Supplementary Material S1

Solubility calculations

The necessary data to carry out copper oxalate solubility calculations in the system $Cu(OH)_2$-$H_2C_2O_4$-[HNO_3/NaOH]-H_2O have been previously published. (S1.5) In the present study the investigation has been extended to include the equilibrium constants one needs to consider when acetate ions are added to the system.

The pH of the system is controlled by either adding nitric acid or sodium hydroxide. The notation used in the text for various parameters and species are summarized in Table S1.1. The following parameters are controlled by the user: (a) the solid phases $CuC_2O_4 \cdot 0.5H_2O$ (CuHOx) and $Cu(OH)_2$, were considered, (b) the activity of the species Ox^{2-} and Ac^-, (c) the pH range (0-12), (d) the global ionic strength (the ionic species concentration is corrected by adding the necessary amount of $NaNO_3$).

The considered chemical equilibria involve dissolution, protonation and complexation reactions. The dissolution reactions and corresponding equilibrium constants used in this study are summarized in Table S1.2. The protonation and complexation reactions are presented in Table S1.3 with their equilibrium constants selected from the literature(S1.1, S1.2). When necessary, the constants were extrapolated to T = 25 °C and ionic strength $\mu = 0.0$ mole/L. The nitrate complexes were not considered.

The activity coefficients, f_i, were calculated using the extended Debye and Hückel formula:

$$-\log(f_i) = AZ_i^2 \mu^{1/2} /(1 + Bd_i \mu^{1/2}) \qquad [1]$$

The A and B parameters are respectively 0.5114 and 0.3291 at 25 °C. The equivalent diameters of the hydrated ions d_i are presented in Table S1.4. (S1.3)

The calculation algorithm is summarized below. For each pH value, (Ox^{2-}) and (Ac^-) activities, the protonation equilibria are first considered (reactions R1 to R4, Table S1.3) this allows calculation of (H^+), (OH^-), $([HOx^-])$, $([H_2Ox])$ and $([HAc]^0)$. Then (Cu^{2+}) is calculated according to the solubility equilibrium (reaction D1, Table 2). The activities of the copper containing complexes are finally calculated according to

the complexation equilibria (reactions R5 to R16, Table S1.3). The concentrations of dissolved species are then calculated using the appropriate activity coefficient according to the following equation:

$$\{M_i\} = (M_i) / f_i \qquad [2]$$

The total analytical concentrations of dissolved copper, oxalate and acetate, {Cu}, {Ox} and {Ac} are calculated by adding the contribution of the appropriate dissolved species according to the three following equations :

$$\{Cu\} = \{Cu^{2+}\} + \{[Cu(OH)]^+\} + \{[Cu(OH)_2]^0\} + \{[Cu(OH)_3]^-\} + \{[Cu(OH)_4]^{2-}\} +$$
$$2\{[Cu_2(OH)_2]^{2+}\} + \{[CuOx]^0\} + \{[Cu(Ox)_2]^{2-}\} + \{[Cu(HOx)]^+\} + \{[Cu(Ac)]^+\} + \qquad [3]$$
$$\{[Cu(Ac)_2]^0\} + \{[Cu(Ac)_3)]^-\} + \{[Cu(Ac)_4]^{2-}\}$$

$$\{Ox\} = \{Ox^{2-}\} + \{[HOx]^-\} + \{[H_2Ox]^0\} + \{[CuOx]^0\} + 2\{[Cu(Ox)_2]^{2-}\} + \qquad [4]$$
$$\{[Cu(HOx)]^+\}$$

$$\{Ac\} = \{Ac^-\} + \{[HAc]^0\} + \{[Cu(Ac)]^+\} + 2\{[Cu(Ac)_2]^0\} + 3\{[Cu(Ac)_3)]^-\} \qquad [5]$$
$$+ 4\{[Cu(Ac)_4]^{2-}\}$$

The ionic balance, IB, is then calculated by adding the concentrations of dissolved species multiplied by their charge :

$$IB = \{H^+\} - \{OH^-\} - 2\{Ox^{2-}\} - \{HOx^-\} - \{Ac^-\} + 2\{Cu^{2+}\} + \{[CuOH]^+\} -$$
$$\{[Cu(OH)_3]^-\} - 2\{[Cu(OH)_4]^{2-}\} + 2\{[Cu_2(OH)_2]^{2+}\} - 2\{[Cu(Ox)_2]^{2-}\} + \qquad [6]$$
$$\{[Cu(HOx)]^+\} + \{[Cu(Ac)]^+\} - \{[Cu(Ac)_3)]^-\} - 2\{[Cu(Ac)_4]^{2-}\}$$

