

Malachite Crystallisation in a Diffusing-Reacting System

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The crystallisation of malachite has been studied in a system involving the counter diffusion of Cu^{2+} and CO_2 through a silica gel column at 25 °C. In such a system supersaturation is a function of time and position along gel column. Under these conditions kinetic variables are required in order to justify nucleation behaviour. Supersaturation rate has revealed as the most important parameter controlling nucleation features (waiting time, position of the precipitate, and metastability levels). The results presented here confirm the general nucleation behaviour reported by Prieto et al., (1989, 1991, 1994) for other carbonates. On the other hand, supersaturation changes during crystallisation process control the morphological evolution of malachite crystals.

Introduction

Malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) is an interesting mineral frequently employed in catalyzers, coatings, pigments, and pesticides industry. When malachite crystals present suitable properties, they may also be used in jewelry stone-cutting (Balitsky et al., 1990). In nature, malachite occurs as a secondary mineral in supergenic deposits and associated to other copper phases (tenorite, cuprite, azurite, etc.). In these geological settings, the crystallisation of copper carbonates is strongly controlled by the partial pressure of CO_2 in the system. This paper deals with the nucleation and growth behaviour of malachite in a diffusion-reaction system. The crystallisation experiments have been carried out in a porous silica gel transport medium. The silica gel technique has extensively been used as a method of growing crystals of sparingly soluble salts (carbonates, sulphates, etc.). However, no previous work, in the knowledge of the authors, on the crystallisation of malachite in a porous medium has been carried out.

In the system employed, mass transfer only occurs by diffusion. Under such conditions, high supersaturation levels are reached before nucleation occurs. However, supersaturation is never constant, but evolves with time. Understanding crystallisation phenomena when supersaturation is time dependent requires evolutionary variables. According to Prieto et al., (1989), one of the most important kinetic parameters in diffusing-reaction systems is the supersaturation rate, i.e. the rate at which the system moves from equilibrium. Under identical conditions, supersaturation rate determines the maximum supersaturation reached at nucleation. On the other hand, supersaturation evolution exerts a clear control on the growth mechanisms. Changes in growth mechanisms will be reflected by the crystal morphologies, which will evolve during crystallisation process.

Experimental methods and calculations

Crystallisation experiments were carried out at 25°C in a double diffusion-reaction system as shown in figure 1. The horizontal branch was occupied by a column of poly-merised silica hydrogel. The gel column was 150 mm long and 9 mm in diameter. The gel was prepared by the acidification of a Na_2SiO_3 solution (Merck Sp. Gr.: 1.059 g/cm³, pH = 11.2) with HCl (1 N) solution to desired pH (5.5 in all the experiments). The reservoirs A and B were filled with 8 cm³ of the reagents solutions. Since the gelling process involves formation of NaCl as a soluble by-product, in order to minimise the number of foreign ions present, CuCl_2 and Na_2CO_3 solutions were used as reagents. Before diffusion starts, the gel column is a homogeneous medium with zero reagents concentration. However, as soon as the experiment starts, the column becomes non homogeneous in pH and concentration. Both the pH and the total C concentration profiles along the gel column for successive periods of time were known from previous works (Prieto et al., 1988, 1989). Independent experiments were carried out to determine the extent of Cu diffusion.

These diffusion experiments were terminated at 100 hour intervals, the gel was removed from the column and sliced into 10 mm wide slices, according to the protocol described by Prieto et al., (1988). Each slice was chemically analysed by means of an atomic absorption spectrometer (UNICAM 919). Finally, to determinate the actual concentration of the interstitial solutions, the measured concentrations of the constituents, were referred to the 'effective water' (95.6%) per gel volume unit (Prieto et al., 1989). The growth evolution of the crystals was monitored by optical microscopy. A month after nucleation, the crystals were recovered by dissolving the silica gel in a NaOH solution. The crystals were confirmed to be malachite by x-ray powder diffraction and their morphologies were studied by scanning electron microscopy.

