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THERMAL ANALYSIS OF CALCITE EQUILIBRATED WITH AQUEOUS SOLUTIONS OF MAGNESIUM, STRONTIUM, BARIUM AND ZINC CHLORIDES

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ABSTRACT

The interactions between calcite particles and aqueous solutions containing $MgCl_2$, $SrCl_2$, $BaCl_2$ and $ZnCl_2$ in various concentrations were investigated by thermal analysis of the solid fraction (TGA and DTG). In these systems calcite powder had been equilibrated with the solution for twenty days while the suspension had been shaken before the thermal treatment. Topochemical substitution of Ca by Mg or Zn was detected from the shift of the decarboxylation DTG peak to lower temperatures. This shift is correlated with the amount of sorbed Mg or Zn. Such a correlation was not observed with Sr or Ba and it was concluded that in these systems topochemical substitution played only a minor role during the interactions between calcite and these cations.

INTRODUCTION

In previous publications the interactions between calcite particles and aqueous solutions of different salts were studied by percolation and equilibration techniques[1-3]. In the first system the aqueous solutions were continuously percolated by slow gravity flow through a coloumn of calcite. In the second system the aqueous solutions were shaken together with the ground calcite for 3, 10 or 20 days. The resulting products depended on whether the reaction was carried out in the percolation or the equilibration technique. After equilibrating calcite with 1M solutions of $SrCl_2$, $BaCl_2$ and

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$ZnCl_2$, new carbonate phases strontianite, witherite and smithsonite, respectively, were identified by X-ray diffraction and by IR spectroscopy. However, they were obtained in very small amounts relative to that of calcite. No new phase was detected either by X-ray or by IR spectroscopy after equilibrating calcite with $MgCl_2$.

During these studies we found that in addition to the formation of new phases, sorption of the various metallic cations by the calcite and the release of Ca into the aqueous solutions also occur. These sorption reactions may be topochemical substitutions of crystalline Ca by the different cations (absorption) but they may also be surface reactions (adsorption), namely, cation exchange of Ca or H by the cations of the soluble chloride salts, and specific or hydrolytic adsorptions[4]. It is expected that cation exchange and specific adsorption will have no effect on the decarboxylation of the calcite. On the other hand, topochemical substitution should lead to shifts in the decarboxylation temperature[5,6]. In order to obtain a better understanding of the sorption mechanism, we studied the thermal properties of calcite by TGA and DTG, after its equilibration with salt solutions of various concentrations.

EXPERIMENTAL

A natural calcite from Makhtesh Ramon, Israel was used in the present study. It was ground to 840 µm. The equilibration method was previously described[1-3]. 20 ml of aqueous solutions containing 0.10, 0.25, 0.50 and 1.00M of chloride salts were added to 10 g ground calcite samples. The suspension was then shaken for 20 days. At the end of this period the solid fraction was thoroughly washed, air dried and analyzed on a Mettler TA 3000 (TGA and DTG). 10 mg air-dried samples were used for each run. Samples were dissolved by HCl and Mg, Ca, Sr, Ba or Zn were determined by atomic absorption (Perkin Elmer 403).

RESULTS AND DISCUSSION

Chemical analysis of the solid samples showed that the metallic cations of the various salts were sorbed by the calcite particles (Table 1). The sorbed cations may be located either on the external surfaces of the calcite crystals (adsorption), or substituting Ca cations inside the calcite crystal (absorption), or they may form separate phases. In the present study the concentrations of the various salts which were used for the equilibration, were very small compared to their concentrations in our previous studies[1-3] and only small amounts of the new carbonate phases precipitated. $BaCO_3$ is the least soluble of the carbonates studied here, and consequently it shows by XRD the highest concentrations in the solid fraction, relative to the other carbonates. The decarboxylation peak of witherite is located at about 755°C, but cannot be detected for small amounts of witherite because it is obscured by the calcite peak. It is clearly seen in the DTG curve of the 1M $BaCl_2$ treated calcite. Extremely small peaks at 845 and 860°C in the DTG curves of $SrCl_2$ and $ZnCl_2$ treated calcite, respectively, can be due to the presence of negligible amounts of new carbonate phases. The latter shifts to 905°C with increasing Zn concentrations.