Then the necessary concentration of NaOH or HNO$_3$, required to reach the pH is given by :

$$\{NaOH\} = IB \quad \text{if IB} < 0, = 0 \text{ otherwise} \qquad [7]$$

$$\{HNO_3\} = IB \quad \text{if IB} \geq 0, = 0 \text{ otherwise} \qquad [8]$$

Finally, the total ionic strength μ (mole/L) is calculated according to :

$$\mu = 0.5 \sum \{M_i\} Z_i^2 \qquad [9]$$

and the total concentration of $NaNO_3$ required to equilibrate the ionic strength μ_s is given by

$$\{NaNO_3\} = \mu_s - \mu \qquad\qquad [10]$$

Negative values of $\{NaNO_3\}$ do not have any physical significance. They indicate that the spontaneous μ obtained with the chosen pH and (Ox^{2-}) conditions is larger than the imposed value and the result must be discarded. These calculations can be made in a 20 to 50°C temperature range. Figure S1.1 and table S1.5, show the distribution of species for the precipitation experiment without acetate, with 50% of the nitrate replaced with acetate and with 100% of the nitrate replaced by acetate.
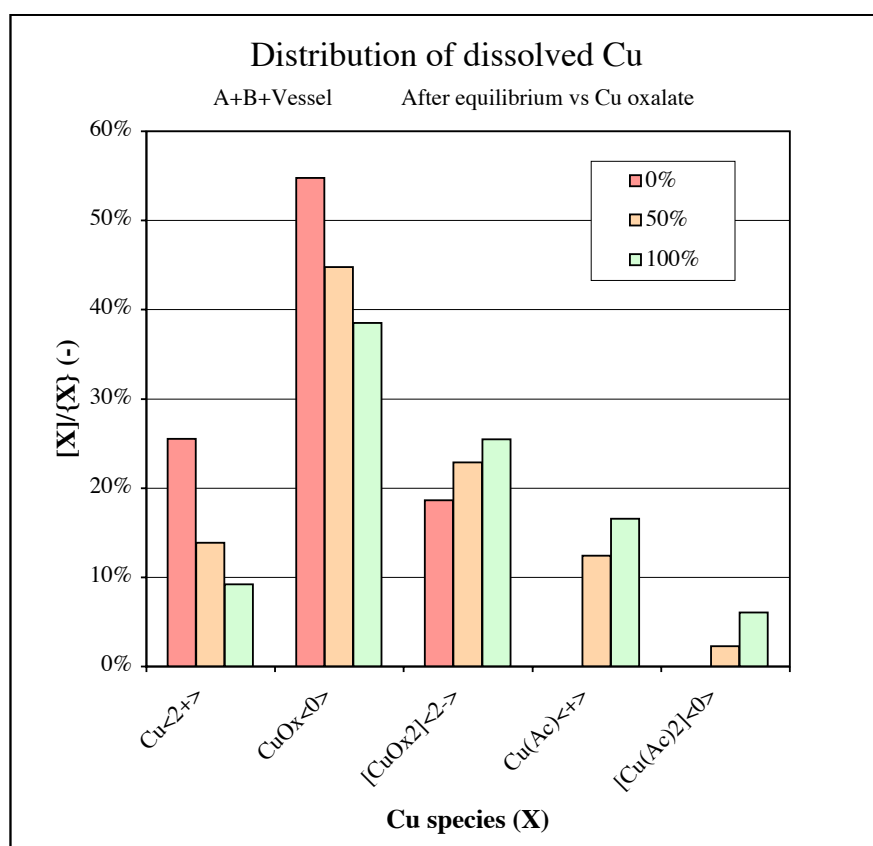
Figure S1.1   Distribution of dissolved Cu species after reaching equilibrium *vs* CuOx•0.5H₂O (moolite) for various acetate/(acetate + nitrate) ratios. Experimental conditions: initial composition $\{Cu\}_0 = \{Ox\}_0 = 10.15$ [mM]; $\{Na\}_0 = \{Ac\}_0 + \{NO_3\}_0 = 20.30$ [mM]; $T = 30$ [°C]. Calculated final compositions and pH, see Table S1.5.

