

Stability relations of malachite and azurite

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ABSTRACT. Stability relations of malachite and azurite are calculated and shown in Eh-pH diagrams, using ΔF (Gibbs free energy) values listed in Garrels and Christ (1965). The malachite/azurite transition is very sensitive to small chemical changes in the environment: equilibrium is reached at $P_{\text{CO}_2} = 10^{-3.45}$ atm., i.e. close to normal values, whereas the precipitation of both minerals from cupric-ion-bearing solutions takes place at pH values between 6 and 8, depending CO_2 partial pressures. It is shown that stability relations of these minerals can be better explained in terms of activities of the carbonate and bicarbonate ion.

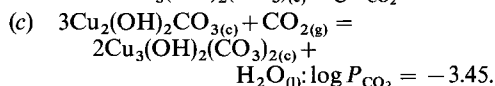
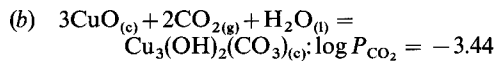
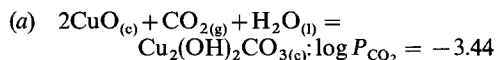
Azurite can be formed only under relatively acid conditions at relatively high carbonate activities. Since the latter imply mostly basic conditions, this explains why malachite is the more common form of copper carbonate and that azurite can be formed only under rather unusual conditions. It also explains the frequent alteration of azurite into malachite, due to small changes in carbonate/bicarbonate activities. These alterations include pseudomorphs of malachite after azurite.

KEYWORDS: malachite, azurite, stability relations.

It is generally recognized that malachite is more stable under atmospheric conditions than azurite. This is not only indicated by a much wider distribution and more frequent occurrence of malachite relative to azurite, but also by numerous pseudomorphs of malachite after azurite. Pseudomorphs of azurite after malachite seem to be extremely rare.

The stability relations of malachite and azurite have to be explained in terms of either partial pressure diagrams or Eh-pH diagrams. In this paper an attempt is made to explain these by means of Eh-pH diagrams.

Partial pressure diagrams. Stability relations of malachite $\text{Cu}_2(\text{OH})_2\text{CO}_3$ and azurite $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ were partially explained by Garrels and Christ (1965) in terms of a $\log P_{\text{O}_2}$ - $\log P_{\text{CO}_2}$ partial pressure diagram. However, using data for Gibbs free energies as listed by Garrels and Christ, the following CO_2 equilibrium partial pressures can be calculated for the transition tenorite(CuO)/malachite, tenorite/azurite and malachite/azurite:



A comparison of the $\log P_{\text{O}_2}$ - $\log P_{\text{CO}_2}$ diagram in fig. 1 with the diagram given by Garrels and Christ (1965, fig. 6.7, p. 156) shows that in fig. 1 the malachite stability field has entirely disappeared. It is not known why and how this discrepancy occurred.

Fig. 1 shows that at a CO_2 partial pressure in excess of $10^{-3.44}$, tenorite is unstable; reactions (a) and (b) show that it can be converted into either malachite or azurite. Reaction (c) however shows that, to the left of the vertical line for $P_{\text{CO}_2} = 10^{-3.45}$, malachite would be stable and, to the right of that line, only azurite. It would appear then that the malachite stability field is reduced to zero. This can be confirmed by plotting the cuprite(Cu_2O)/malachite linear curve, $\log P_{\text{CO}_2} = -22.4 - \frac{1}{2} \log P_{\text{O}_2}$; this curve passes exactly through the point in the diagram where the tenorite, cuprite and azurite fields come together, and it does not give rise to a separate malachite stability field (dashed line in fig. 1).

The above reactions (a) to (c) do not appear to be very helpful in explaining the stability relations of malachite and azurite in terms of P_{CO_2} . The diagram would only suggest that azurite is the stable phase at P_{CO_2} partial pressures in excess of $10^{-3.45}$ atm.