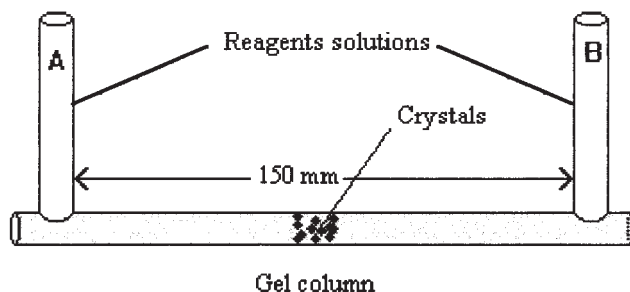
The deviation of a crystallisation system from equilibrium is usually given in terms of supersaturation – f and different expressions can be used for its evaluation. In this work the expression employed to evaluate the supersaturation of the interstitial solution with respect to malachite was:

$$\beta = \frac{a(\text{Cu}^{2+})^{\nu\text{Cu}^{2+}} \cdot a(\text{CO}_3^{2-})^{\nu\text{CO}_3^{2-}} \cdot a(\text{OH}^-)^{\nu\text{OH}^-}}{K_{sp}} \quad (1)$$

where $\nu\text{Cu}^{2+} = 2$, $\nu\text{CO}_3^{2-} = 2$ and $\nu\text{OH}^- = 2$; $a(\text{Cu}^{2+})$, $a(\text{CO}_3^{2-})$ and $a(\text{OH}^-)$ are the activities of the free ions in the solution, and K_{sp} is the thermodynamic solubility product ($K_{sp} = 10^{-33.78}$).

Equation (1) shows that, in order to calculate supersaturation, knowledge of the activities of the free ions is required. The activity coefficients of Cu^{2+} , CO_3^{2-} and OH^- were 3

Fig. 1. Experimental set up



determined by using the Debye-Hückel formula. This method of calculation has been extensively explained for other systems in previous papers (Prieto et al., 1989, 1991). In this work calculation of ionic activity coefficients was carried out by means of a specially designed computer program. It requires a detailed aqueous especiation model, where the following chemical species have been considered:

charged species: Cu^{2+} , CO_3^{2-} , HCO_3^- , Na^+ , Cl^- , H^+ , OH^- , NaCO_3^- , CuOH^+ , CuCl^+ .

uncharged species: H_2CO_3^0 , NaHCO_3^0 , NaOH^0 , CuCO_3^0 .

Since the crystallisation system studied is non-homogeneous and evolutionary, the supersaturation is a function of both the position in the gel column and the diffusion time. According to Prieto et al., (1991, 1994), in these systems nucleation kinetics strongly depends on the rate at which the system moves from equilibrium, i.e. the super-saturation rate. This parameter is given by the first derivative of the supersaturation function, $d\beta/dt$. In this work, the supersaturation profiles are used as initial data to calculate values of supersaturation rate following the protocol described by Prieto et al., (1991).

Results

Table I shows the results of malachite nucleation experiments for various concentrations of the mother liquors. Nucleation density, time and location of the first precipitates are reported. As can be observed, there is a clear relationship between the waiting period for nucleation and the concentration of the mother liquors, higher initial concentrations of the reagents resulting in shorter waiting periods. Figure 2A shows the supersaturation profiles along the gel column at nucleation time when mother liquors $\text{CuCl}_2(0.5\text{M})$ — $\text{Na}_2\text{CO}_3(0.5\text{N})$ were used. The location of the first precipitate is outlined in the upper part of the graphic. In all the runs, the maximum supersaturation values correspond to the slices closer to the CuCl_2 reservoir. However, it quickly decreases to reach a mini-mum in slice 7, from where it slowly decreases to the Na_2CO_3 reservoir, showing a local maximum in slice 8. The corresponding pH profile is shown in figure 2B. The first pre-cipitate location does not coincide with the position of the maximum supersaturation level within the gel column, but with the region where pH increases from a value of 5.5 to 6. This position coincides with the supersaturation local maximum. Similar behaviour has been observed in all the experiments.

