Transformation of Vaterite into Cubic Calcite in the Presence of Copper(II) Species

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By a simple washing of vaterite with ultrapure water, it transforms rapidly into cubic calcite. When the solid is washed with Cu^{2+} solutions, the transformation depends on the concentrations of the copper solutions applied in the process. For concentrations of 10^{-4} mol dm^{-3}, a certain delay in the transformation process is detected, and the obtained cubic calcite seems to be in the form of $Cu_xCa_{1-x}CO_3$. For concentrations of 10^{-3} mol dm^{-3}, the vaterite structure remains stable with time, and this stability seems to be correlated with the saturation of the surface by Cu^{2+} in place of Ca^{2+}. For concentrations of 10^{-2} mol dm^{-3}, a mixture of vaterite, aragonite, cubic calcite, and malachite is obtained during the transformation process.

Introduction

Vaterite and cubic calcite are two different forms of calcium carbonates ($CaCO_3$). The first one possesses an orthorhombic structure, whereas the second a rhombohedral structure. It is well-known that the vaterite transforms into cubic calcite by simple washing with water.[1−8]

Copper adsorption on carbonate surfaces has received significant attention during the past two decades. For instance, Heydemann[9] found that the adsorption of Cu^{2+} onto calcite surfaces is complex indicating a mechanism of multiple steps. Kitano et al.[10] found that the extent of copper adsorption on calcite is much less significant in sea water than in pure water and depends on the preparation procedures that are used. Terjesen et al.[11] demonstrated that copper is capable of significantly influencing dissolution rates of $CaCO_3$. Franklin and Morse[12] showed that in distilled water Cu sorption into calcite is 90% complete during the first 3 min of interaction. The general behavior found for Cu^{2+} and Mn^{2+} on calcite surfaces shows certain differences. Indeed, in the interaction of manganese with calcite, the coprecipitate $Ca_xMn_{1-x}CO_3$ is observed to form in sea water, while relatively pure $MnCO_3$ is formed in distilled water. In contrast to results concerning copper, the same authors noted that copper uptake is directly proportional to the concentration of Cu^{2+} in solution. In this context, a precipitate in form of $Cu_xCa_{1-x}CO_3$ may then be deposited on the calcite surface. Morse[13] reported that in distilled water, the amount of adsorbed copper on calcite increases linearly with the concentration of Cu remaining in solution. He also indicated that removal of Cu from solution may be due to the formation of a precipitate on the calcite surface since the total Cu adsorbed concentration exceeds that needed for monolayer coverage.

In a recent work,[8] it was demonstrated that the presence of Cu^{2+} ions at low concentrations (10^{-4} mol dm^{-3}) in vaterite can be used as probes to follow the transformation of this solid into cubic calcite in pure water as a function of time. These ions do not form a precipitated phase on vaterite and cubic calcite, but they interact favorably with the $CaCO_3$ structure. Indeed, when a Cu^{2+} solution is added onto vaterite, these are stages of removal of the metal from solution. An initial rapid uptake occurs in the first few minutes, while