Tables

Table S1.1 Notations summary

Symbol	Meaning
(M_i)	Activity of species M_i (mole/L)
$\{M_i\}$	Concentration of species M_i (mole/L)
CuOxH	Neutral hemihydrated copper oxalate
H_2Ox	Oxalic acid, $H_2C_2O_4$
HAc	Acetic acid, CH_3CO_2H
$Cu(OH)_2$	Copper hydroxide
d_i	Equivalent diameter of hydrated ions at 25 °C (nm)
f_i	activity coefficient of M_i species
μ	Ionic strength (mole/L)
Z_i	Ionic charge of M_i species

Table S1.2 Dissolution reactions and equilibrium constants

Reaction number	Reaction	$\log K_{298}$
D1	$CuOx \cdot 0.5H_2O \rightarrow Cu^{2+} + Ox^{2-} + 0.5H_2O$	-9.677
D2	$Cu(OH)_2 \rightarrow Cu^{2+} + 2OH^-$	-19.320

Table S1.3 Reactions in solution and equilibrium constants

Reaction number	Reaction	$\log K_{298}$
R1	$OH^- + H^+ \rightarrow H_2O$	13.997 a)
R2	$Ox^{2-} + H^+ \rightarrow [HOx]^-$	1.252 a)
R3	$[HOx]^- + H^+ \rightarrow [H_2Ox]^0$	4.266 a)
R4	$Ac^- + H^+ \rightarrow HAc$	4.757 a)
R5	$Cu^{2+} + OH^- \rightarrow [Cu(OH)]^+$	6.00 b)
R6	$Cu^{2+} + 2OH^- \rightarrow [Cu(OH)_2]^0$	10.70 b)
R7	$Cu^{2+} + 3OH^- \rightarrow [Cu(OH)_3]^-$	14.20 b)
R8	$Cu^{2+} + 4OH^- \rightarrow [Cu(OH)_4]^{2-}$	16.40 b)
R9	$2Cu^{2+} + 2OH^- \rightarrow [Cu_2(OH)_2]^{2+}$	17.63 b)
R10	$Cu^{2+} + Ox^{2-} \rightarrow [Cu(Ox)]^0$	5.71 a)
R11	$Cu^{2+} + 2Ox^{2-} \rightarrow [Cu(Ox)_2]^{2-}$	10.08 a)
R12	$Cu^{2+} + Ox^{2-} + H^+ \rightarrow [Cu(HOx)]^+$	7.60 a)
R13	$Cu^{2+} + Ac^- \rightarrow [Cu(Ac)]^+$	2.22 a)
R14	$Cu^{2+} + 2Ac^- \rightarrow [Cu(Ac)_2]^0$	3.63 a)
R15	$Cu^{2+} + 3Ac^- \rightarrow [Cu(Ac)_3]^-$	4.14 a)
R16	$Cu^{2+} + 4Ac^- \rightarrow [Cu(Ac)_4]^{2-}$	4.36 a)

a) Data from Kortly (S1.1); each time it was necessary, the constants were extrapolated to T = 25 °C and μ = 0.0 mole/L.
b) Data calculated from Baes and Mesmer (S1.2)

Table S1.4 Equivalent diameters d_i of hydrated ions at 25 °C

Ion	d_i(nm)	Ion	d_i(nm)
Cu^{2+}	0.60 b)	$[Cu_2(OH)_2]^{2+}$	0.50 a)
H^+	0.90 b)	$[Cu(Ox)_2]^{2-}$	0.50 a)
OH^-	0.35 b)	$[Cu(HOx)]^+$	0.50 a)
Ox^{2-}	0.45 b)	Ac^-	0.45 a)
$[HOx]^-$	0.40 a)	$[Cu(Ac)]^+$	0.40 a)
$[Cu(OH)]^+$	0.30 a)	$[Cu(Ac)_3]^-$	0.65 a)
$[Cu(OH)_3]^-$	0.30 a)	$[Cu(Ac)_4]^{2-}$	0.71 a)
$[Cu(OH)_4]^{2-}$	0.45 a)		

a) Data estimated analogically to other similar ions on the chemical point of view and with identical charge.
b) Data from Kielland (S1.4).

Table S1.5   Final compositions after equilibrium *vs* CuOx•0.5H$_2$O.

Acetate ratio [%]	{Cu}$_e$ [mM]	{Ox}$_e$ [mM]	pH$_e$ [-]
0	0.22	0.22	5.59
50	0.27	0.27	6.82
100	0.31	0.31	6.97

References

S1.1 Kortly, S.; Sucha, L. *Handbook of Chemical Equilibria in Analytical Chemistry*; Ellis Horwood: Chichester, 1985; Chapter 5, Chapter 6.