In all the experiments the supersaturation level reached at nucleation time and location is always very high. However, it markedly depends on the initial concentration of the mother liquors. For example, in the case of mother liquors $\text{CuCl}_2(0.5\text{ M})$ — $\text{Na}_2\text{CO}_3(0.5\text{ N})$, the supersaturation at nucleation time and location takes a value of 94 400, while when the mother liquors are $\text{CuCl}_2(0.1\text{ M})$ — $\text{Na}_2\text{CO}_3(0.1\text{ N})$, its value is 35 000, around three times lower. However, the supersaturation level reached in these experiments always is extremely high, even when low concentrated mother liquors are employed.

Table I

Initial concentrations and experimental data for the nucleation of malachite

Initial Concentration CuCl_2 — Na_2CO_3	Waiting time (hours)	Precipitate location (slices)	Super- saturation Threshold	Super- saturation Rate (hours^{-1})	Density
0.5 M—0.5 N	220	8	94 400	4700	60—70
0.3 M—0.3 N	270	8	50 250	717	45—55
0.1 M—0.1 N	700	8	35 000	487	25—35

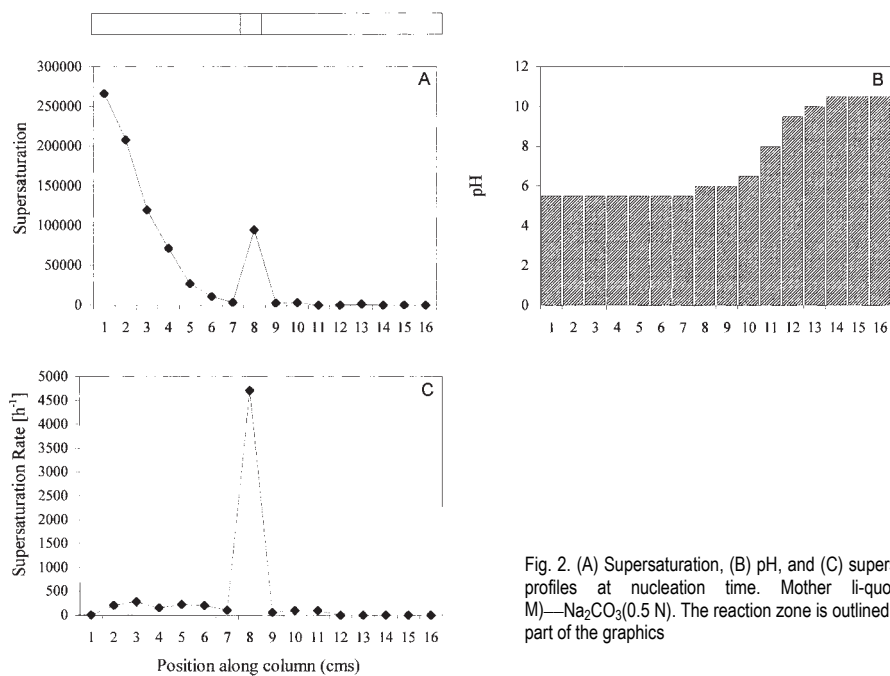


Fig. 2. (A) Supersaturation, (B) pH, and (C) supersaturation rate profiles at nucleation time. Mother liquors: $\text{CuCl}_2(0.5 \text{ M})\text{—Na}_2\text{CO}_3(0.5 \text{ N})$. The reaction zone is outlined in the upper part of the graphics