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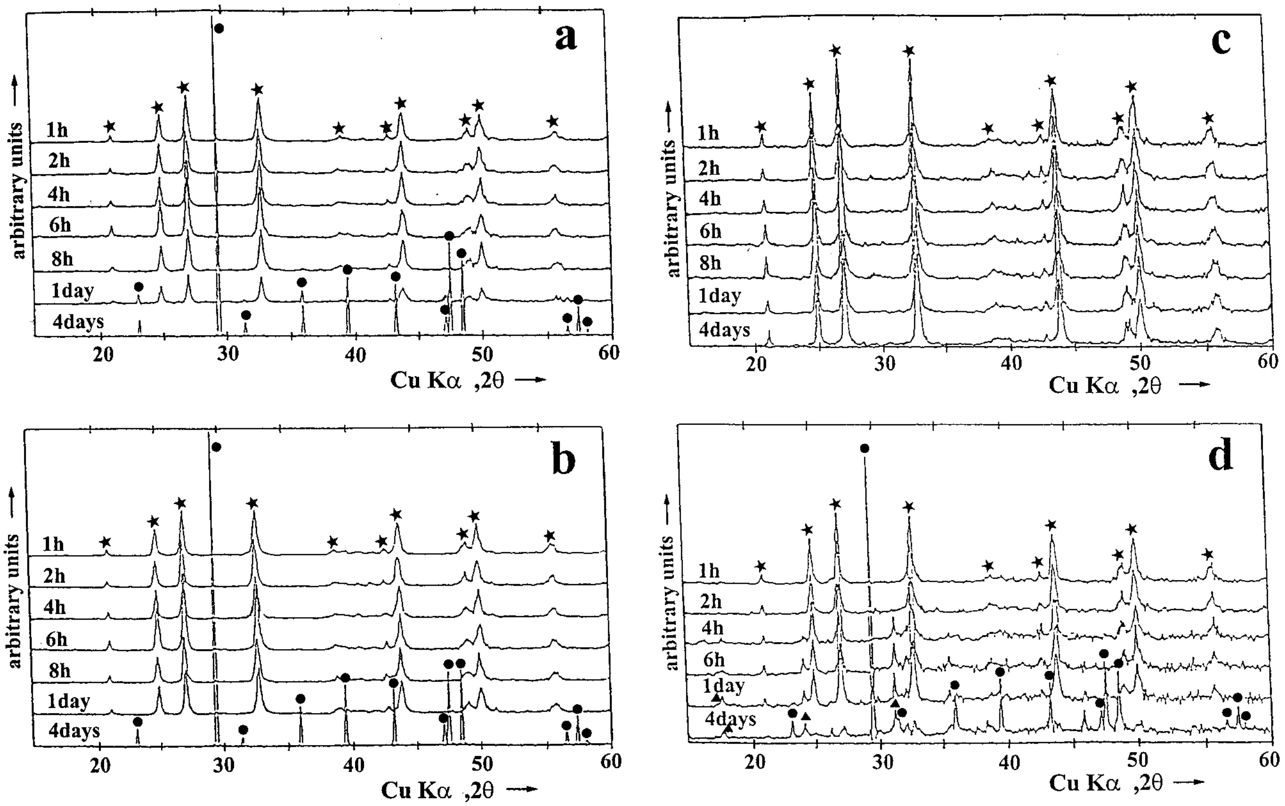

Figure 1. XRD patterns obtained during the transformation process of vaterite as a function of time after washing the solids with (a) pure Milli-Q water; (b) 10^{-4} mol dm^{-3}; (c) 10^{-3} mol dm^{-3}; (d) 10^{-2} mol dm^{-3} Cu^{2+} solutions. (★) vaterite; (●) cubic calcite; (▲) malachite.

during a second stage there is apparently a relative slowing of the uptake process until the mineral sites are saturated with metal ions. The amounts of copper adsorbed on the carbonates increase with concentration of the specific metal, and an increase in the calcium concentration of the filtrate is also observed. This phenomenon is due not just to the dissolution of the carbonate but also to an exchange process between Ca and Cu in the solid structure.

The purpose of this work is to investigate by different spectroscopic techniques the behavior of copper(II) ions of different solution concentrations added onto vaterite during its transformation into cubic calcite in pure water.

Experimental Section

Cu^{2+}/vaterite samples with different copper(II) concentrations are prepared in ultrapure water, by adding 10^{-4}, 10^{-3}, and 10^{-2} mol dm^{-3} of $CuCl_2$ solutions to a known amount of vaterite (2 g/0.5 dm^3). These latter solutions are shaken to obtain homogeneous carbonate phases at 293 K. Samples are filtered at different lapses of time on a 45 μm Sartorius filter. Subsequently, they are studied by the following techniques.

Ultrapure water is prepared as follows: A Milli-Q Plus water purification system (Millipore) is currently used in our laboratory to provide up to 1.5 L/min of ultrapure water on demand for chemical analysis and synthesis. A $QPAK_2$ purification pack (Millipore) is used for this compact Milli-Q Plus system pretreated by resin deionized water; it contains a 0.5 μm prefilter to protect other purification media from colloidal, organic, bacterial, pyrogenic, and particulate contamination often entrained in water pretreated by regenerated ion-exchange resin; this pack also contains activated carbon, nuclear-grade ion-exchange resin and Organex-Q organic scavenger mixture.

