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THERMOPHYSICAL INVESTIGATIONS OF THE POLYMORPHOUS PHASES OF CALCIUM CARBONATE

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Abstract

1. Results of thermodynamic and kinetic investigations for the different crystalline calcium carbonate phases and their phase transition data are reported and summarized (vaterite: V; aragonite: A; calcite: C).

A → C: T_{tr}=455±10°C
$\Delta_{tr}H$=403±8 J mol^{-1} at T_{tr}
V → C: T_{tr}=320–460°C, depending on the way of preparation
$\Delta_{tr}H$= –3.2±0.1 kJ mol^{-1} at T_{tr}
$\Delta_{tr}H$= –3.4±0.9 kJ mol^{-1} at 40°C
$S_V^{\ominus}$= 93.6±0.5 J $(K\ mol)^{-1}$
A → C: E_A=370±10 kJ mol^{-1}; XRD only
V → C: E_A=250±10 kJ mol^{-1}; thermally activated, iso- and non-isothermal, XRD

2. Preliminary results on the preparation and investigation of inhibitor-free non-crystalline calcium carbonate (NCC) are presented.

NCC → C: T_{tr}=276±10°C
$\Delta_{tr}H$= –15.0±3 kJ mol^{-1} at T_{tr}

T_{tr} – transition temperature, $\Delta_{tr}H$ – transition enthalpy, S^{Θ} – standard entropy, E_A – activation energy.

3. Biologically formed internal shell of *Sepia officinalis* seems to be composed of ca 96% aragonite and 4% non-crystalline calcium carbonate.

Keywords: calcium carbonate (amorphous, non-crystalline, polymorphs), kinetics, phase transition, sepia officinalis, thermodynamics

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Introduction

Despite of the importance of calcium carbonate and although it belongs to the most simple chemical compounds the formation processes of different polymorphous phases have only been understood incompletely until now. The reasons seem to be found in the fact, that besides non-crystalline calcium carbonate three crystalline polymorphous modifications are known. In addition to the thermodynamically stable calcite there are the increasingly metastable modifications aragonite and vaterite, respectively. The crystal structure of the mentioned carbonates is reliably investigated [1–3]. While some organisms should be able to stabilize amorphous or better non-crystalline calcium carbonate, its stability in the non-biological range was questionable [4]. According to Addadi *et al.* [4] the following distribution of the mentioned natural solid phases of calcium carbonate within the biological and non-biological range is presented:

	biological	non-biological
Calcite	very common	very common
Aragonite	very common	rare
Vaterite	rare	very rare
non-crystalline $CaCO_3$	rare	non-existent

(further on called: calcite: C; aragonite: A; vaterite: V; non-crystalline $CaCO_3$:NCC).

Independently of the variety of the structure and morphology, various sequences in the formation of the solid carbonates are to be considered. Especially in the biological system the modification to be formed is specified via selected chemical agents. Phase formations are inhibited or activated. Also the stability of formed metastable phases seems to be steadily maintained by energy delivery.

Preliminary results concerning the actors controlling the phase formation are given [5, 6]. Generally, reliable knowledge for controlled phase formation is lacking.

For the crystalline phases of calcium carbonate it is well-known that on the basis of the preselected precipitation temperature the formed carbonate phase can be specified [7, 8]. All the three crystalline modifications can be prepared reliably and roentgenographically pure. In addition, for calcite and aragonite there are pure inorganic mineralization products from different deposits. In the case of aragonite, for comparing investigations, material of biological origin are also available.

The non-crystalline phase of $CaCO_3$ is very important, because probably non-crystalline calcium carbonate could be formed, first of all, in biological systems [5, 6]. On the other hand, on the basis of the non-crystalline phase, the known crystalline modifications should be producible. Including the non-crystalline phase the number of possible phase transitions is substantially extended. Thus, there are new interesting possibilities to study the influence of chemical agents on the sequence of transitions. Preliminary results of preparation and phase transitions of NCC are given in this paper.

The transition of the calcium carbonate phases can be activated via different modes. The thermally activated transition should proceed directly between the solid phases possibly always while forming thermodynamically stable calcite. It should be suitable to obtain reliable information on transition enthalpy $\Delta_{tr}H$, transition temperature T_{tr} and transition kinetics. Possibilities to influence the transition result by activators or inhibitors are not given in thermal activation. However, it is described in literature [7–10], that the metastable modifications of calcium carbonate within the temperature range of 25 and 100°C during a period of one day should transform into a more stable modification also with the saturated aqueous solution. This process is called crystallization with phase transition in the following and is suitable to simulate mineralization processes, i.e. to study the influence of activators or inhibitors on the sequence and process of phase transition. The thermal power exchanged during phase transition could be used for the process screening, if the crystallization is carried out in sufficiently sensitive and long-time stable calorimeters.