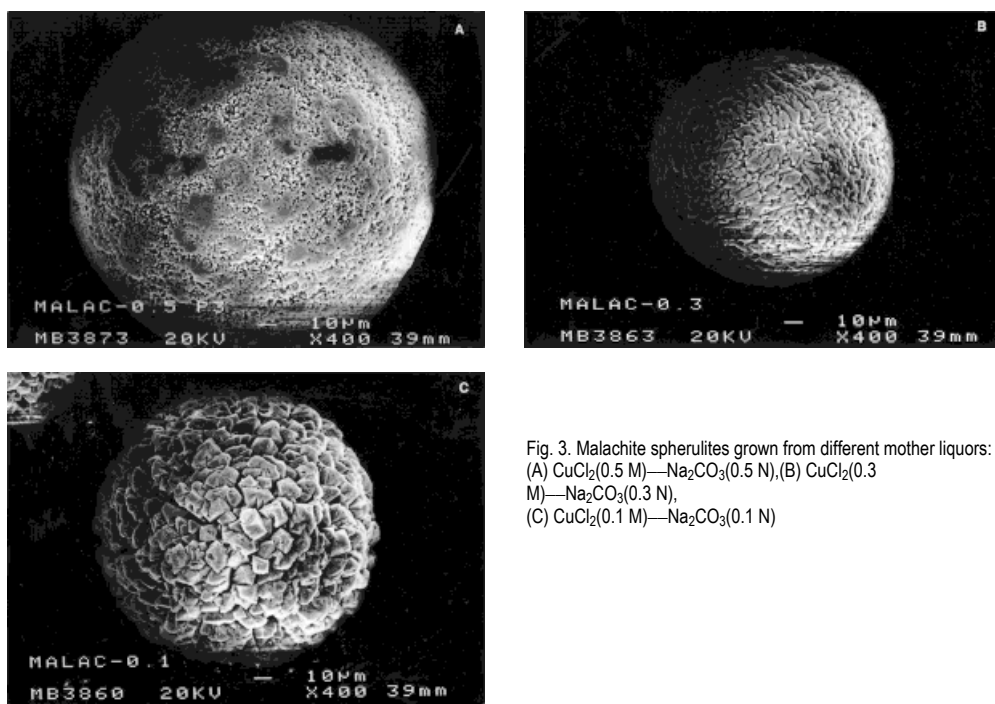


Fig. 3. Malachite spherulites grown from different mother liquors: (A) $\text{CuCl}_2(0.5 \text{ M})\text{—Na}_2\text{CO}_3(0.5 \text{ N})$, (B) $\text{CuCl}_2(0.3 \text{ M})\text{—Na}_2\text{CO}_3(0.3 \text{ N})$, (C) $\text{CuCl}_2(0.1 \text{ M})\text{—Na}_2\text{CO}_3(0.1 \text{ N})$

Supersaturation levels have a clear influence on crystal growth behaviour of malachite. In all the experiments conducted malachite crystallised as spherulites, whose size ranged from 100 to 150 μm . However, different features have been distinguished on the spherulitic surfaces, depending on the initial concentration of the reagents. When malachite grows from mother liquors with high initial concentrations $\text{CuCl}_2(0.5 \text{ M})\text{—Na}_2\text{CO}_3(0.5 \text{ N})$, it forms spheres with a very rough surface (figure 3A). Smaller concentrations of the mother liquors $\text{CuCl}_2(0.3 \text{ M})\text{—Na}_2\text{CO}_3(0.3 \text{ N})$ lead to the formation of spheres with wavy surfaces, that could correspond to poorly defined individual crystallites (figure 3B). Finally, when the concentration of the mother liquors is even smaller, malachite crystallises as spherulites, built up by individual crystallites exhibiting prismatic morphologies with well developed flat faces –f110g; f111g or f011g (figure 3C).

Discussion

As it has been mentioned above, the system described here is non homogeneous and evolutionary. The mass-transfer progress leads to a continuous change of pH, ions concentration and, therefore, supersaturation level at any point in space and time. Moreover, the fact that mass transfer mainly occurs by ionic diffusion determines that very high degrees of supersaturation can be reached before nucleation occurs. Such an effect is specially strong when the salt that crystallises is sparingly soluble. This is the case of malachite, whose solubility product is very low, $10^{-33.78}$. The very high supersaturation degrees reached in these experiments at nucleation time and location (Table I) have to be interpreted as a result of both the limited mobility imposed by the crystallisation medium and the low solubility of the substance. In solutions of such a sparingly soluble substance, growth units are relatively distant from one to another. Only under very high supersaturation levels a high probability of nucleation is achieved.

