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Thermochimica Acta 277 (1996) 175–186

thermochimica
acta

Phase transformation of calcium carbonate polymorphs

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Received 11 April 1995; accepted 12 September 1995

Abstract

The phase composition of mineral aragonite and synthetic vaterite samples was determined qualititavely by using IR-spectrophotometric and X-ray diffraction analyses. The transformation of aragonite, A, and vaterite, V, into the stable modification calcite, C, was followed using differential scanning calorimetry analysis. In order to determine the kinetics and mechanisms of these phase transformations, a number of experimental DSC curves were elaborated mathematically and the stationary point theory was applied. The activation energy, Ea, and the enthalpy, ΔH, were found to be, respectively, 234.5 ± 5.6 kJ mol^{-1} and 122 Jg^{-1} for the phase transformation $A \rightarrow C$, and 252.8 ± 48.7 kJ mol^{-1} and -21.2 Jg^{-1} for the $V \rightarrow C$ transformation.

Keywords: Aragonite; Calcite; Calcium carbonate; DSC; Phase transformation; Vaterite

1. Introduction

Calcium carbonate, like many other similar simple chemical compounds, forms different anhydrous polymorphs (calcite, aragonite and vaterite) and hydrated modifications (calcium carbonate monohydrate and calcium carbonate hexahydrate). All of these are found in nature. The occurrence of vaterite, μ-CaCO$_3$, the least stable of the polymorphs under normal conditions, is mainly of biogenic origin [1]. The polymorphic modifications of calcium carbonate and the factors affecting their formation have been the subject of study for many years. It is of great importance to understand the formation and stability conditions for all calcium carbonate crystal modifications, as

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SSDI 0040-6031(95)02748-3

well as the rules of their phase transformations, especially in the studies of complex metamorphic and sedimentation processes in geology.

As every polymorph contains a certain amount of energy, the amount of energy equal to the difference in energy contents of the two polymorphs is released or captured during the transformation from one form into the other [1,2]. In the study of the phase transformation one can apply this fact by measuring the rate of transformation at higher temperatures and/or pressures. For this purpose, various methods of analysis can be employed [1,3,4].

In this study, differential scanning calorimetry, DSC, under dynamic non-isothermal conditions was used to examine the kinetics and mechanisms of the phase transformation of aragonite and vaterite into calcite. The activation energies for these transformation processes were calculated using the Ozawa method and the values of kinetic parameters obtained for the phase transformation of mineral aragonite into calcite were compared with those obtained for pure aragonite, synthesized in laboratory [5]. The effect of other polymorphs on the phase transformation of vaterite into calcite was also examined.

2. Experimental

2.1. Materials

Aragonite, A. A sample of natural mineral aragonite was composed of tightly packed needles and was slightly brown. A typical analysis of the sample is shown in Table 1.

Vaterite, V. Vaterite particles were prepared by pouring 500 ml of a 5 mM $CaCl_2$ solution into the same volume of a freshly prepared 5 mM Na_2CO_3 solution. Both solutions were adjusted to pH 10 by means of NaOH or HCl solution before they were mixed together under good stirring. The suspension was filtered through a 0.22 μm membrane filter about 10 minutes after the mixing. The crystals were washed several times with small portions of water and dried at 378 K for one hour. The process was carried out at room temperature. All solutions were made from analytical grade chemicals and triply distilled water [6].

Table 1
Chemical analysis of a sample of mineral aragonite

Analysis	Mass %
SiO_2 + insoluble	0.26
CaO	54.76
MgO	0.72
Fe_2O_3	0.20
Al_2O_3	0.15
Loss on ignition at 1273 K	44.07

Mixture of vaterite and calcite, VC. The method of preparation was the same as that described for vaterite. In this case, however the crystals were left in longer contact with the mother liquor.

Mixture of vaterite and aragonite, VA. The sample was synthesized by carbonation of calcium nitrate and monethanolamine at 303 K, according to Langelin et al. [7].