The scanning electron micrographs of the solids during their different phases of transformation are taken on a JEOL JSMT 330A microscope. Each sample is ground to a fine powder which is suspended in water.

The specific areas of solids are determined by the BET method using a Quantasorb Junior apparatus, and the gas adsorbed at 77 K is pure nitrogen.

The structures of solids are analyzed by X-ray diffraction (XRD) techniques in a Siemens D5000 diffractometer equipped with a copper anode. Such an apparatus allows working with samples under a given atmosphere at different temperatures. The values of 2θ are used to estimate the observed reflections of maximum intensity.

Infrared (IR) spectra are scanned on a Perkin-Elmer FTIR Model 1600 spectrophotometer. The pressed samples are obtained using KBr disks, each one containing 1.5 mg of sample + 120 mg of KBr.

The electron paramagnetic resonance (EPR) measurements are performed at 77 and 293 K on a Varian E9 spectrometer. A cavity operating with a frequency of 9.3 GHz (X-band) is used. The magnetic field is modulated at 100 kHz. Precise g values are determined by comparison with a reference sample ($g = 2.0028$).

Results and Discussions

X-ray Diffraction. Figure 1 shows the changes in X-ray diffraction (XRD) patterns of Cu/vaterite during its transformation into cubic calcite. In the absence of copper and before washing, the XRD spectrum obtained is characteristic of the vaterite phase. After 6 h of washing, certain lines corresponding to the cubic calcite phase appear, whereas the intensities of those corresponding to vaterite decrease. A complete transformation of vaterite into cubic calcite is achieved after 24 h of washing. This observation is already confirmed by other techniques in a previous study.[8]

When vaterite is washed with Cu^{2+} ion solutions, the rate of the transformation process of this solid into cubic calcite is much slower when compared to that observed in the transformation of the pure solid. The time of the transformation rate increases with an increase of copper concentration on the vaterite solid.

The transformation into cubic calcite needs more than 24 h when vaterite is washed with a 10^{-4} mol dm^{-3} Cu^{2+} solution. Only two phases of vaterite and cubic calcite are observed by the XRD technique during this transformation process. Such a result indicates that copper is incorporated into the cubic calcite structure in place of Ca to give a solid solution of $Cu_xCa_{1-x}CO_3$. Franklin and Morse[14] have already demonstrated the formation of this latter solid when a Cu^{2+} solution is added to cubic calcite.

When vaterite is washed with a 10^{-3} mol dm^{-3} Cu^{2+} solution, the transformation is not observed even after a long time of washing. Only the XRD lines ascribed to vaterite are detected. The solid structure is then stable for this concentration of copper. This stability seems to be related to the surface saturation of Cu^{2+} in place of Ca^{2+} leading therefore to the formation of one layer or more on the vaterite surface which would be responsible of the nontransformation of the solid.

When vaterite is washed with a 10^{-2} mol dm^{-3} Cu^{2+} solution, another phase besides vaterite and cubic calcite is detected during the transformation process. Indeed, after 4 h of washing, broad XRD lines with weak intensities appear in addition to those already attributed to vaterite and calcite phases. These new lines are assigned to the malachite phase [$Cu_2(CO_3)(OH)_2$]. But, since these lines are broad and weak, these XRD characteristics indicate the presence of the malachite phase in the form of a not well-crystallized solid. The amount of the new solid reaches a maximum after 24 h of washing. The malachite possesses a monoclinic structure where there are four molecules in one unit. In this structure, there are two slightly different sites of copper where each copper has two hydroxyl and two carbonate oxygen atoms as neighbors, approximately at the corners of a square. In addition, one copper has two more oxygen atoms whereas the other has two additional hydroxyls.