S1.2 Baes, C. F.; Mesmer R. E. *The Hydrolysis of Cations*; Wiley & Sons: New York, NY, 1976.

S1.3 Linsday, W. L. *Chemical Equilibria in Soils*; Wiley & Sons: New York, NY, 1979; Chapter 2

S1.4 Kielland, J. *J. Am.Chem. Soc.*, **1937**, *59*, 1675.

S1.5 Rubattel, S.; Lemaître, J.; Bowen, P.; Ring, T. A. *J. Crystal Growth*, **1994,** *135*, 135
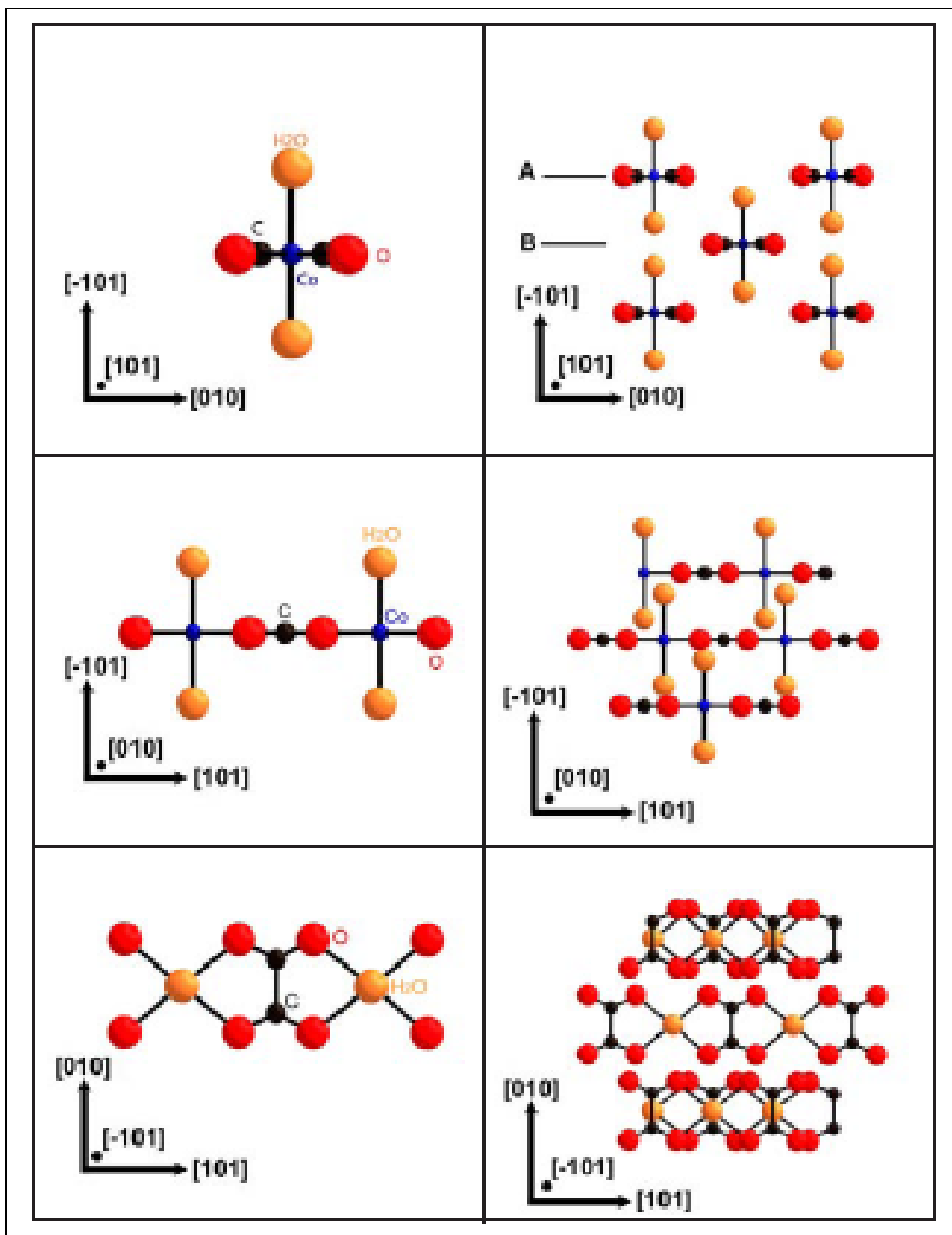
Supplementary material S2