2.2. *Methods*

The samples were characterized by infra-red spectrophotometry (Perkin-Elmer FT-IR-spectrophotometer Mo 2000), X-ray diffraction (Philips X-ray diffractometer with a proportional counter and Cu Kα radiation), differential thermal analysis, DTA, (Netzch), thermogravimetric, TG, (Perkin-Elmer TGS-2 with a TADS microcomputer) and granulometric analysis (median d_{50}, Coulter Counter Multisizer II).

The phase transformation was followed by using DSC. The DSC analysis was carried out under dynamic non-isothermal conditions in flow using extra pure nitrogen with a Perkin-Elmer DSC-4 differential scanning calorimeter. The measurements were performed in the temperature interval from 623 to 772 K, with K min^{-1} heating rates 2.5, 5.0, 10.0, 15.0 and 20.0 K min^{-1} and the cooling rate 320 K min^{-1}. The rate of nitrogen flow was 30 $\text{cm}^3\text{min}^{-1}$ and the mass of samples ranged from 4.11 to 10.14 mg. The choice of the top temperature, 772 K, was limited by the characteristics of the instrument.

2.3. *Mathematical elaboration of DSC curves*

In order to determine the kinetics and mechanisms of the phase transformation of aragonite and vaterite into calcite, DSC curves (Figs. 1 and 2) were elaborated mathematically using the stationary point theory for a number of experimental kinetic curves.

For the quantitative analysis of the experimental data, the degree of transformation, α, defined as

$$\alpha = \Delta H_{partial}/\Delta H_{total} \tag{1}$$

was calculated. In eq. (1), $\Delta H_{partial}$ is the enthalpy at the time t and ΔH_{total} is the total enthalpy of the system. These values were obtained by determining the partial and the total surface area of a DSC curve. The rate of the phase transformation, v, was calculated by

$$v = \mathrm{d}\alpha/\mathrm{d}t. \tag{2}$$

These data are shown in Fig. 3 as a function of absolute temperature, T. The curves obtained were used in determining the stationary point parameters necessary for calculating the activation energy, Ea. The activation energy for the transformation process was calculated using the Ozawa method:

$$\mathrm{d}(\ln q)/\mathrm{d}(1/T_m) = -\mathrm{Ea}/R, \tag{3}$$

where Ea is the activation energy (J mol^{-1}), R is the gas constant (J mol K^{-1}), q is the linear heating rate (K s^{-1}) and T_m is the temperature (K) at which the maximum transformation rate is achieved [5].

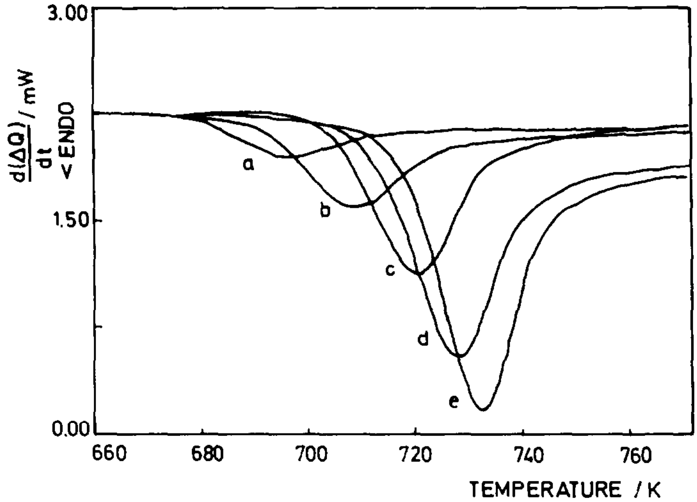

Fig. 1. DSC curves of sample A obtained at different heating rates: (a) 2.5 K min^{-1}, (b) 5.0 K min^{-1}, (c) 10.0 K min^{-1}, (d) 15.0 K min^{-1}, (e) 20.0 K min^{-1}.