Although in all the experiments carried out nucleation occurs under very high supersaturation levels, the actual supersaturation degree depends on the boundary conditions (in this case, the initial concentration of the mother liquors). In non homogeneous systems, “critical supersaturation” (Walton, 1969) is a meaningless concept. To understand nucleation behaviour a dynamic concept of supersaturation is required. Prieto et al., (1991, 1994) developed the concept of threshold supersaturation β_{th} , which is related to the evolutionary history of the system and has to be applied whenever supersaturation gradients exist. As demonstrated by these authors, the actual threshold supersaturation depends on the rate at which the system is moving away from equilibrium — i.e., the supersaturation rate.

Both values of supersaturation threshold and supersaturation rate at nucleation time and location for malachite crystallisation in a silica gel system, are shown in table I. As it was to be expected, there also is a clear correlation between the supersaturation rate and the supersaturation threshold values. When $(\text{CuCl}_2(0.5 \text{ M})\text{—Na}_2\text{CO}_3(0.5 \text{ N}))$ mother liquors were used, nucleation occurred at a supersaturation value of 94 400, however, when the concentrations of the mother liquors were $\text{CuCl}_2(0.1 \text{ M})\text{—Na}_2\text{CO}_3(0.1 \text{ N})$, the supersaturation had a value of 35 000 at the nucleation time and location. In the first case, the supersaturation rate was 4700, while in the second case it was 490. The much smaller supersaturation rate in the second experiment determines that, even though the waiting period was longer, nucleation occurred under much lower supersaturation.

Similar results have been reported in previous papers (Prieto et al., 1989, 1991, 1994) for the crystallisation of other carbonates (SrCO_3 , BaCO_3 , CaCO_3 , CdCO_3 etc.). However, although carbonate nucleation has been proved to occur under very high supersaturation when diffusion-reaction systems are considered, the metastability levels reached in malachite crystallisation are specially high compared to other carbonates. This fact is directly related to the extremely low solubility of this phase. As mentioned above, malachite solubility product takes a value of $10^{-33.78}$, while other carbonates solubility products are in the range from 10^{-8} to 10^{-9} . Lower solubility products imply lower nucleation probability and, therefore, higher metastability levels.

The supersaturation rate distribution along the diffusion column at nucleation time allows to justify the location of the first precipitate. As can be observed in figure 2C the maximum supersaturation rate coincides with the sloping segment in the pH profile and hence with the reaction zone. The reagents concentration ratio is not irrelevant for a stochastically controlled system of limited particle mobility (Henisch & Garcia-Ruiz, 1986; Prieto et al., 1991). The distribution of “cation containing” species is pH-dependent. The increase in the pH value from 5.5 to 6 also determines an increase in the CO_3^{2-}

and OH^- ions concentration, while both are very low for smaller pHs. The low concentration of CO_3^{2-} ions in the slices closer to the CuCl_2 reservoir determines that, although

supersaturation is maximum because of a high concentration of Cu^{2+} ions, the nucleation probability will be very low. When pH increases, an strong increase of the CO_3^{2-} and

OH^- activity is observed. This leads to an increase of the nucleation probability, which will be reflected by the supersaturation rate. The malachite nucleation behaviour described here confirm again the relationship found by Prieto et al., (1991) between supersaturation rate and supersaturation threshold as a general rule.

Supersaturation evolution does not only control the nucleation behaviour of malachite, but plays an important role during the crystal growth process. The morphologies shown by malachite agree with the early stages of growth occurring under very high supersaturation levels. The spherulitic morphologies and the curved and rough surfaces observed involve a continuous growth mechanism which is characteristic of interfaces with high kinetic roughness. In the case of mother liquors with initial concentrations of $\text{CuCl}_2(0.1 \text{ M})$ — $\text{Na}_2\text{CO}_3(0.1 \text{ N})$, the progressive decrease of supersaturation as a result of both the growth process and the decrease in supersaturation rates with increasing diffusion time, leads to a transition to growth controlled by two dimensional nucleation and, eventually, by helicoidal dislocations (Sunagawa, 1987). As a result, individual crystals with flat faces develop on the surface of the spherulites. When mother liquors with higher initial concentrations are considered, the decrease of the supersaturation level

during the growth process is not important enough to allow the system to leave the growth region controlled by a continuous growth mechanism.

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