The formation of malachite phase during the transformation process of vaterite is probably due to the presence of Cu^{2+} ions in excess in solution and its acid character. Indeed, in one side, the formation of such a phase is observed at high copper(II) concentrations ($>10^{-3}$ mol dm^{-3}) rather than at low ones. Franklin and Morse[16] have demonstrated that the uptake of copper by the surface of calcite is directly proportional to the concentration of Cu in solution. From a concentration of 1.3×10^{-5} mol dm^{-3}, a precipitate of the form $Cu_xCa_{1-x}CO_3$ may be deposited onto the calcite surface in distilled water, whereas in sea water a malachite phase can be formed. Since in our case, the formation of malachite is obtained in distilled water, this result is in disagreement with the suggestion of Franklin and Morse.[16] On the other side, when a 10^{-2} mol dm^{-3} Cu^{2+} solution is added to vaterite, the pH value is about 4.8 and remains constant until 24 h of washing; subsequently it increases to finally reach a value of 7.3. The acid character of the solution that remains for a relatively long time in contact with the vaterite surface is probably responsible for the solid surface dissolution and the formation of the malachite phase. Conversely, such a phenomenon cannot be detected with lower copper(II) concentrations (10^{-4} and 10^{-3} mol dm^{-3}) because in both cases the initial pH values measured increase rapidly from 5.0 to 7.2 within only a few seconds of contact between the copper solution and the vaterite.

Scanning Electron Microscopy (SEM). Figure 2 illustrates the SEM images taken after washing the vaterite with a solution of 10^{-2} mol dm^{-3} of Cu^{2+} ions at different lapses of time. The image exhibits clearly the presence of four phases: remaining vaterite in small amounts; transformed cubic calcite; aragonite (needle-like structure); and malachite (in the form of small particles deposited on other phases).

When vaterite is washed with a 10^{-3} mol dm^{-3} Cu^{2+} solution, the corresponding SEM image reveals that vaterite remains stable after washing for a relatively long time (ca. 4 days) with Milli-Q water.

Specific Areas. Figure 3 shows the variation of specific areas of vaterite washed with different copper(II) concentrations. In the absence of Cu^{2+} ions in solution, the specific area changes from 16.7 to 2.0 m^2 g^{-1} when vaterite transforms completely into cubic calcite.[8]

When vaterite is washed with a 10^{-4} mol dm^{-3} Cu^{2+} solution, the area decreases slightly (15.7 m^2 g^{-1}) after a washing period of 3 days. This result can be explained by the formation of a $Cu_xCa_{1-x}CO_3$ solid solution when Cu^{2+} ions replace Ca^{2+} ions on the surface of $CaCO_3$ particles during the transformation process of vaterite. This phase is completely different from that obtained when Cu^{2+} ions are directly added on a pure cubic calcite. Indeed, the specific area obtained in this case (2.4 m^2 g^{-1}) is slightly higher than that determined for a pure cubic calcite (2 m^2 g^{-1}). Therefore, the copper ions replace only the calcium ions of the cubic calcite surface without incorporation into the bulk of the solid.

When the vaterite is washed with a 10^{-3} mol dm^{-3} Cu^{2+} solution, the specific area increases from 16.7 to 24.4 m^2 g^{-1}. Compared to that obtained above, this high value can be explained by a complete replacement of Ca^{2+} by Cu^{2+} on the vaterite surface. In this case, all the Ca^{2+} ions are replaced by Cu^{2+} ions, forming then a layer of $CuCO_3$ on the solid surface. These species, which form barriers between the spherical vaterite particles, stop the dissolution of the vaterite process and as a consequence stop the transformation process. When such a solution is used to wash directly pure cubic calcite, the specific area obtained (2.8 m^2 g^{-1}) is completely different from that obtained for vaterite. This result confirms that the vaterite structure remains stable for this Cu^{2+} concentration.

After washing the vaterite with a 10^{-2} mol dm^{-3} Cu^{2+} solution, the specific area increases to 33.4 m^2 g^{-1}. This increase is closely related to the formation of the malachite phase after the achievement of the transfor-