With regard to the role of P_{CO_2} , Kern and Weisbrod (1967, p. 284) came to the following conclusion, by calculating a pH- $\log(\text{Cu}^{2+})$ -diagram: 'at very low Cu^{2+} concentration, azurite, malachite or tenorite will be precipitated, and in such circumstances the CO_2 content of the atmosphere above the solution has scarcely any influence on the precipitation of these mineral phases'. They also state that malachite and azurite will crystallize under very similar conditions which are only slightly dependent on P_{CO_2} .

Eh-pH diagrams. Garrels and Christ (1965, p. 239) give the Eh-pH diagram for the system

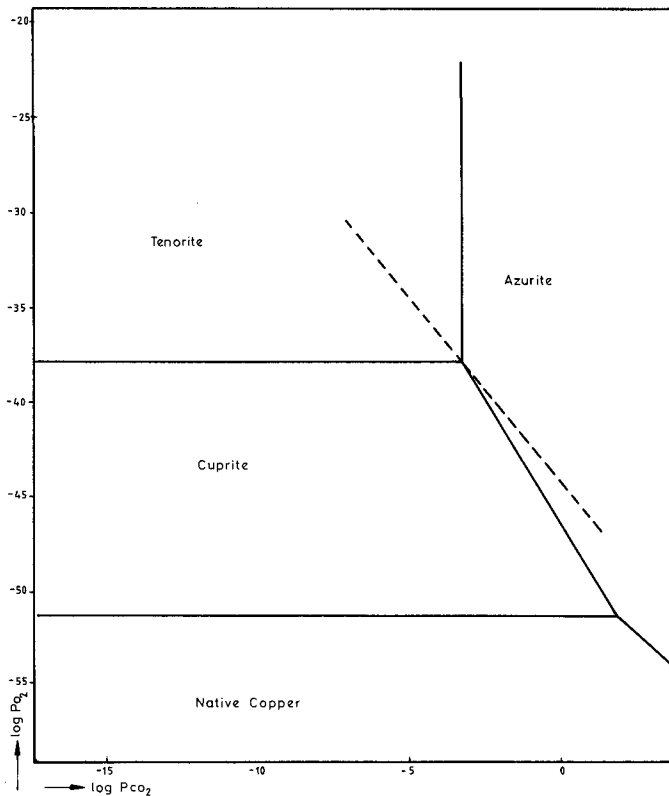


FIG. 1. $\log P_{\text{O}_2}$ - $\log P_{\text{CO}_2}$ diagram of copper compounds at 25°C, and 1 atm. total pressure. The dashed line gives the irrelevant cuprite/malachite boundary for $\log P_{\text{CO}_2} = -22.4 - \frac{1}{2} \log P_{\text{O}_2}$ (see text).

Cu-H₂O-O₂ at 25°C and 1 atmosphere total pressure, in which a large field for tenorite appears.

If CO₂ is added ($P_{\text{CO}_2} = 10^{-3.5}$, i.e. practically the same value as for the malachite-azurite equilibrium, fig. 1) the tenorite field is replaced entirely by malachite (fig. 7.2, p. 240). It is interesting to consider the role of azurite in this diagram: if under the same conditions, the reactions Cu²⁺/azurite, cuprite/azurite and CuO₂²⁻/azurite are calculated, it will be seen that the malachite and azurite fields almost entirely overlap each other, but that under these conditions malachite is the stable modification (one has to carry out the calculation to the third decimal for pH-values).

The coincidence of the two fields, is complete if a CO₂ partial pressure of $10^{-3.45}$ atm. i.e. the malachite/azurite equilibrium partial pressure mentioned for reaction (c). At CO₂ partial pressures higher than $10^{-3.45}$ atm., azurite occupies the field and for values less than $10^{-3.45}$ atm., malachite is the stable phase. Fig. 2 shows the position of the fields for CO₂ partial pressures varying from 10^{-1}

to 10^{-6} atm. Activities of total dissolved copper species were kept at 10^{-6} .

