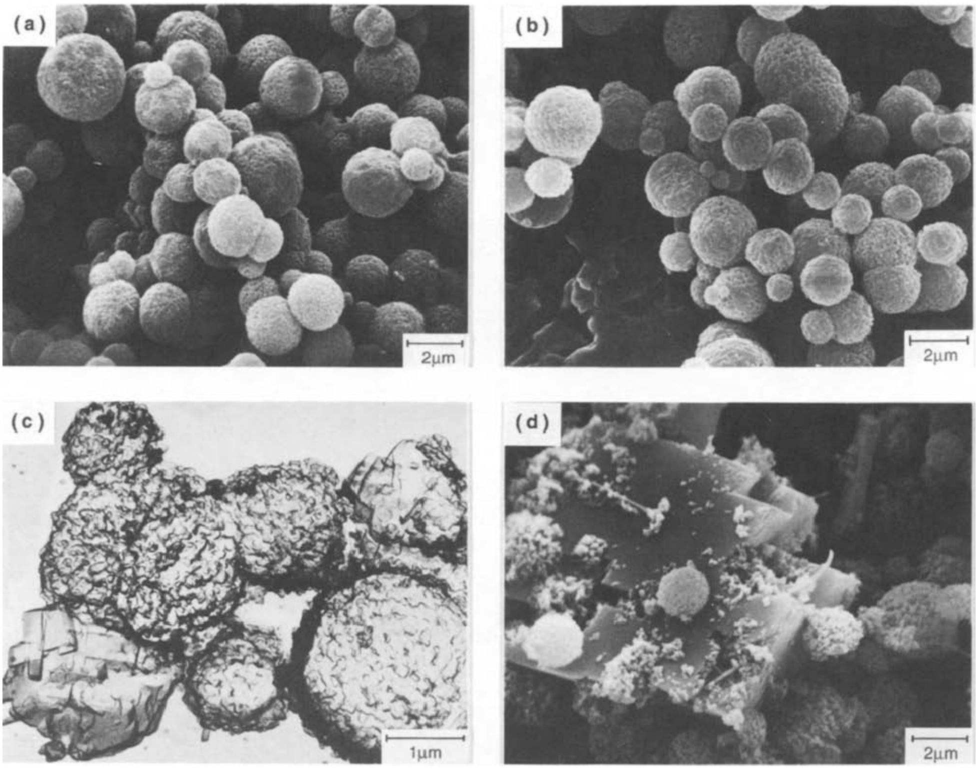

Fig. 6. Scanning electron micrographs of genuine and polymorphically transformed vaterite. (a) Spherulites of genunie vaterite prepared by precipitation at high pH from a highly diluted aqueous $CaCl_2/(NH_4)_2CO_3$ solution. (b) Calcite spherulites obtained by the thermally induced polymorphic transition of vaterite (final temperature 733 K; heating rate, 5 K min^{-1}). (c) Morphological changes observed after grinding spherulitic vaterite for 20 min at room temperature. (d) Vaterite/calcite mixture obtained by keeping spherulitic vaterite in water for 20 h at room temperature.

parameters have been evaluated using the method described in refs. 21 and 22: activation energy $E_a = 50.3$ kcal mol^{-1}, pre-exponential factor $A = 1.15 \times 10^{14}$ min^{-1}. The $g(\alpha)$ function best describing the mechanism of the process has been determined as $g(\alpha) = -\ln(1-\alpha)^{0.5}$. Concomitant morphological studies reveal the following: after the thermally induced transformation of vaterite into calcite (heated up to 733 K, heating rate 5 K min^{-1}) no morphological changes can be observed (see Figs. 6(a) and 6(b)). This can be explained by the minute structure changes accompanying this process, i.e. no extended diffusion paths of Ca^{2+} or CO_3^{2-} ions are necessary for the formation of calcite. Therefore no drastic morphological changes can be expected. Comparative studies on tribochemically treated vaterite (period of grinding, 20 min) reveal that the morphological features change (Fig. 6(c)). The parent morphology is even fully altered if vaterite is kept in twice-distilled water for 20 h at room temperature (Fig. 6(d)), These findings confirm that the wet-chemical, mechanical and thermochemical reactivities of vaterite are distinct.