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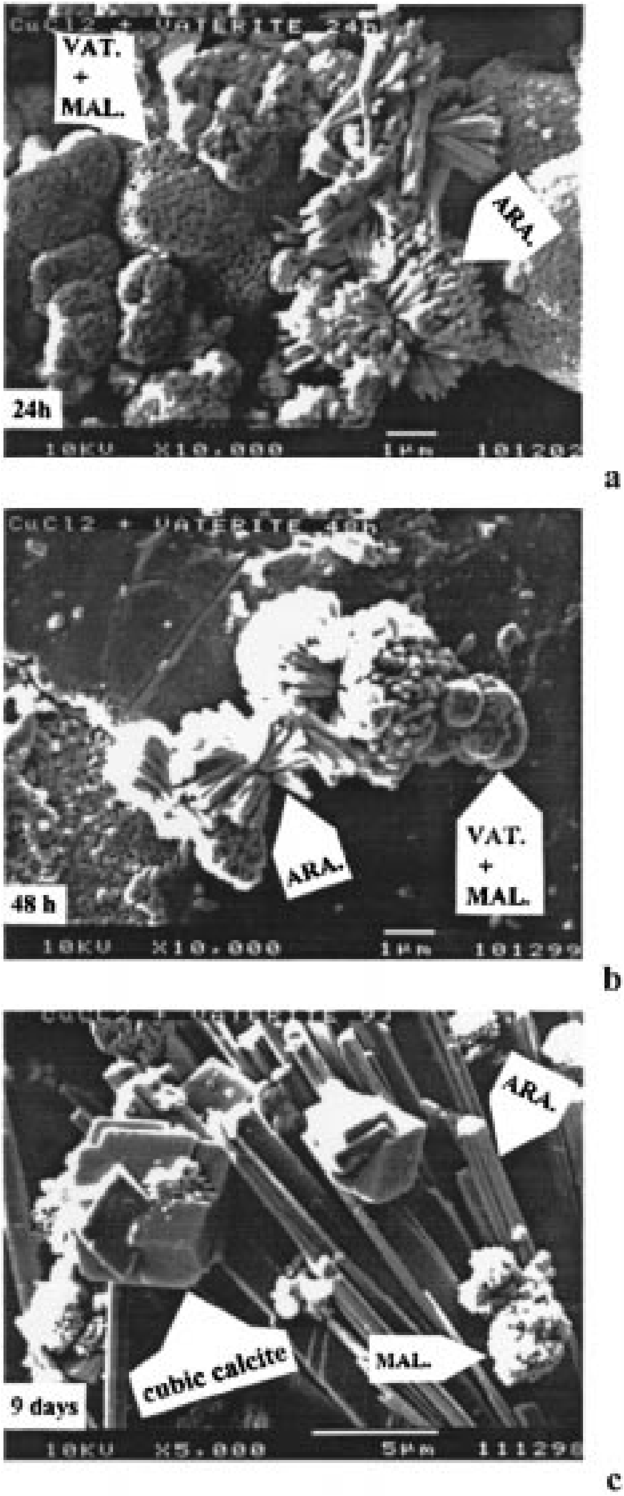

Figure 2. Scanning electromicrograph of vaterite taken after washing solids with a 10^{-2} mol dm^{-3} Cu^{2+} solution for (a) 24 h, (b) 48 h, and (c) 9 days. Vat.: spherical micropellets; Ara.: needlelike structures; Mal.: small particles deposited on other phases; cubic calcite: rhombohedric crystals.

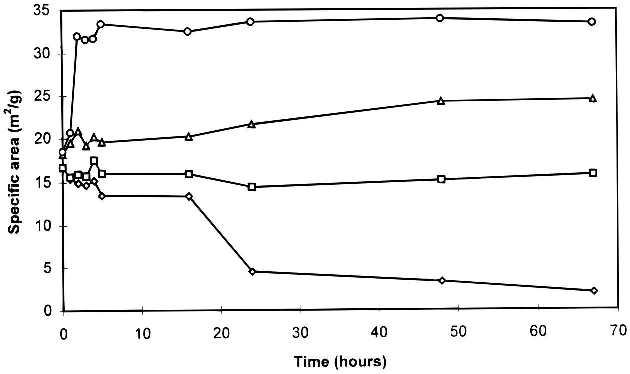

Figure 3. Variation of the specific surface area during the transformation process of vaterite as a function of time after washing solids with (◇) pure Milli-Q water; (□) 10^{-4} mol dm^{-3}; (△) 10^{-3} mol dm^{-3}; (○) 10^{-2} mol dm^{-3} Cu^{2+} solutions.