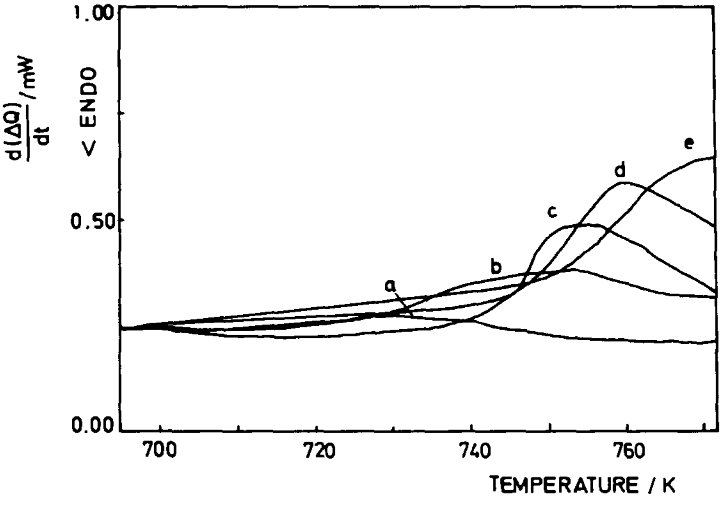

Fig. 2. DSC curves of sample V obtained at different heating rates: (a) 2.5 K min^{-1}, (b) 5.0 K min^{-1}, (c) 10.0 K min^{-1}, (d) 15.0 K min^{-1}, (e) 20.0 K min^{-1}.

3. Results and Discussion

3.1. Analysis of samples

In order to estimate the phase composition of the samples qualitatively, the IR-spectra and X-ray diffractograms of the samples were compared with the corre-

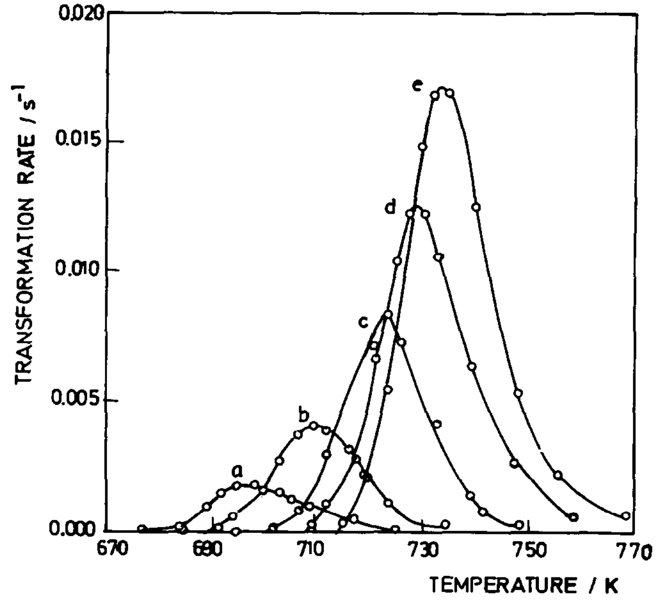

Fig. 3. Plots of transformation rate, v, as a function of absolute temperature, T, for sample A. Curves correspond to those in Fig. 3.

sponding literature data [8, 9]. Figures 4 and 5 show the infra-red spectra and the X-ray diffraction powder patterns of the samples A ($d_{50} = 4.4$ μm), V ($d_{50} = 2.3$ μm), VC ($d_{50} = 3.4$ μm) and the VA ($d_{50} = 4.4$ μm) in the range 1200–650 cm^{-1} and $24 \leq 2\Theta \leq 31$ in which the most intensive absorption bands and reflections, respectively, of calcium carbonates appear. These analyses yielded spectra characteristic of aragonite (A), pure vaterite (V), predominantly vaterite with some calcite (VC) and with some aragonite (VA) present in the sample.