As mentioned before and confirmed by temperature-dependent XRD measurements the morphologies of parent vaterite and its polymorphic transition product calcite (temperature range of transition 693–753 K) are identical. At 700 K the CO_2 partial pressure over $CaCO_3$ is in the 1 Pa range [28, 29]. Under vacuum conditions, i.e. 10^{-4} Pa, $CaCO_3$ starts to decompose at this temerature. However the temperature of the polymorphic transition increases slightly under vacuum conditions. Therefore, at about 700 K three co-existing phases (vaterite, calcite and calcium oxide) can be generated experimentally. This has been confirmed by temperature-dependent XRD measurements using a Guinier–Lenné camera. Moreover, this observation of simultaneously occurring polymorphic transition and decomposition should allow interest kinetic studies; both phases (vaterite and calcite) are isomorphological. However, there must be a detectable difference between the decomposition of vaterite under vacuum conditions below the transition temperature and the decomposition of calcite obtained by the polymorphic transition of the former, i.e. isomorphous ex-vaterite. In turn the morphology of the parent phases (rhombohedral calcite or spherulitic vaterite) should clearly influence the kinetics of the decomposition process.

In summary, the presented experimental results lead to the following questions:

(i) Does the morphology of a solid influence the course and the kinetics of its heterogeneous decomposition?

(ii) Does the simultaneity of polymorphic transition and decomposition influence the course and kinetics in an observable manner?

(iii) If one of the mentioned questions finds a positive answer, a cardinal question arises: Do kinetic equations and derived mechanistic interpretations refer to real phenomena, or do they lead to ambiguous or even obscure interpretations!

This cardinal question seems to be justified since several hundred papers on the decomposition of calcite have been in the literature. The present investigations prove, however, that under vacuum conditions it should be possible to decompose vaterite to calcium oxide. Consequently, two sets of experiments have been carried out in order to verify the influence of morphological features as well as the simultaneity of polymorphic transition and decomposition on the reaction kinetics.

Influences of morphological features

The influence of morphological features has been studied by comparing the decomposition of rhombohedral forms, i.e. normal calcite and vaterite (which under the given experimental conditions transforms into calcite

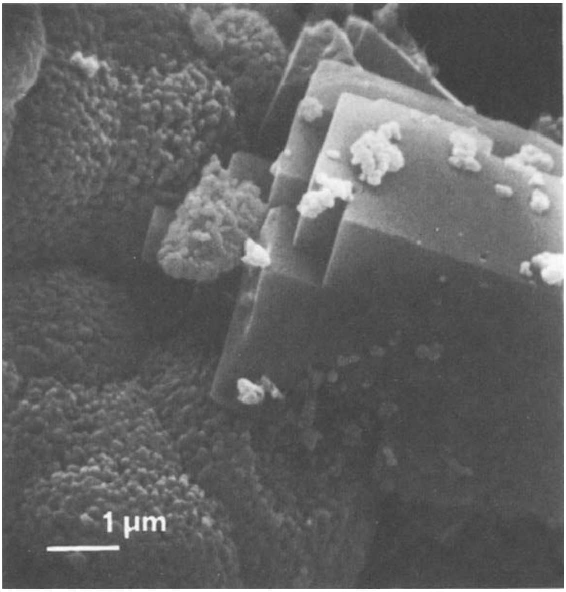

Fig. 7. Scanning electron micrograph of spherulitic vaterite (or calcite) and rhombohedral calcite.

before the beginning of the decomposition). In Fig. 7 both morphologies are presented. The decomposition of the calcite samples was measured under isothermal conditions at different temperatures. In Fig. 8 a set of thermogravimetric measurements is summarized. The courses of the curves show clear differences with respect to the different temperatures and to the different morphologies. Corresponding kinetic data have been derived by the mentioned method [21, 22]. They are compiled in Table 1. Although the α versus t plots are distinctly different, the derived kinetic parameters do not differ significnatly. It has to be mentioned, that the commonly applied comparison of one kinetic parameter (preferably the activation energy) cannot be used as a tool for discriminating between processes. The characterization of position and shape of α versus t (isothermal measuremetns) or α versus T (non-isothermal measurements) plots is based on the following three parameters: activation energy E_a, frequency factor A and the function $g(\alpha)$ referring to the mechanism of decomposition. In the presented case the decomposition of the two different parent calcites is best described by the same $g(\alpha)$ function, ie. $g(\alpha) = \alpha$. In terms of solid state kinetics all reactions would be zero order, because the rate of the decomposition $d\alpha/dt = k(1 - \alpha)^0$ is constant. Consequently the calculated kinetic parameters do not reflect the essential differences between the real courses of the decompositions of spherulitic and rhombohedral calcite. The fact that the morphology of the parent phase clearly influences the kinetics