mation process. Indeed, XRD techniques show that non-well-crystallized malachite forms during the washing of vaterite with a high copper concentration (10^{-2} mol dm^{-3}); in addition, malachite prepared in the laboratory at 293 K is generally amorphous and has a specific area of about 55 m^2 g^{-1}, whereas well-crystallized malachite (as a natural malachite or a solid obtained after calcination under air at 1073 K of amorphous $Cu_2(CO_3)(OH)_2$ solids) possesses a specific area of about 1 m^2 g^{-1}. After the transformation process, XRD data show the presence of a malachite phase as well as vaterite and calcite at the same time. The simultaneous presence of these three phases can explain why the specific area (33.4 m^2 g^{-1}) obtained after the washing is lower than 55.4 m^2 g^{-1}. In addition, when pure cubic calcite (2 m^2 g^{-1}) is washed with such a solution, the specific area of the concerned solid drastically increases to 33 m^2 g^{-1}. This value is nearly the same as that obtained in the case of vaterite. Such a result also indicates the formation of the malachite phase directly from cubic calcite. Consequently, the acid character of the 10^{-2} mol dm^{-3} Cu^{2+} solution is responsible, as in the case of vaterite, the dissolution of cubic calcite.

From these results, it is obvious that the copper ions replace the calcium ones in vaterite before its transformation into cubic calcite. For a low copper concentration, all the Ca ions on the surface are not totally replaced by Cu^{2+} and the transformation into cubic calcite is possible. On the contrary, when all the Ca^{2+} ions on the vaterite surface are substituted, the course of the transformation is stopped.

Infrared. Figure 4 shows the IR spectra obtained after washing vaterite with different Cu^{2+} solution concentrations. When vaterite is washed with a 10^{-4} mol dm^{-3} Cu^{2+} solution, the transformation of vaterite into cubic calcite is similar to that obtained for pure vaterite.[8] The band at 744 cm^{-1}, which is characteristic of vaterite, disappears with time whereas the 712 cm^{-1} band attributed to cubic calcite appears. For washing with a 10^{-3} mol dm^{-3} Cu^{2+} solution no change in the general features of the IR spectrum attributed to vaterite is observed with time during washing. This finding confirms that vaterite remains stable for this copper concentration. On the contrary, for washing with a 10^{-2} mol dm^{-3} Cu^{2+} solution, the IR spectrum of vaterite changes. The spectrum obtained is in fact the superposition of two spectra: the first one is characterized by a band of 712 cm^{-1} and is attributed to cubic calcite; the other is assigned to both malachite and aragonite with specific IR bands at 817 and 855 cm^{-1}, respectively. These bands are assigned from IR spectra recorded separately for the above-mentioned solids (Figure 5).

EPR. Figure 6 shows the EPR spectra obtained when vaterite is washed with a 10^{-2} mol dm^{-3} solution. All

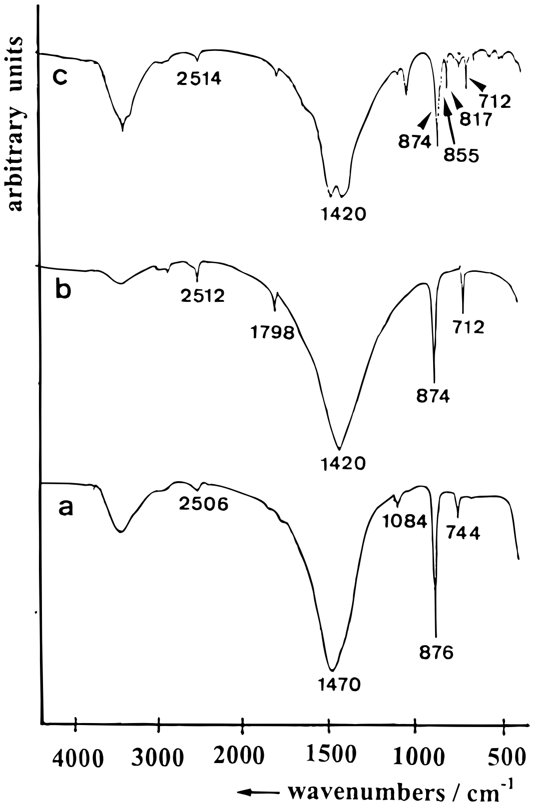

Figure 4. IR spectra obtained during the transformation process of vaterite as a function of time after washing solids with (a) 10^{-3} mol dm^{-3}; (b) 10^{-4} mol dm^{-3}; (c) 10^{-2} mol dm^{-3} Cu^{2+} solutions.