TABLE 1
Concentration of M^{2+} (M = Mg, Sr, Ba or Zn) in natural calcite and calcite equilibrated with 0.10, 0.25 and 0.50 molar solutions of MCl_2 (expressed in m mole M^{2+} per mole Ca^{2+}), temperature range of decarboxylation reaction (in °C), DTG peak maximum (in °C) and weightloss (from TGA, in weight%)

Salt in equilibrium system	Concentration of aqueous solution (in M)	Concentration of sorbed M^{2+} in calcite, in M^{2+}/Ca^{2+} molar ratio $\times 10^{-3}$	Temperature range of decarboxylation (in °C)	Peak temp. (in °C)	Weight loss (weight%)
Natural calcite		7*	604 - 866	790	43.4
$MgCl_2$	0.10	11	601 - 854	787	41.5
	0.25	13	602 - 836	771	40.0
	0.50	15	595 - 832	767	38.9
$SrCl_2$	0.10	6	608 - 853	777	42.1
	0.25	7	605 - 855	794	42.5
	0.50	3	575 - 869	782	42.2
$BaCl_2$	0.10	20	593 - 854	795	42.0
	0.25	24	601 - 858	794	42.0
	0.50	26	603 - 861	765	39.8
	1.00	39	600 - 840	755,785	
$ZnCl_2$	0.10	9	613 - 846	783	40.6
	0.25	22	588 - 825	763	42.0
	0.50	37	589 - 807	758	39.0

* Mg in natural calcite

In our previous study[3] the presence of $BaCl_2.2H_2O$ in the 1M $BaCl_2$ treated calcite and of $Zn_5(OH)_8Cl_2$ in the 1M $ZnCl_2$ treated calcite were identified by IR, XRD and DTA. In the present study the presence of $BaCl_2.2H_2O$ was shown by the DTG curve (90°C) only after equilibration of the calcite with a 0.5M solution whereas the presence of $Zn_5(OH)_8Cl_2$ (160°C) was shown after equilibration of the calcite with only 0.25M solution. In both cases the peaks were extremely small indicating that negligible amounts of these salts were formed. It may therefore be concluded that the greatest fraction of the metallic cations which are determined in the solid samples do not form separate phases, but are part of the calcite phase.

The principal peak in the DTG curve of untreated calcite is between 604 and 866°C, with a maximum at 790°C. This peak is due to the decarboxylation of the calcite. It is associated with a weightloss of 43.4%.

All samples of calcite equilibrated with the various salt solutions, show the characteristic decarboxylation DTG peak of this mineral. Weightloss which is associated with this peak, becomes smaller after the equilibration. In most of the DTG curves the location of this peak was shifted in relation to the peak of the pure calcite. Table 1 summarizes temperature ranges and locations of the DTG peak maxima of the decarboxylation reaction. The Table also shows the concentrations of the "foreign" cations in the calcite (expressed in molar ratio between the substituting cation and Ca). The Table shows that in the case of Mg and Zn, there is a correlation between the amount of sorbed cation and the location of the peak. The latter shifts to lower temperatures with increasing sorption. These two metallic cations possess radii smaller than that of Ca and their carbonate salts form crystals with the calcite structure. It is therefore concluded that the shift in the location of the decarboxylation peak maximum is due to topochemical substitution of Ca with these cations which occurs during the equilibration.

Sr and Ba have radii larger than that of Ca and their carbonate salts crystallize with the aragonite structure. In the case of Ba, after the equilibration of the calcite with a 1M solution, the DTG curve showed two peaks at 755 and 785°C. The former may be attributed to the witherite and the latter to calcite with a small topochemical substitution of Ca by Ba. After equilibration of the calcite with a 0.5M solution, the DTG curve showed one peak at 765°C. This peak results from the overlapping of the decarboxylation peaks of both species, calcite and witherite.

In the case of Sr we did not obtain a correlation neither between the concentration of the equilibrium solution and the sorbed Sr nor between the latter and the location of the decarboxylation peak. On the other hand, the shoulder at 845°C, which may be attributed to strontianite, intensifies with the concentration of the equilibrium solution and the end of the decarboxylation peak shifts to higher temperatures (Table 1), indicating that more strontianite is formed. Scanning microprobe analysis of the treated samples showed that small amounts of the sorbed metallic cation were equally dispersed on the whole calcite crystals. We suggest that in this system the "specific" adsorption of Sr on the surface of the calcite crystal is more significant than the topochemical substitution.

CONCLUSIONS

During the equilibration of calcite with aqueous solutions of $MgCl_2$, $SrCl_2$, $BaCl_2$ or $ZnCl_2$ topochemical substitution of Ca by the various cations may occur. This substitution shifts the decarboxylation peak of the calcite to lower temperatures. Topochemical substitution of Ca by Mg or Zn is significant. The radii of these two elements are smaller than that of Ca but the crystal structure of their carbonates is similar to that of calcite. In the case of Ba, whose radius is larger than that of Ca, the precipitation of witherite is the principal reaction which occurs during the equilibration. Witherite has the aragonite crystal structure. It is the least soluble of the carbonates studied here. In the case of Sr whose radius is only slightly larger than that of Ca, the thermal analysis did not supply conclusive results on topochemical substitution and it seems that the "specific" adsorption of Sr on the surfaces of the calcite crystals is more significant than the topochemical substitution.

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