The following overview about our investigations therefore presents:

- results of thermodynamic and kinetic investigations for the different calcium carbonate phases;
- results on crystallization with phase transition via aqueous solution observed by thermal screening;
- peculiarities of biomineralization products by the example of biologically formed aragonite;
- preliminary results on the preparation and investigation of NCC as prerequisite for interesting simulation alternatives of the biological mineralization processes.

Results and discussion

Thermodynamic and kinetic investigations of the phase transitions between the crystalline phases

Results on the changes of the thermodynamic variables during the phase transition of aragonite into calcite (A → C) are reported in literature [11], the scattering of which is considerable. Therefore, it seemed to be necessary to investigate the thermally activated phase transition of carefully prepared and characterized aragonite and comparably reliable samples from natural deposits in the Czech Republic, Spain and Morocco, respectively. It has been stated in accordance with all the mentioned samples [12], that the phase transition is observable at $T_{tr}=455\pm10°C$, and the molar phase transition enthalpy is $\Delta_{tr}H=403\pm8$ J mol^{-1}. Comparing determinations of $\Delta_{tr}H$ at a temperature of 40°C, measurement of dissolution enthalpy of aragonite and calcite in acid or EDTA solutions led to the unexpected value of about 100 J mol^{-1} for $\Delta_{tr}H$. The observed difference between high-temperature and room-temperature values of $\Delta_{tr}H$ [12], seemed to be too low on the basis of the heat capacities known from literature [11]. By precision measurements of heat capacity [13] it could be shown that ΔC_p increases in the corresponding temperature range, but is considerably smaller than 1 J (K mol)$^{-1}$. The difference of the $\Delta_{tr}H$ values between room temperature and high temperature was measured more exactly by difference drop experiments of aragonite

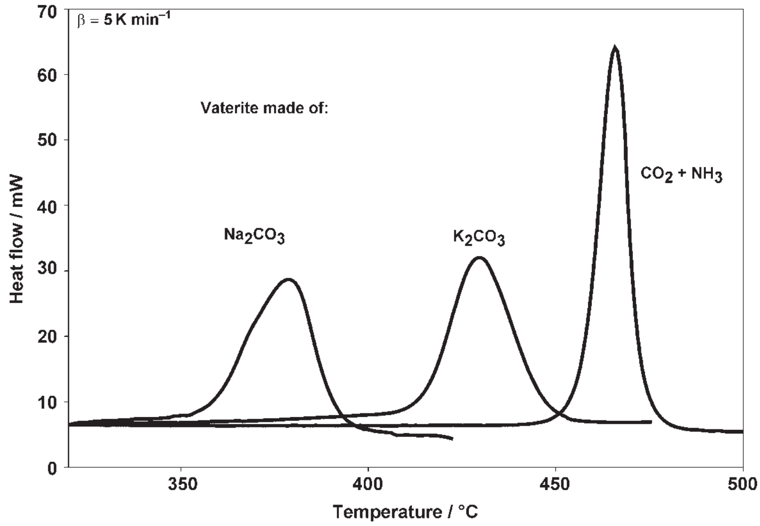

Fig. 1 Thermally activated phase transition of differently precipitated vaterites

vs. calcite in a DSC 111 (SETARAM) [13]. The obtained value of $\Delta(\Delta_{tr}H)$= 200± 40 J mol^{-1} sufficiently confirmed the value for phase transition enthalpy which has been obtained from dissolving experiments near room temperature.

The investigations on the thermally activated phase transition of vaterite into calcite (V→ C) showed that the considerably less stable vaterite causes problems during investigation. By precipitating of calcium carbonate from $CaCl_2$ with different alkali carbonates and with NH_3 and CO_2, respectively, several roentgenographically phase-pure vaterite samples are prepared. Samples from natural mineralization processes are not available for purposes of comparison. At sufficient coincidence for all prepared vaterite samples a unified value of $\Delta_{tr}H$= –3.12±0.1 kJ mol^{-1} could be measured for the thermally activated phase transition, while the phase transition temperatures T_{tr} being dependent on precipitating agent (Fig. 1) were between 320 and 460°C [14]. The highest value of transition temperature and at the same time most marked transition peak has been observed with the samples prepared with NH_3 and CO_2. Otherwise, with decreasing molar mass of alkali ion a considerable reduction of T_{tr} and a broadening of transition curve take place (Fig. 1). The observed different metastability of the prepared vaterite versions has been considered to be caused by contaminations by foreign ions. However, it could not been excluded that water strongly bound in the vaterite samples has essential impact on the observed differences. Drying tests over a period of 2 h at 250°C did not lead to a complete removal of the water. As thermogravimetric measurements showed, the removal of the residual water content of 1 mass% was carried out together with phase transition only.