At $P_{\text{CO}_2} = 10^{-3.45}$ and pH = 6.95 azurite and malachite can coexist. The same is valid for the basic side of the diagram: at $P_{\text{CO}_2} = 10^{-3.45}$ and pH = 13.05 azurite and malachite can coexist. The corresponding transition from cuprite to coexisting malachite and azurite at $P_{\text{CO}_2} = 10^{-3.45}$ is given by the equation $Eh = 0.670 - 0.0592 \text{ pH}$. The relationship between the malachite and azurite stabilities shown in fig. 2, and the CO₂ partial pressure of $10^{-3.45}$ is unfortunately extremely close to the normal or average CO₂ partial pressure of the atmosphere of $10^{-3.5}$.

An equally unfortunate situation is the fact that the precipitation of azurite from a Cu²⁺-bearing solution takes place at equilibrium pHs varying from 6.13 to 6.95 for P_{CO_2} values varying from 10^{-1} to $10^{-3.45}$ respectively, and that the precipitation of malachite from a Cu²⁺-bearing solution takes place at equilibrium pHs varying from 6.95 to 7.59 for P_{CO_2} values varying from $10^{-3.45}$ to 10^{-6} (or

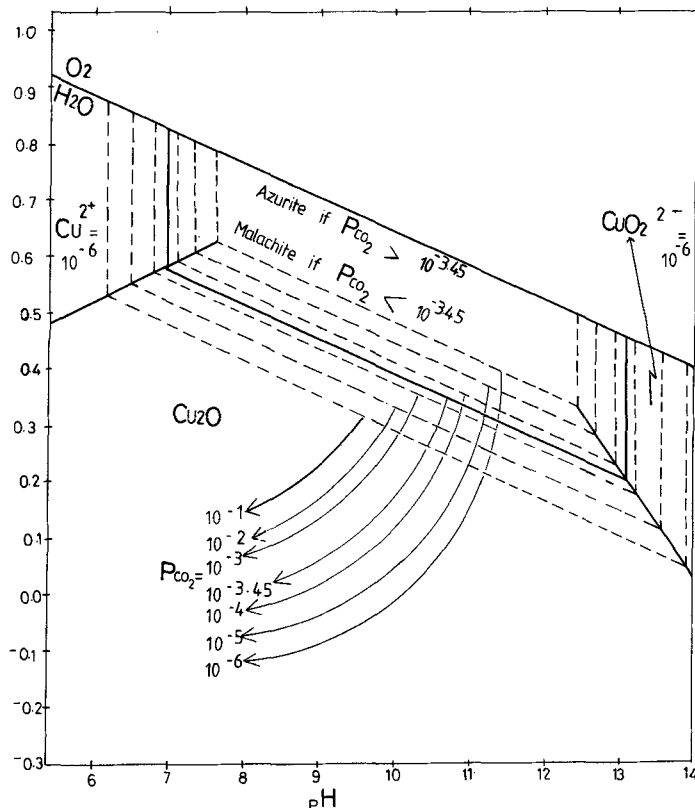


FIG. 2. Partial Eh-pH diagram of the system Cu-O-H-CO₂ at 25°C and 1 atm, total pressure. Total dissolved copper ion: 10⁻⁶ molal. The diagram shows the stability fields of malachite and azurite as a function of P_{CO₂}. Equilibrium is reached at P_{CO₂} = 10^{-3.45} atm, with corresponding pH = 6.95, pH = 13.05 and Eh = +0.670–0.0592 pH (straight lines).

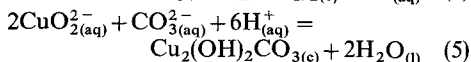
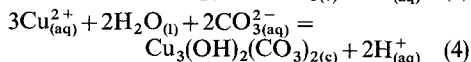
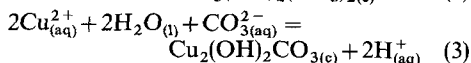
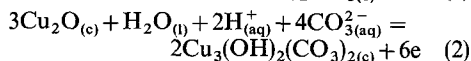
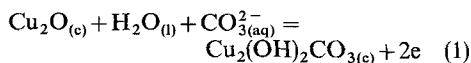
lower), respectively. Except for the CuO₂²⁻ side of the diagram, all the other P_{CO₂} and pH values occur in a very normal and common natural range, so that it only can be concluded that very small changes in environmental conditions are responsible for the occurrence of either malachite or azurite.