3.2. *The aragonite-calcite phase transformation*

Aragonite, an orthorhombic polymorph of $CaCO_3$, is metastable at low temperatures and atmospheric pressures. It transforms into calcite upon heating and on a laboratory time scale this reaction is relatively rapid above 698 K but slow below about 648 K. The transformation process is irreversible involving a change in primary coordination from 9 to 6. A slight displacement of atoms is sufficient to cause the transformation. The kinetics and mechanism of this transformation have been extensively studied and many different techniques and methods of characterization have been employed [10–24]. The experiments of Carlson [10], Carlson and Rosenfeld [11], Gillet et al. [13] and McTigue and Wenk [18] show that the mechanism involves heterogeneous nucleation and interface-controlled growth, both being controlled topotactically. Calcite nuclei form preferentially at the crystal surface or at the defects, such as cleavages, fractures and twin boundaries. An increase in

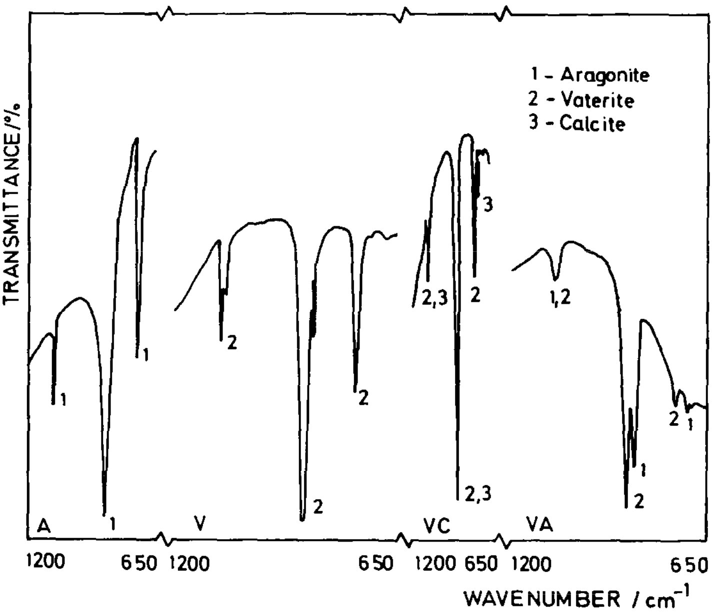

Fig. 4. IR-spectra of the examined samples in the region 650–1200 cm^{-1} showing the most intense absorption bands of aragonite (1), vaterite (2) and calcite (3). Samples A and V are pure aragonite and vaterite, and samples VC and VA are mixtures of vaterite and calcite, and of vaterite and aragonite, respectively.

volume of 8%, producing mechanical effects around the calcite grains has also been observed [11, 13].

The aragonite-calcite phase transformation is an endothermal process as it is seen both from the DSC (Fig. 1) and DTA (Fig. 6) curves. A single rather symmetrical endothermal peak in the temperature range 675.9 – 768.7 K was observed.

The enthalpy of the phase transformation, ΔH, determined from the DSC curve, scanned at the heating rate 10 K min^{-1}, was found to be 122 J g^{-1} and the activation energy, Ea, for the same process was calculated to be 234.5 ± 5.6 K min^{-1}. The value for Ea is lower, and the value for ΔH is much higher than the already published values (Ea = 296.4 kJ mol^{-1}, $\Delta H \cong 50$ J g^{-1}) for pure aragonite synthesized in laboratory [5]. The differences obtained can be ascribed to the effect of impurities and occluded water that was contained in mineral aragonite (Table 1 and Fig. 6). Thermogravimetric analysis shows a loss of mass of 1.04% corresponding to the loss of occluded water. The water appears to be released uniformly during the transformation, causing no distortion of the DSC curve. The impurities affect the stability of the individual polymorphic modification and cause a decrease in activation energy of the aragonite-calcite transformation. It is well known that the presence of water has a large accelerating effect on the aragonite-calcite transformation. Apart from the sample purity, the effect of the degree of crystalline perfection (fine and most perfect crystals are the most difficult to transform), the grain size and shape, the surface morphology and the previous thermal and deformational history should also be considered [4, 11, 25].