The residual water content has also been decisive for the observed differences between the heat capacity [15] of vaterite and calcite. Only above 55°C and increasing with temperature a very small, positive C_p difference between calcite and vaterite is measurable. The only very small differences of heat capacity are determining for the small temperature dependence of phase transition enthalpy. By dissolution experiments of vaterite and calcite in EDTA solution a value of $\Delta_{tr}H= -3.4\pm0.9$ kJ mol^{-1} for phase transition enthalpy at a temperature of 40°C has been obtained [15].

From performed heat capacity measurements within the temperature range from 5 to 300 K for the standard entropy of vaterite at T=298.15 K a value of S^0= 93.6±0.5 J (K mol)$^{-1}$ could be determined [16].

Summarizingly, the investigations show, that:

- at the phase transition calcite is generally formed;
- vaterite reacts very sensitively to preparation effects, while in the case of aragonite no appropriate effects were observable;
- the phase transition enthalpy for aragonite in calcite is small endothermal, for vaterite, however, it is exothermal and high enough to accomplish a thermal screening of phase transition during crystallization near room temperature.

The comprehensive investigations on thermally activated solid phase transition ($A \to C$) and ($V \to C$) represent an interesting basis for kinetic evaluations. However, it is well known from literature [17], that the determination of kinetic parameters or of statements concerning the mechanism of solid-phase transition exclusively on the basis of DSC measurements at different heating rates offers only insufficient conditions for an objective evaluation. By means of mathematical criteria alone the applicability of selected model functions can only be truly confirmed in exceptional cases. It is doubtless more reliable, beside the dynamic DSC measurements to include also isothermal calorimetric investigations and results of an alternative independent method (e.g. X-ray investigations) into the kinetic evaluation.

For the two interesting thermally activated phase transitions, isothermal and non-isothermal calorimetric and roentgenographic investigations have been carried out. From the calculated curves for the fractional extent of reaction (α) as a function of temperature the activation energy E_A of phase transition has been determined model-independently for the different vaterite samples [14]. With the exception of vaterite from Na_2CO_3 a value of $E_A(V \to C)$=250±10 kJ mol^{-1} was obtained. For the easier thermally activated vaterite from Na_2CO_3 (T_{tr} near 320°C) the activation energy should be lower by about 30 kJ mol^{-1}. All the transition curves can be well described by a model corresponding to the formation and growth of nuclei of the thermodynamically stable calcite phase [14].

For the transition ($A \to C$) a value for the activation energy of $E_A(A \to C)$= 370±10 kJ mol^{-1} was obtained from thermal and X-ray investigations [17]. Compared to the previously reported one this value is still subjected to serious uncertainties, since the isothermal calorimetric investigations at present are performed at an increased experimental expenditure. The phase transition enthalpy of aragonite is so small that measurable signals during isothermal transition can be discriminated from the noise of available devices only by large-scale measurements.

Crystallization experiments

From investigations on phase formation [7, 8] and phase stability as a function of temperature and time [9, 10] it seems evident that the thermodynamically less stable crystalline phases and vaterite are converted into the stable modification of calcite. It is assumed that also NCC under the mentioned conditions transforms into one of the crystalline modifications. These crystallization processes should be investigated by an experimentally reliable method for the determination of thermodynamic and kinetic parameters. Furthermore, the effect of additives on the course of processes should be calculable. It is questionable, whether during conversion of a metastable phase in each case the thermodynamically more stable or the next less metastable phase is formed. Also a symposium on the occasion of '100 Years Ostwald Step Rule' indicated, that there are no generalizing results concerning the course of phase transition phenomena [18, 19].