Reaction (c), the transition malachite/azurite in terms of P_{CO₂} and H₂O, cannot be included in fig. 2 because reaction (c) is Eh- and pH-independent. In the following calculations it is shown that the malachite/azurite stability relations can be explained by calculating the stability fields as a function of activities of CO₃²⁻ and/or HCO₃⁻, and not of P_{CO₂}. In that case the transition malachite/azurite is pH-dependent. This is of particular interest in cases where calcareous hostrock is present (limestones, dolomites, calcareous schists, etc.).

The diagram of the system Cu-O-H-CO₃²⁻

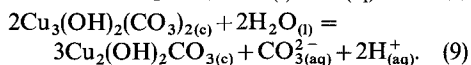
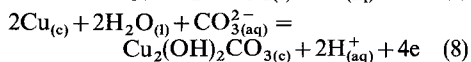
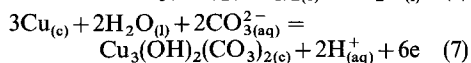
was first calculated for activities of total dissolved copper species 10⁻⁶ and dissolved CO₃²⁻ 10⁻⁴. The transitions native copper/Cu²⁺, native copper/cuprite and cuprite/CuO₂²⁻ remain the same as given by Garrels and Christ (1965) in several of their diagrams.

The chemical reactions involving CO₃²⁻ are given below:





$$\text{pH} = 8.80. \quad (9)$$



The corresponding Eh-pH equations or equilibrium Eh and pH values for Cu^{2+} and $\text{CuO}_2^{2-} = 10^{-6}$ and for $\text{CO}_3^{2-} = 10^{-4}$ are as follows:

$$\text{Eh} = +0.15 \quad (1)$$

$$\text{Eh} = -0.0232 + 0.02 \text{ pH} \quad (2)$$

$$\text{pH} = 5.10 \quad (3)$$

$$\text{pH} = 3.26 \quad (4)$$

$$\text{pH} = 11.62 \quad (5)$$

$$\text{pH} = 11.35 \quad (6)$$

$$\text{Eh} = +0.224 - 0.0197 \text{ pH} \quad (7)$$

The result of these calculations is presented in fig. 3. Since the transition from Cu^{2+} to azurite is at $\text{pH} = 3.26$ (eq. 4), and to malachite at $\text{pH} = 5.10$ (eq. 3), equation (3) is irrelevant, and from left to the right in the diagram, Cu^{2+} , azurite, malachite, and CuO_2^{2-} occur. In the same way, the transition from CuO_2^{2-} to azurite is also irrelevant.

The native copper-cuprite- CuO_2^{2-} -configuration in the diagram makes the transition native copper/azurite (eq. 7) relevant and the transition native copper/malachite (eq. 8) irrelevant.

The six relevant reactions were also calculated for $\text{CO}_3^{2-} = 10^{-6}$, and the resulting equations plotted in fig. 3 as dashed lines. At decreasing CO_3^{2-} activity, the azurite field decreases, whereas the Cu^{2+} field and the malachite field increase. The reason that the malachite/ CuO_2^{2-} and the