X-ray powder diffraction of cobalt oxalate dehydrate - precipitated with different PMMA concentrations
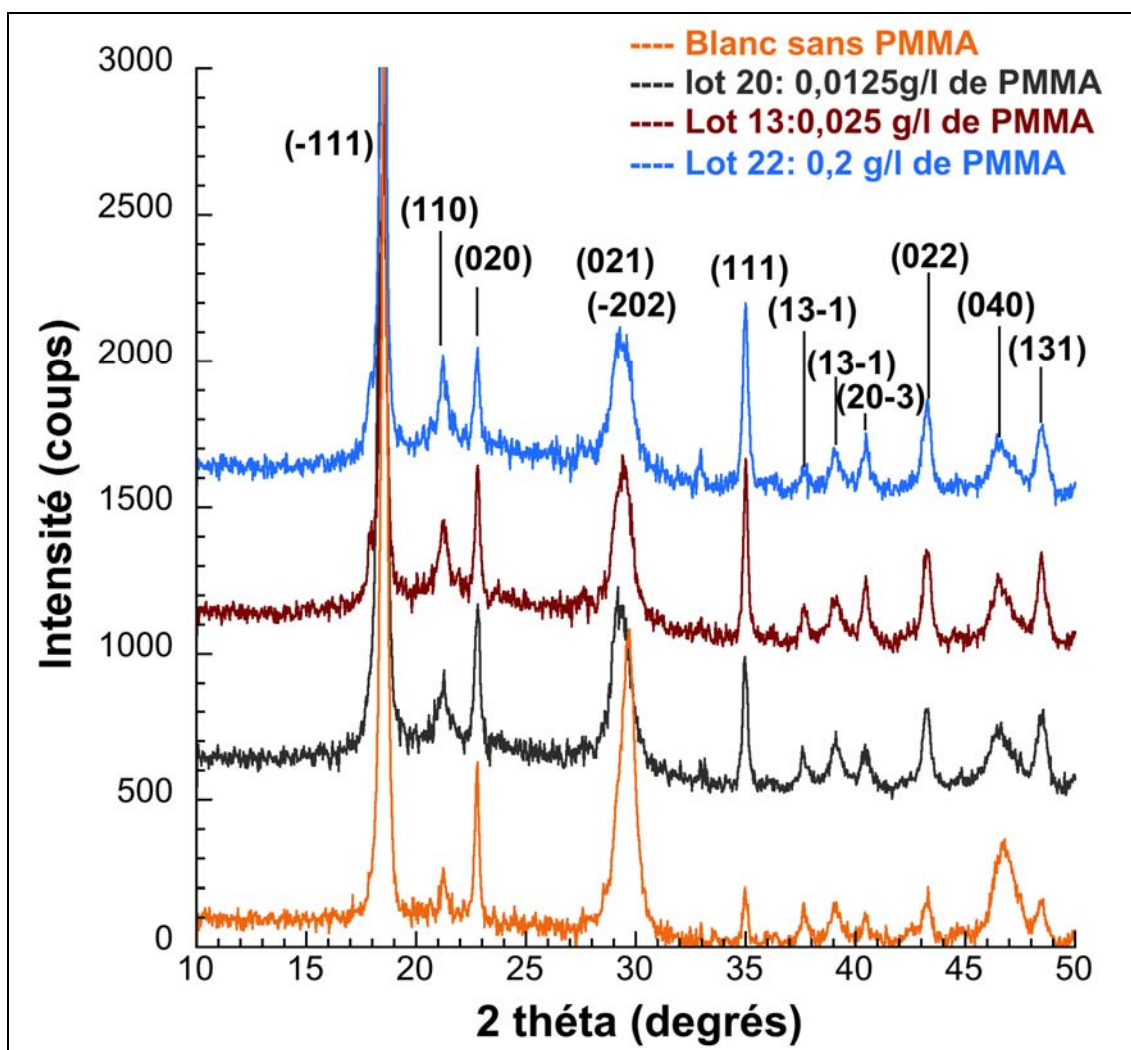
Supplementary material S3

Cobalt oxalate crystallographic monoclinic structure

Avond, G.; Pezerat, H.; Lagier, J.; Dubernat, J. *Re*V. *Chim. Mine´r.***1969**, *6*, 1095-1106.

Supplementary material S4

Thermogravimetric analysis of PMMA and cobalt oxalate dehydrate (OCD)