For aragonite and vaterite attempts have been made to study the crystallization by means of thermal detection in a high-efficient calorimeter (Micro-DSC II, SETARAM). The investigations of aragonite were difficult, since the comparably small phase transition enthalpy in combination with the expected large transition times requires the detection of extremely low thermal efficiency. Also as a result of additional roentgenographic measurements on the starting, intermediate and final sample the following result seems reliable. Within the temperature range between 10 and 90°C naturally mineralized aragonite does not tend to transform, while synthetically prepared aragonite transforms to calcite in a solution of high ionic strength near 90°C. Since the investigated aragonite samples are responsible for these differences, further investigations are needed on the crystallization process (A → C).

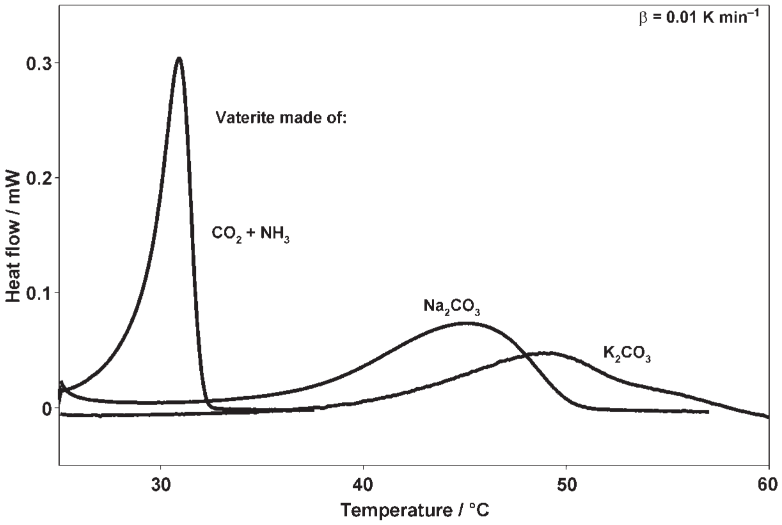

Fig. 2 Crystallization of differently precipitated vaterite via saturated solution

In comparison with aragonite interesting results on the prepared vaterite versions both as a function of temperature and of time could be elaborated by means of calorimetric screening of the transition process [15]. Measurements in the Micro-DSC II at comparable heating rates showed, that the various vaterite versions indicated a very different transformation tendency (Fig. 2). This result is also confirmed by the time dependence of transition observed at isothermal measurements. Compared with, at high temperatures, thermally activated phase transition a reversed sequence concerning starting temperature of transition is observed for the various prepared vaterites. Additional X-ray measurements confirm, that calcite is always formed during the transition of vaterite. The enthalpy of transition $\Delta_{tr}H=-3.4\pm 0.2$ kJ mol^{-1}, which follows from the calorimetric measurements, shows no sample-dependent differences and corresponds to the obtained value for phase transition from the dissolution experiments at 40°C.

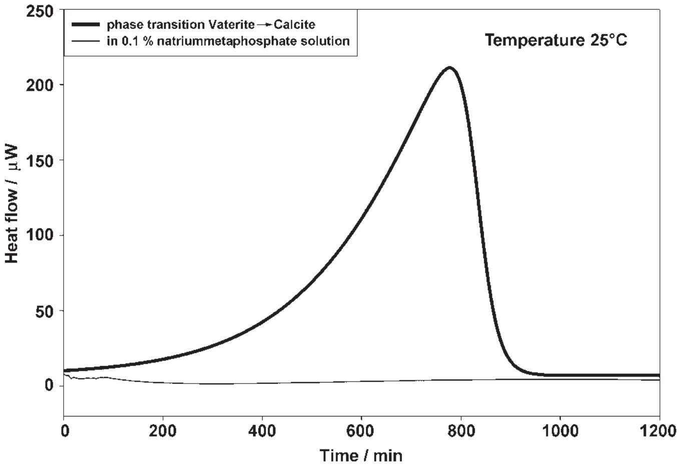

Fig. 3 Sodium metaphosphate as inhibitor of crystallization of vaterite in saturated solution

A reliable kinetic modeling of results seems to be important, for preliminary investigations to utilize the calorimetric method to study the influences of additives on crystallization processes have been successful. Thus, the reliably measurable transition of vaterite to calcite at 25°C could be completely prevented by an 0.1% addition of sodium hexametaphosphate (Fig. 3). Comparable tests on biologically interesting macromolecules as additives are under investigation at present.

Obviously, the calorimetric method substituted by X-ray investigations seems to be suitable to study the course and the sequence as well as the possibility of influencing transitions by different additives qualitatively and quantitatively. In relation to the non-crystalline calcium carbonate the importance of this method will become considerably higher.