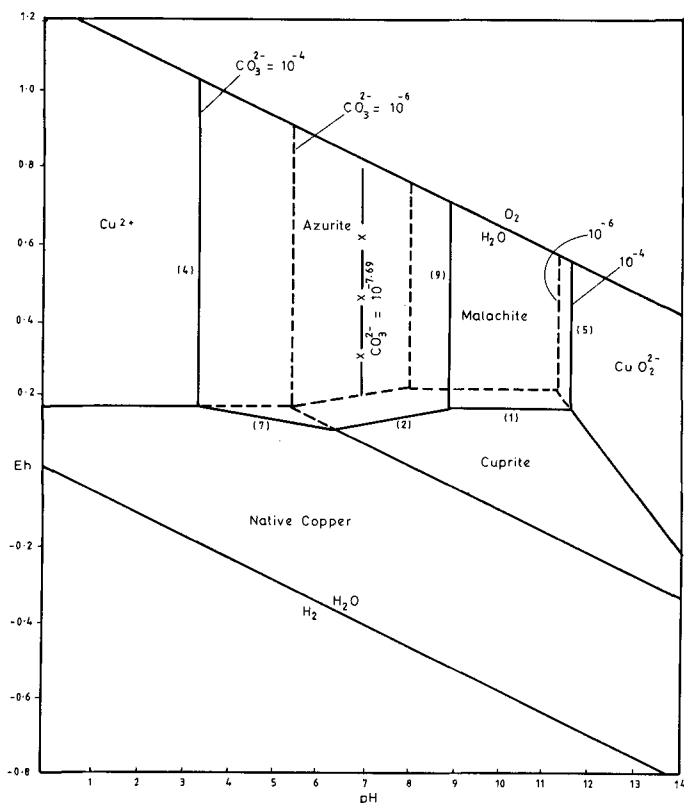


FIG. 3. Eh-pH diagram of the system Cu-O-H-CO₃²⁻ at 25°C and 1 atm. total pressure. Total dissolved copper ion: 10⁻⁶ molal. Straight lines: log(molality) CO₃²⁻ = -4. Dashed lines: log(molality) CO₃²⁻ = -6. Figures in parentheses refer to chemical reactions mentioned in text.

malachite/azurite borders shift to the left and the Cu^{2+} /azurite border to the right is given by equations (5), (9), and (4): in equations (5) and (9) CO_3^{2-} and H^+ are on the same side of the reaction equation, whereas in reaction (4) they are on different sides, resulting in the opposite behaviour if the conditions change.

Since the azurite field decreases with decreasing CO_3^{2-} activity, there must be a certain CO_3^{2-} activity at which the azurite field disappears completely, so that the Cu^{2+} field and the malachite field are bordering. This value can be calculated by considering the reactions (4) and (9):

Reaction (4):

$$\Delta F_{298}^\circ(r) = -1.364 \log [\text{H}^+]^2 \cdot [\text{CO}_3^{2-}]^{-2} \cdot [\text{Cu}^{2+}]^{-3} = -26.57 \text{ kcal/mole.}$$

For $\text{Cu}^{2+} = 10^{-6}$ molal:

$$+1.48 = 2 \log [\text{H}^+] - 2 \log [\text{CO}_3^{2-}] \quad (a)$$

Reaction (9):

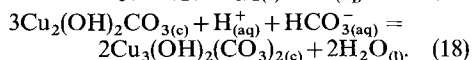
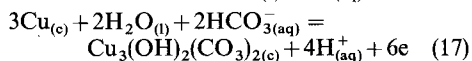
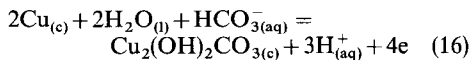
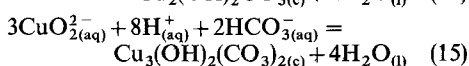
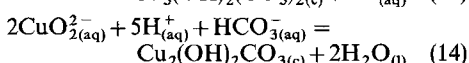
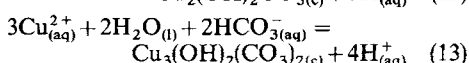
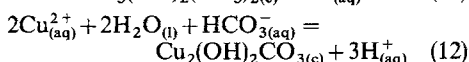
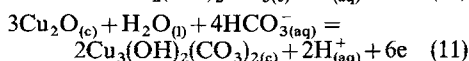
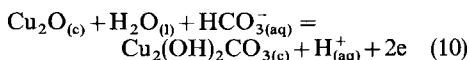
$$\Delta F_{298}^\circ(r) = -1.364 \log [\text{H}^+]^2 \cdot [\text{CO}_3^{2-}] = +29.44 \text{ kcal/mole.}$$

Or: $-21.58 = 2 \log [\text{H}^+] + \log [\text{CO}_3^{2-}]$. (b)

From equations (a) and (b) H^+ and CO_3^{2-} are calculated: $\text{CO}_3^{2-} = 10^{-7.69}$ molal and the corresponding pH = 6.95. Thus if the conditions $\text{Cu}^{2+} = 10^{-6}$ and $\text{CO}_3^{2-} = 10^{-7.69}$ are chosen, no azurite field remains; only at higher CO_3^{2-} activities can azurite be stable. The conditions calculated above were also plotted in fig. 3.