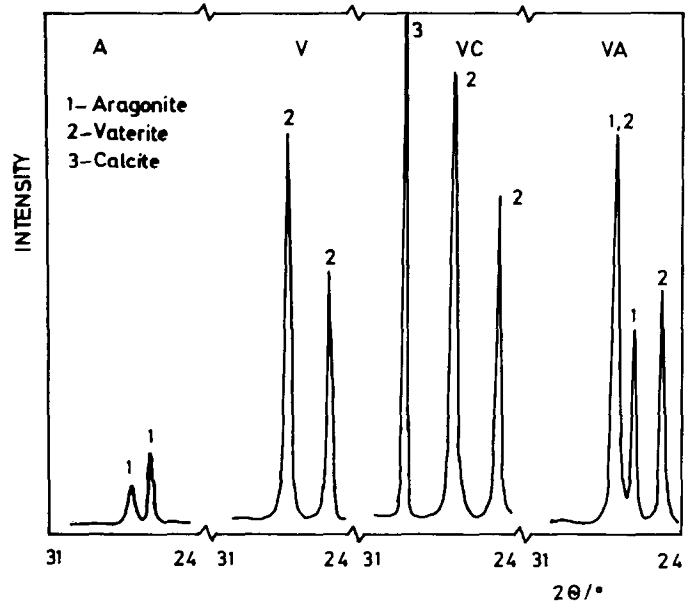

Fig. 5. X-ray diffraction powder patterns in the range $24 \leq 2\Theta \leq 31$ for the examined samples. Sample A consists of aragonite, sample V of vaterite, sample VC is a mixture of vaterite and calcite, and sample VA is a mixture of vaterite and aragonite.

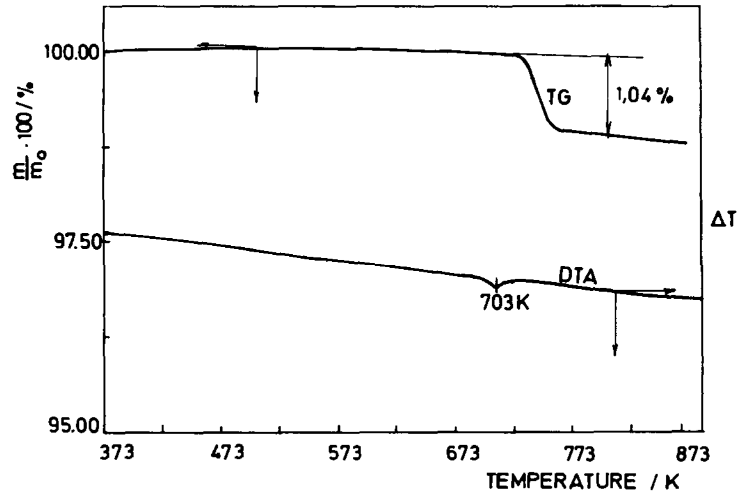

Fig. 6. DTA and TG curves of sample A. Differential thermal analysis shows an endothermal peak at 703 K at which the transformation aragonite → calcite takes place.

3.3. *The vaterite-calcite phase transformation*

Vaterite is a hexagonal crystal modification of calcium carbonate. It is found as a rare mineral in metamorphic rocks and sediments [26]. Irregularities in the structure of its crystal lattice were often reported [26–28]. Natural vaterite is usually less pure than either calcite or aragonite and impurity atoms are associated with its crystal defects [26, 28]. The vaterite structure is relatively unstable and any further distortion of the lattice, as may be produced by heating or even by grinding, is sufficient to bring about the transformation into calcite at all temperatures [28–29], along with a decrease in volume of about 2% that accompanies the transformation. Although the thermal transformation of vaterite into calcite has been examined by several workers, there is little information in the literature about the kinetics and mechanism, and about the effect that the presence of other polymorphs could have in this process.