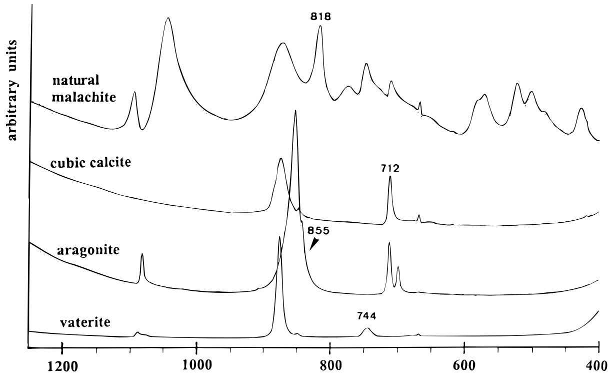

Figure 5. IR spectra recorded for vaterite, aragonite, cubic calcite, and natural malachite.

the signals observed correspond, without ambiguity, to isolated clusters of Cu^{2+} ions.[15-18]

For vaterite washed with a 10^{-4} mol dm^{-3} solution, the spectra obtained after washing the solid were widely studied in previous work.[8] Briefly, before washing the solid, the copper(II) ions are isolated in vaterite and localized in sites with distorted octahedral symmetries and 5-fold coordination. After washing the solid, clusters of Cu^{2+} are formed from the isolated species and are localized in the bulk of the cubic calcite.

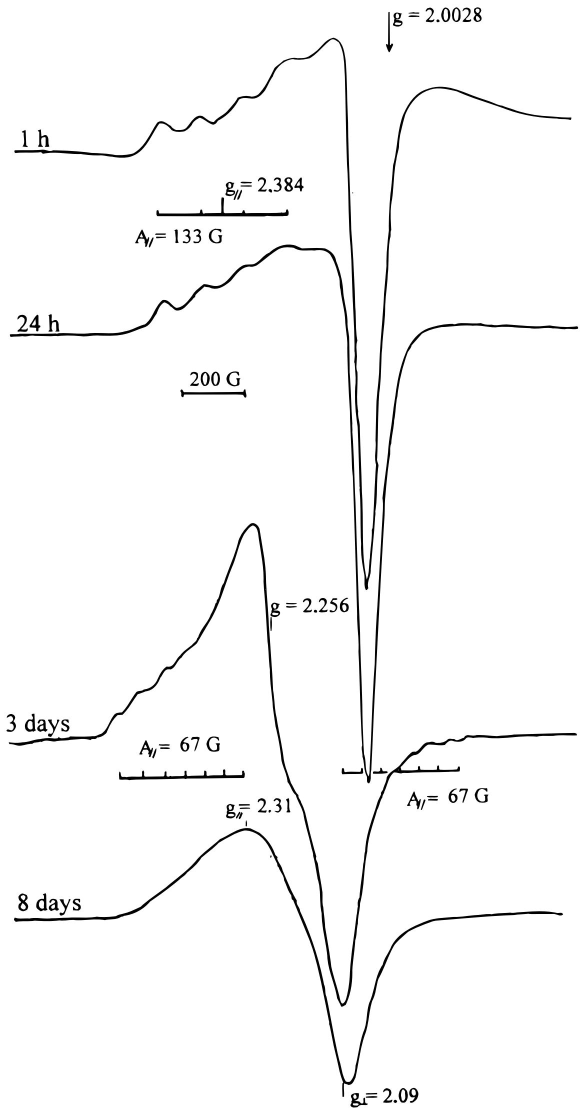

Figure 6. EPR spectra recorded at 77 K of vaterite after washing solids with a 10^{-2} mol dm^{-3} Cu^{2+} solution.