There is a similarity here with fig. 2, where the same vertical line for pH = 6.95 separated the field for $\text{Cu}^{2+} = 10^{-6}$ on the left hand side and the field for azurite/malachite on the right hand side, for a CO_2 equilibrium partial pressure of $10^{-3.45}$. In fig. 2, at decreasing CO_2 partial pressure, the azurite field disappears: here at decreasing activity of CO_3^{2-} , the azurite field disappears.

Similar calculations were carried out taking the bicarbonate ion. The chemical reactions involving bicarbonate species are as follows:



The activities of dissolved copper species were kept the same as in the previous calculation, i.e. 10^{-6} . The activity for the bicarbonate ion taken here was 10^{-3} . The corresponding Eh-pH equations or equilibrium pH values are as follows:

$$\text{Eh} = +0.425 - 0.0295 \text{ pH} \quad (10)$$

$$\text{Eh} = +0.344 - 0.0197 \text{ pH} \quad (11)$$

$$\text{pH} = 6.51 \quad (12)$$

$$\text{pH} = 6.30 \quad (13)$$

$$\text{pH} = 12.09 \quad (14)$$

$$\text{pH} = 11.85 \quad (15)$$

$$\text{Eh} = +0.447 - 0.044 \text{ pH} \quad (16)$$

$$\text{Eh} = +0.408 - 0.039 \text{ pH} \quad (17)$$

$$\text{pH} = 8.25. \quad (18)$$

These equations are plotted in fig. 4. Similar to the calculations involving CO_3^{2-} , a few equations do not apply, i.e. equations (12), (15), (16), and (17). The five relevant reactions were also calculated for a lower bicarbonate activity of 10^{-4} . The outcome is given by dashed lines in fig. 4. A similar trend occurs as in fig. 3: at decreasing HCO_3^- activity, the azurite field decreases in size and the malachite field increases. Thus, here also, a HCO_3^- activity can be calculated for which the azurite field has entirely disappeared:

Reaction (13):

$$\Delta F_{298}^\circ(r) = -1.364 \log [\text{H}^+]^4 \cdot [\text{HCO}_3^-]^{-2} \cdot [\text{Cu}^{2+}]^{-3} = +1.61.$$

For $\text{Cu}^{2+} = 10^{-6}$ molal:

$$+19.18 = 2 \log [\text{HCO}_3^-] - 4 \log [\text{H}^+]. \quad (c)$$

Reaction (18):

$$\Delta F_{298}^\circ(r) = -1.364 \log [\text{H}^+]^{-1} \cdot [\text{HCO}_3^-]^{-1} = -15.34.$$

Or: $-11.25 = \log [\text{HCO}_3^-] + \log [\text{H}^+]$. (d)

From equations (c) and (d), H^+ and HCO_3^- are calculated. The results are: $\text{HCO}_3^- = 10^{-4.30}$ molal and pH = 6.95. Thus for conditions $\text{Cu}^{2+} = 10^{-6}$ and $\text{HCO}_3^- = 10^{-4.30}$, no azurite field remains; only at higher HCO_3^- activities can azurite be stable. The conditions calculated above are also plotted in fig. 4. Here again, a similarity exists with figs. 2 and 3; the vertical line for pH = 6.95 is the same as in fig. 2 for the CO_2 equilibrium partial pressure of $10^{-3.45}$, and also the same as in fig. 3. In fig. 4 an azurite field appears at HCO_3^- activity higher than $10^{-4.30}$, at