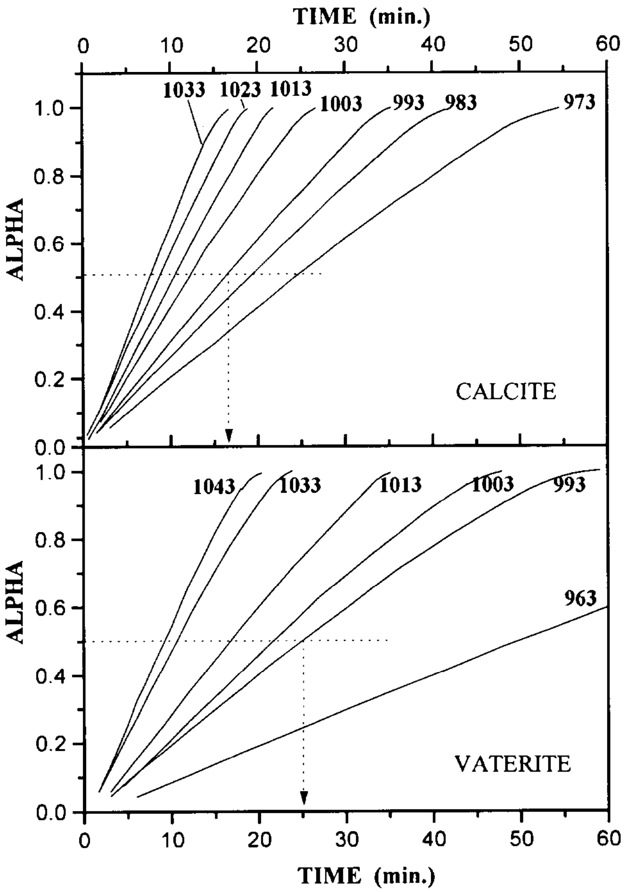

Fig. 8. Comparison between α vs. time plots of the isothermal decompositions of morphologically different calcium carbonate samples, i.e. rhombohedral calcite and spherulitic vaterite. Note the faster decomposition of rhombohedral calcite, where $\alpha = 0.5$ is reached after 16.5 min, whereas for spherulitic vatertie $\alpha = 0.5$ is only reached after 25.1 min ($T = 993$ K).

TABLE 1

Kinetic parameters for the isothermal decomposition of vaterite and spherulitic calcite under inert gas atmosphere

Phase	A/min^{-1}	$E/\text{cal mol}^{-1}$	$f(\alpha)$	$g(\alpha)$
Calcite	2.05×10^7	40157	$k(1-\alpha)^0$	α
Vaterite	9.57×10^7	44088	$k(1-\alpha)^0$	α

is not indicated by comparison of both parameters (*A* and *E*) of the particular process.

Influences of the "simultaneity" of polymorphic transition and decomposition

To start this set of experiments three different forms of calcium carbonate have been prepared or used: spherulitic vaterite, as described before, rhombohedral calcite (Merck p.a.) and spherulitic calcite obtained by heating vaterite up to 770 K in a CO_2 atmosphere (101.3 kPa). It has been reported that under the given CO_2 pressure the decomposition of calcium carbonate begins only at 1175 K [30]. The comparison between the kinetics of the decomposition of vaterite and spherulitic calcite, i.e. parent phases with identical morphologies but different structures, sheds light upon the so-called Hedvall effect [31]. This effect should accelerate a process if a polymorphic transition and a chemical reaction occur simultaneously, i.e. heterogeneous decomposition occurs. The comparison between spherulitic calcite, i.e. "ex-vaterite", and rhombohedral calcite are indicative of the influence of morphological features on the kinetics under vacuum conditions. In Fig. 9 the isothermal thermogravimetric measurements at 803 and 823 K are summarized. In Table 2 the kinetic parameters for the three different samples are compiled.