When vaterite is washed with a 10^{-3} mol dm^{-3} solution, the spectrum obtained is similar to that observed in the case of vaterite containing a low copper concentration ($g_{\|} = 2.384$; $g_{\perp} = 2.078$; $g_{iso} = 2.180$; $A_{\|} =$ 133 G; $A_{\perp} = 30$ G; $A_{iso} = 64$ G). After washing, this signal does not change with time even after 10 days. This phenomenon can be explained by the stability of the vaterite structure for such a copper concentration. These results confirm those obtained for this solid using XRD technique where no transformation of vaterite phase after washing is detected. In addition, since only one signal of isolated Cu^{2+} ions is detected and it is similar to that obtained in the case of 10^{-4} mol dm^{-3} solution, it is then evident to suggest that all the Ca^{2+} ions of vaterite are replaced by copper(II) leading then to the formation of a $CuCO_3$ layer as a coating which would be responsible for structure stability of vaterite.

For vaterite washed with a 10^{-2} mol dm^{-3} solution, the EPR signal observed after 24 h of washing is similar to those obtained with the preceding solutions. After 3 days of washing, the signal transforms into a complex spectrum constituted of three signals. The first one is symmetric ($\Delta H = 75$ G) and centered at $g = 2.256$ with a weak anisotropic feature and inverted g values ($g_{\|} <$

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$g_\perp$); the second one is strongly anisotropic with an axial symmetry ($g_{\|} = 2.31$; $g_\perp$=2.09) and is manifested by the absence of the hyperfine structure arising from the coupling between the single electron and the nuclear spin of copper(II) ($I = {}^3/_2$); and the third is identified by the presence of numerous weak lines in each side of the spectrum which are separated by ca. 67 G. For a long time of washing, the intensity of the first signal decreases and finally disappears after 8 days, whereas that of the third one remains relatively weak.

The first signal is similar to that already obtained when vaterite is washed for a period of 8 days with a 10^{-4} mol dm^{-3} Cu^{2+} solution.[8] This signal was attributed to Cu^{2+} ions located in rhombohedral sites in cubic calcite. Contrary to that observed for a low copper concentration, this signal disappears after washing the solid for 8 days with the 10^{-2} mol dm^{-3} Cu^{2+} solution and the intensity of the second signal increases. Since the two signals are correlated, it is then evident to attribute the second one to specific sites of copper(II) in calcite after complete structural stabilization of this latter solid.

Since after the transformation process of vaterite, the malachite phase is formed in a small amounts with cubic calcite, it is then interesting to attribute an EPR signal to copper(II) present in solid [$Cu_2(CO_3)(OH)_2$]. Since the Cu^{2+} signal, which is observed at the beginning of washing of vaterite, has a parallel hyperfine splitting constant (133 G) nearly double that observed for the weak narrow lines (67 G) obtained after washing the solid, this suggests that the third signal corresponds to a dimer of Cu^{2+} ions.[19] Fine structure is not observed because the intensity of the corresponding signal is relatively weak when it is compared to that attributed to copper(II) in cubic calcite. Such a dimer can be assigned to copper(II) species in the malachite phase [$Cu_2(CO_3)(OH)_2$]. In fact, the intensity of the third signal decreases after washing the solid for a period of 8 days. XRD technique methods also show that the amount of malachite phase decreases in the same range of washing.

On the other hand, a synthesized (amorphous) and a natural (crystallized) malachite have been studied with EPR. The signals obtained are symmetric and centered respectively at $g \sim 2.055$ with $\Delta H = 600$ G and $g = 2.007$ with $\Delta H = 50$ G. Consequently, the signals of such species can be present in the spectrum obtained after washing vaterite but their intensities, compared to those of other signals, ought be weak.

Conclusion

In this work different techniques are used to follow the transformation of vaterite washing with cupric solutions. The transformation depends intimately on the copper concentration. Thus, for a 10^{-4} mol dm^{-3} concentration, the transformation occurs with the formation of only cubic calcite. For a 10^{-3} mol dm^{-3} copper(II) concentration, the vaterite structure remains stable; and this stability is due to the formation of $CuCO_3$ layers on the solid surface. Such a coating stops the dissolution of spherical particles of vaterite which is responsible for the transformation. For a 10^{-2} mol dm^{-3} Cu^{2+} solution, the vaterite transforms in a first stage into aragonite, malachite, and cubic calcite; subsequently, the aragonite phase disappears, whereas malachite remains in small amounts in addition to pure crystals of cubic calcite.

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