Upon heating above 730 K, vaterite transforms directly and irreversibly into calcite. With increasing heating rate, the exothermal effect also increases and the maximum is shifted towards higher temperatures. At higher heating rates ($\geq 10\,\mathrm{K\,min^{-1}}$) these effects do not end within the operating temperature range (see Fig. 2), so that the degree of transformation and consequently its differential change were not determined with sufficient accuracy. The presence of the vaterite modification was identified in quenched samples after DSC analysis (fig. 7).

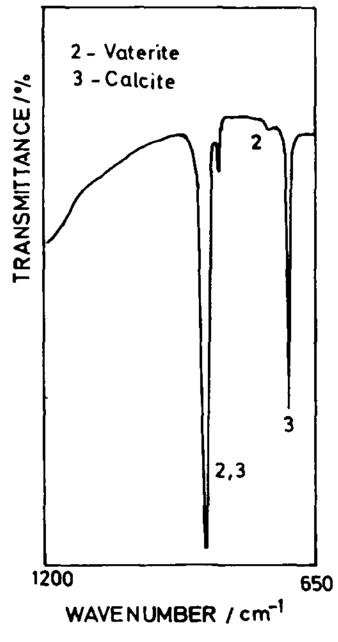

Fig. 7. Infra-red spectra of the quenched sample V after DSC analysis, carried out at the heating rate of 10.0 $\mathrm{K\,min^{-1}}$.

The activation energy and the enthalpy of the phase transformation of pure vaterite were calculated from the curves analogous to those in Fig 3. The values of maximum transformation rate at different heating rates were used to calculate the activation energy, Ea. These values were found to be $252.8 \pm 48.7\,\mathrm{kJ\,mol^{-1}}$ and $-21.2\,\mathrm{J\,g^{-1}}$, respectively. The value for ΔH was determined from the DSC curve scanned at the heating rate of $5\ \mathrm{K\,min^{-1}}$. According to Turnbull [26], ΔH for an ideal crystal showing no X-ray line broadening is $-22.8 \pm 1.2\ \mathrm{J\,g^{-1}}$. Considering the broad and shallow DSC peaks obtained in our measurements, and the difficulties in processing these DSC curves mathematically, we may conclude that the two values are in good agreement.

The presence of calcite in vaterite (sample VC) favours the phase transformation, whereas the presence of aragonite (sample VA) brings about a slight shift of the peaks towards higher temperatures (Figs. 8 and 9).

Thermogravimetric analysis of the samples indicates a slight loss of mass ($\leq 1.28\%$) up to approximately 773 K, corresponding to the loss of water incorporated into the solid phase during precipitation of calcium carbonate (Fig. 10), which often occurs with samples precipitated spontaneously [30].

In order to understand the phase transformation mechanism and the crystal microstructure induced by transformation stresses, some additional methods, such as transmission electron microscopy, should be applied.

4. Conclusions

The phase transformation of mineral aragonite into calcite is an endothermal process, as determined by DSC and DTA analysis, giving an endothermal peak in the

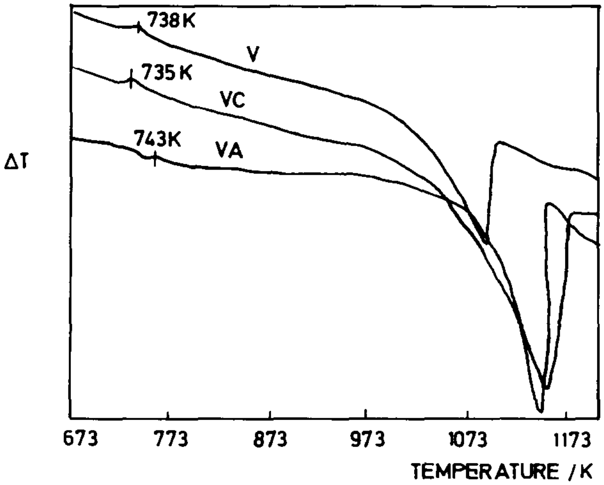

Fig. 8. DTA curves of samples V, VC and VA. The presence of calcite promotes the transformation of vaterite (peak at 735 K, sample VC). On the other hand, aragonite delays this process (peak at 743 K, sample VA).