At first sight the measurements reveal that the course as well as the temperature range of the thermogravimetric curves differ significantly. Compared with the decomposition of spherulitic calcite (v/c) the rate of the vaterite (v) decomposition is higher at the same temperature. A detailed analysis of the results obtained leads to the following interpretation of the different processes. In the experiments carried out under nitrogen, the rate of decomposition of rhombohedral calcite is higher than that of spherulitic vaterite already transformed to calcite before decomposition. Under vacuum conditions the situation is more complicated. Up to a reaction degree α of about 0.6 the rate of the vaterite (v) decomposition is slightly higher than that of calcite (c). It seems (compare data in Fig. 5) that the polymorphic transition is faster than the decomposition. Therefore, the measurements can interpreted in such a way that at $\alpha = 0.6$ all vaterite is transformed into calcite. From that point onwards the rate constant of calcite decomposition governs the process.

The determination and comparison of the corresponding kinetic parameters do not offer clearcut mechanistic information. On the one hand the activation energies for the decomposition of vaterite (54 320 cal mol^{-1}) and transformed vaterite, i.e. spherulitic calcite, (44 776 cal mol^{-1}) differ markedly. On the other hand (according to the commonly used method of interpreting kinetic parameters widely described in the literature) a higher

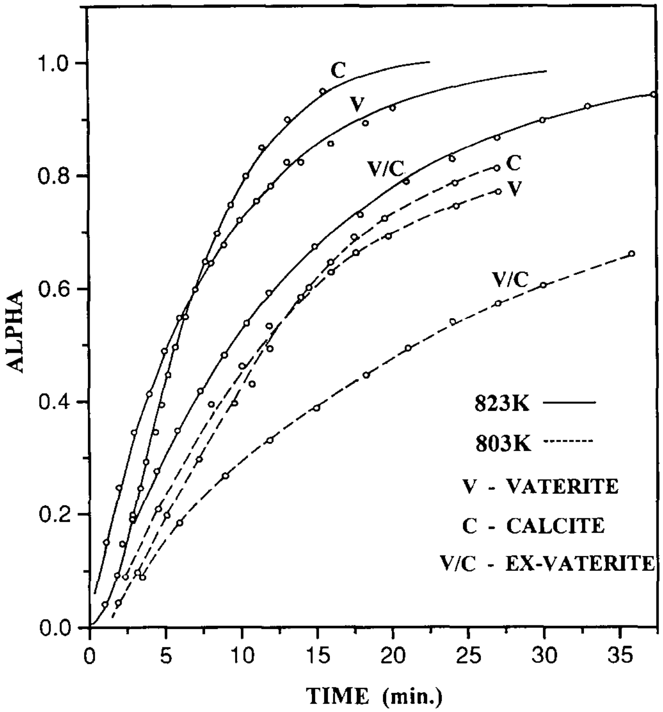

Fig. 9. Isothermal thermogravimetric measurements of spherulitic vaterite (v), rhombohedral calcite (c) and spherulitic calcite (v/c) at 803 and 823 K under vacuum conditions (10^{-4} Pa).

activation energy would lead to a lower reaction rate at constant temperature. The experiments show just the opposite. This dichotomy can be explained by comparison of the pre-exponential factors. Whereas for vaterite $A = 2.07 \times 10^{13}$, a value of $A = 9.72 \times 10^{10}$ has been determined for spherulitic calcite. Consequently, the relatively large increase of the pre-exponential factor for spherulitic calcite leads to a larger increase of the decomposition rate than the decrease imposed by the difference in activation energies.

TABLE 2

Kinetic parameters for the isothermal decomposition of rhombohedral calcite, vaterite and spherulitic calcite under vacuum conditions (10^{-4} Pa)

Phase	A/min^{-1}	E/cal mol^{-1}	$f(\alpha)$	$g(\alpha)$
Calcite (c)	1.83×10^{12}	49455	$k[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
Vaterite (v)	2.07×10^{13}	54320	$k(1-\alpha)$	$-\ln(1-\alpha)$
Calcite[a] (v/c)	9.72×10^{10}	44776	$k(1-\alpha)$	$-\ln(1-\alpha)$

[a] Refers to "ex-vaterite".