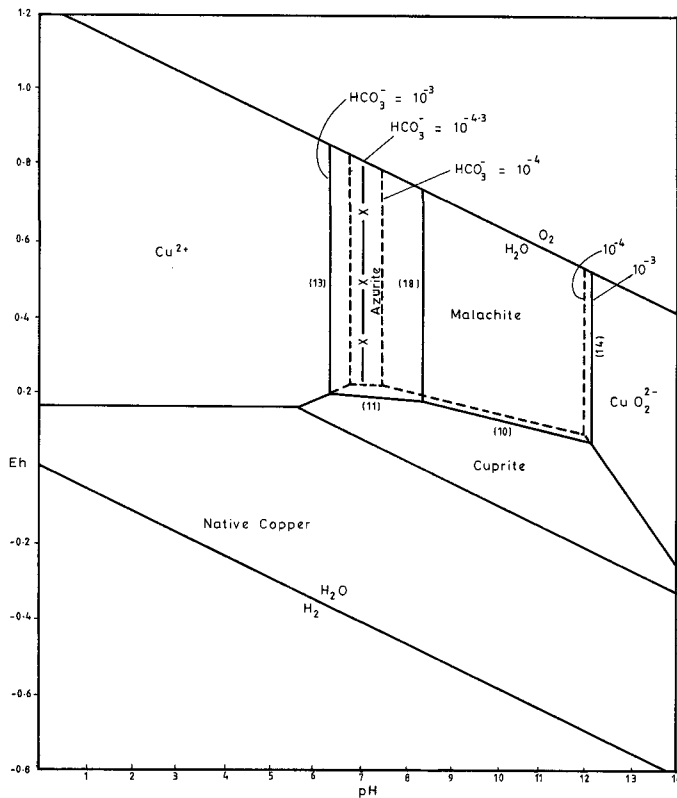


FIG. 4. Eh-pH diagram of the system Cu-O-H-HCO₃⁻ at 25°C and 1 atm. total pressure. Total dissolved copper ion: 10⁻⁶ molal. Straight lines: log(molality) HCO₃⁻ = -3. Dashed lines: log(molality) HCO₃⁻ = -4. Figures in parentheses refer to chemical reactions mentioned in text.

10^{-4.30} it disappears and at HCO₃⁻ activities less than 10^{-4.30} the Cu²⁺ field borders the malachite field.

Conclusions. In terms of CO₂ partial pressures, the malachite/azurite transition is a very sensitive one, since the equilibrium partial pressure is 10^{-3.45} atm., i.e. very close to normal CO₂ partial pressures in the atmosphere. Also the precipitation of azurite and malachite from cupric-ion-bearing solutions is equally sensitive: azurite will be precipitated at pH values between approximately 6 and 7, at P_{CO₂} values > 10^{-3.45} atm., and malachite at pH values between approximately 7 and 8, at P_{CO₂} values < 10^{-3.45} atm., the turning point being at pH = 6.95 with a corresponding P_{CO₂} = 10^{-3.45} atm. For these reasons, minute chemical changes in the environment may influence the formation and stabilities of these minerals. The stability relations of malachite and azurite can be better explained in terms of activities of CO₃²⁻ and/or HCO₃⁻,

although obviously these, in turn, are affected by P_{CO₂}.

The maximum solubility of carbonate in pure water circulating through a pure limestone is approximately 10^{-4.4} molal for CO₃²⁻ and 10^{-4.05} molal for HCO₃⁻. Under such conditions the pH ranges between 9 and 10. The pH of an aqueous system containing calcium carbonate in equilibrium with the atmosphere is 8.4 with corresponding solubilities of CO₃²⁻ and HCO₃⁻ of 10^{-4.9} and 10^{-3.0} molal respectively. These conditions invariably favour the formation of malachite at a realistic activity for the Cu²⁺ ion of 10⁻⁶ (figs. 3 and 4).

Water circulating through impure limestones and dolomites, or through other calcareous rocks, will have much lower carbonate activities, reducing the azurite field substantially. Under such conditions the pH will decrease, but will still be higher than 7, again favouring malachite formation.

Thus azurite can be formed only under relatively acid conditions, at relatively high carbonate activities; these conditions can be considered to be rare since high carbonate activities generally imply basic conditions. Figs. 3 and 4 show why malachite is more abundant than azurite, and that azurite commonly alters into malachite, frequently forming pseudomorphs of malachite after azurite.

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