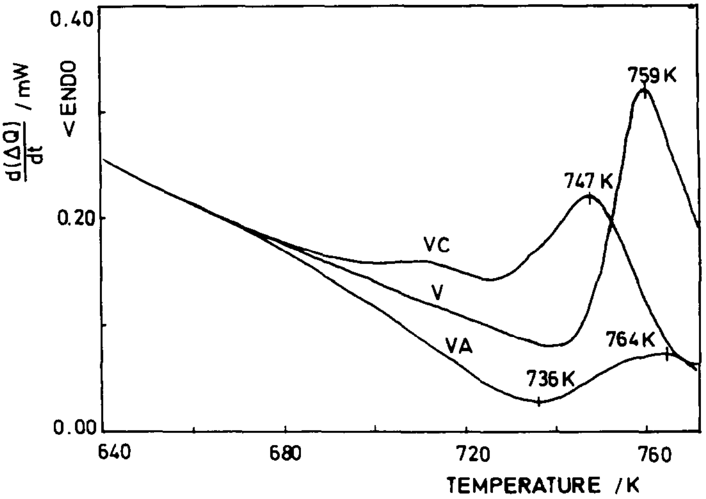

Fig. 9. DSC curves samples V, VC and VA. The transformation of vaterite in the presence of calcite starts and shows a maximum at lower temperatures (747 K, sample VC); aragonite acts in opposite direction (764 K, sample VA).

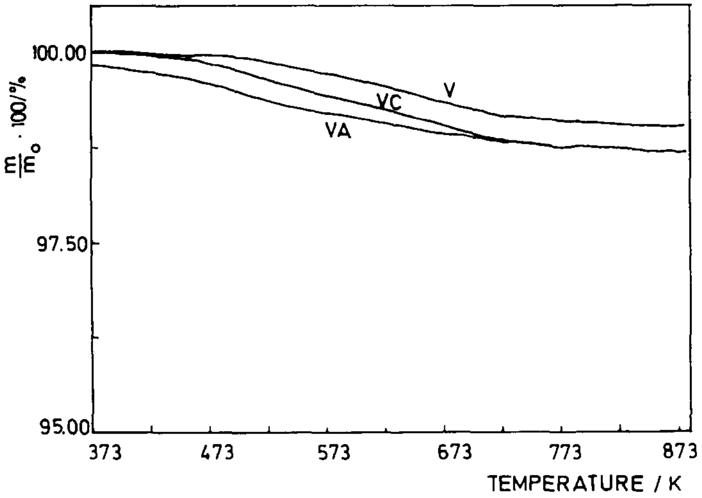

Fig. 10. TG curves of samples V, VC and VA. A loss of mass ($\leq 1.28\%$) obtained corresponds to a loss of water incorporated into these samples.

temperature range 675.9 – 768.7 K. The lower activation energy, $Ea = 234.5 \pm 5.6$ kJ mol^{-1} and the higher enthalpy for the phase transformation, $\Delta H = 122$ J g^{-1}, than those obtained for pure aragonite can be ascribed mainly to the effect of various trace elements present in mineral aragonite.

Vaterite is metastable with respect to the other two polymorphs under standard and geological conditions. Upon heating 730 K it irreversibly transforms into calcite. With increasing heating rate, the exothermal effect also increases, and T_m shifts toward higher temperatures. The value of the activation energy, Ea $= 252.8 \pm 48.7$ kJ mol^{-1}, as well as the enthalpy of its phase transformation into calcite, $\Delta H = -21.2$ J g^{-1}, have been determined. The presence of calcite in vaterite favours its phase transformation, but the presence of aragonite shows a slight inhibitory effect.

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