Preparation and characterization of non-crystalline calcium carbonate

It is well known that from concentrated, oversaturated solutions of calcium chloride under the addition of sodium carbonate, first of all, amorphous, non-crystalline calcium carbonate precipitates. Already in 1916 the first experiments were published [20] and since then repeated in different versions [21–24]. Frequently, measurements of solubility or calcium ion activity for the primary precipitation product were the subject of those papers.

By the addition of crystallization inhibitors during precipitation a non-crystalline precipitate can be formed, which is stable for a longer period of time [25–30]. A further interesting version is the precipitation of carbonate from $Ca(OH)_2$ solution by introducing CO_2 [23], where recently the control of pH value and of conductivity has been found advantageous [31]. With a similar, but considerably modified method the preparation of inhibitor-free NCC was successful. Inhibitor-free material is the decisive precondition for comparing investigations on biomineralization. However, we have to point to the restriction, that the NCC produced and investigated by us has hitherto been characterized excludingly by X-ray and IR spectroscopy. Accordingly, we called the prepared samples ‘non-crystalline’ (mean grain size 40 μm). Further investigations will prove, whether non-crystalline calcium carbonate is concerned or not. Biogeneously formed and also stabilized NCC is described comprehensively [32, 33].

Thermophysical investigations (DTA/TG) of NCC were published in [24] and more recently in [34]. Especially in the latest investigations a considerable influence of the preparation conditions (pH value dependence) on temperature and transition enthalpy have been determined for thermally activated crystallization. The observed values are between $207\leq T_{tr}/°C\leq347$ and $3.9\leq-\Delta_{tr}H/\text{kJ mol}^{-1})\leq12.3$ as well. It cannot be excluded that the observed dependencies are caused by surface contaminations of the samples by $Ca(OH)_2$.

The inhibitor-free NCC prepared by us batchwise showed after preliminary investigations with the TG/DSC 111 reliably corresponding characteristics. After TG-measurements mass reduction in two steps has been observed, which is obviously related with the release of water, where the second step is within the range of crystallization temperature. The crystallization occurred thermally activated near $T_{tr}=276\pm 10°C$, where $\Delta_{tr}H=-15.0\pm3$ kJ mol^{-1} was measured for transition enthalpy. During the process of crystallization calcite is generally formed. By subsequent drying of the starting material at elevated temperature the crystallization process according to the DSC measurements could be limited to a narrower transition range, thus preventing the occurrence of provable modifications of T_{tr} or $\Delta_{tr}H$.

First experiments on the crystallization of NCC in saturated solution have also been successful. This process is much more rapid than the recrystallization of vaterite, and an enthalpy change was measured calorimetrically, which nearly coincides with the given value of $\Delta_{tr}H$ from DSC measurements for thermal activation.

Thermochemical investigations of aragonite of biological origin

Comparing investigations between synthetic and non-biological mineralization products can only be performed for aragonite, because no corresponding vaterite samples are available. The same refers to the biomineralization products. In the form of internal shells of *Sepia officinalis* larger biologically produced samples are available,

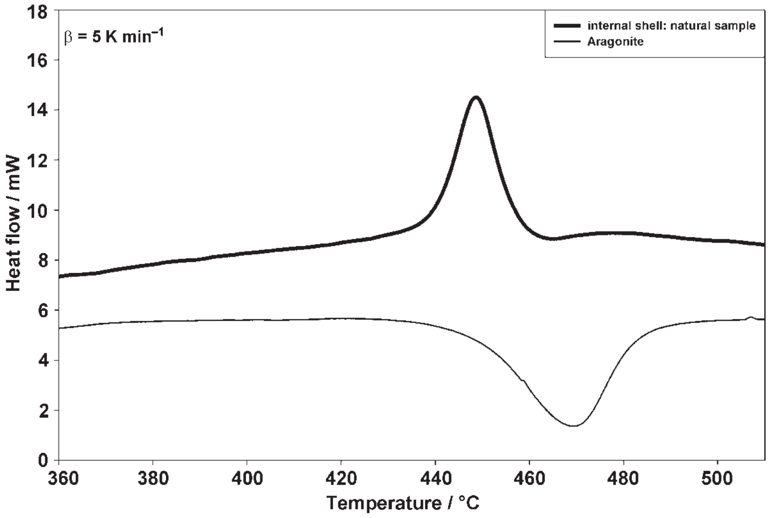

Fig. 4 Thermally activated transition of aragonite and of the starting materials of the internal shell (*Sepia officinalis*)