In the literature the kinetic equation best describing the course of the themoanalytical curve is used for the evaluation of mechanisms. For the studied processes the best fitting equation has the form

$$-\ln(1-\alpha) = kt^{1/n} \tag{1}$$

This kinetic equation describes a model mechanism with the formation of product nuclei as rate-determining step. The value of the exponent n refers to the number of dimensions and the number of steps involved in the formation of the product nuclei if the reaction can be characterized by the growth of spherical nuclei $n = 4$, of cylindrical nuclei $n = 3$ and of plate-like nuclei $n = 2$. According to model mechanisms developed by Mampel [32] if a single nucleus is formed per (small) crystallite $n = 1$. Equation (1) with $n = 1$ best describes the course of the decomposition of spherulitic calcium carbonate particles, be it vaterite or "ex-vaterite" calcite.

The following conclusions may be drawn from the experimental results:

(i) The polymorphic transition of vaterite → calcite influences the rate of the decomposition.

(ii) Although the polymorphic transition influences the real, i.e. experimentally monitored, course of the decomposition, no implications for the mathematical algorithm, i.e. kinetic equation describing the mechanism, are found.

(iii) For rhombohedral calcite, the best fit of the curve is obtained with eqn. (1) and $n = 3$, which refers to a mechanism governed by the formation and growth of cylindrical product nuclei.

Accordingly, morphological investigations on intermediates and products of the described processes clearly show how confined is the application of the widespread evaluation of mechanistic interpretations from kinetic equations [33].

CONCLUSIONS

The characterization of mechanisms of heterogeneous solid state reactions not only implicate the knowledge of compositional, structural and morphological changes, but always reflects the influence of the actual experimental conditions. This is even more pronounced for simultaneously occurring processes such as the described simultaneous polymorphic transition and decomposition. The presented data on the thermochemical reactivity of vaterite do not only focus on the solid state chemical aspects but also on the bioinorganic relevance of this system. However, the mechanistic data lead to the problem of determining kinetic data of heterogeneous solid state reactions. Several conclusions can be drawn from the experimental findings:

(i) The determination of well-defined rate constants cannot be determined unambiguously by the mathematical evaluation of thermoanalytical measurements. Only if the structural mechanism as well as the experimental conditions such as pressure, temperature distribution, etc. are known, may meaningful rate constants be determined (see, for example, ref. 34). However, morphological and structural studies on (preferably) single crystals are then of paramount importance. In the case of a microcrystalline parent material the determination of structural reaction mechanisms as well as corresponding rate constants turns out to lead to ambiguous interpretations. In addition the pressure and temperature dependence of heterogeneous solid state decompositions cannot be considered by the kinetic equations and therefore the evaluation of mechanisms is not reliable (see also ref. 35).

(ii) In the case of simultaneously occurring processes (as shown by the polymorphic transition and decomposition of vaterite) the determination of mechanism and kinetics prove to be even more complicated. There is, however, a crucial inference to be drawn from the set of experimental data: metastable materials prove more reactive if their structure reaches an activated state. Such an activated state may be due to a phase transition, i.e. by the temperature dependent dynamization of one or more structural elements. This phenomenon is known as the Hedvall effect. Its proof is very difficult because it can only be observed in a few systems. Even in the case of the vaterite/calcite system a quantification of this effect would be very difficult, if not impossible. In turn, the influence of the morphology as well as the simultaneity of transition and decomposition on the kinetics may be useful tools for the generation of solids under specific, preferably mild, thermal conditions.

(iii) The use of kinetic parameters such as rate constants, or even more importantly, activation energies for the characterization of heterogeneous solid state process is very limited (see, for example, ref. 36). Too many factors may influence the course of such processes. Therefore the exact description of the reactants, as well as of the experimental conditions, is as important as the evaluation of the said parameters. Under these circumstances, the evaluation of the mechanisms by fitting experimental measurements with kinetic equations seems to be even more doubtful. Again the detailed analysis of compositional, structural and morphological changes (of course studies of this type are very time consuming) leads to more reliable interpretations and thus a more efficient approach for a better understanding of heterogeneous solid state processes. The fact that this knowledge is urgently needed in the fields of modern synthetic pathways for materials design, as well as of materials science, heterogeneous catalysis, energy technology, etc., may be the driving force to invest the necessary time and labour.

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