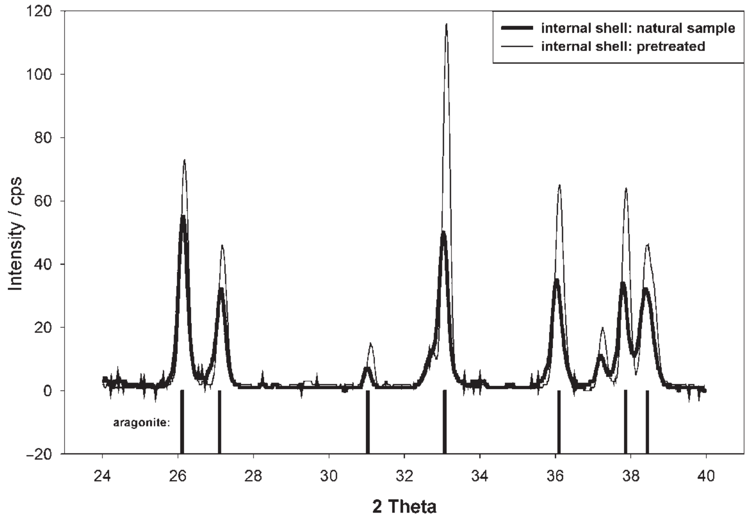

Fig. 5 Modification of the X-ray spectrum of the internal shell (*Sepia officinalis*) by pretreatment with NaOCl

which prove to be almost phase-pure aragonite in X-ray diffraction investigations. Small amounts of halite, which are provable in the untreated starting substance no longer occur already after cleaning of the powdered sample with water. Corresponding to analytical investigations with EDTA much more than 90 mass% $CaCO_3$ was present in the starting substance. The thermogravimetric analysis showed up to 400°C a mass loss of the starting substance by about 6 mass%. Combined DSC/TG measurements in oxidizing (air) and non-oxidizing (CO_2) atmosphere with heating rates of 5 K min^{-1} up to 500°C prove, that the observed mass loss, first of all, occurs due to endothermal water release and, furthermore, to exothermal combustion of organic impurities. Predrying for 3 h at 260°C reduces the water content, but does not eliminate it completely, as the differences of measurement in air and CO_2 atmosphere indicate it.

The observation of an exothermal effect at the DSC measurements near T=440°C was much more striking, the temperature $T_{tr}(A \rightarrow C)$ for the thermally activated, endothermal phase transition of aragonite (Fig. 4). Since the starting substance according to X-ray investigations was converted into calcite in all the cases, it has been assumed that an exothermal process supercompensates the endothermal transition of aragonite into calcite. Although this exothermal effect is not accompanied by a mass change, it has been first tried to eliminate organic intercrystalline matrix from the starting material. It is well-known, that organic components of the starting substance can be eliminated by pretreatment at 100°C with H_2O_2 [35] or with NaOCl [36]. In the case of the internal shell the DSC measurements show that after a pressure digestion with NaOCl at 180°C a considerable reduction of the organic matrix is provable, and the observed exothermal effect near $T_{tr}(A \rightarrow C)$ is considerably decreased.

The steady X-ray control of the sample showed, that by pretreatment no calcite is formed, however the intensities corresponding to aragonite, are markedly increased (Fig. 5). The assumption that the increase of the aragonite content in the pretreatment is caused by the crystallization of non-crystalline calcium carbonate being present in the internal shell, seems to be probable also as a consequence of a Rietveld analysis. Accordingly, the starting substance should contain about 4 mass% of non-crystalline material. Since meanwhile we succeeded in the preparation of inhibitor-free NCC and thus in the determination of crystallization enthalpy, it could be shown on the basis of this enthalpy value that the unexpected exothermal peak (Fig. 4) at $T=T_{tr}(A \rightarrow C)$ should be accomplished by the crystallization of the NCC content in the starting substance. The decrease of the exothermal peaks after pretreatment is understandable as the result of decreasing non-crystalline fractions and thus increasing aragonite fractions.

It has to be the subject of further investigations, to completely control these assumptions and to investigate problems of the process of crystallization of NCC depending on inhibitors or stabilizers. In the biological material of *Sepia officinalis* the crystallization of the residual NCC takes place with the transition of aragonite and thus compared with the NCC prepared by our tests at about 200°C higher. It also remains to be elucidated, why by pretreatment with NaOCl from NCC additional aragonite is formed.

The present phases of the calcium carbonate, the experimental orders and the available results are a necessary basis for further extensive investigations on the possibility to influence the process and sequence of phase transitions in the calcium carbonate system.

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