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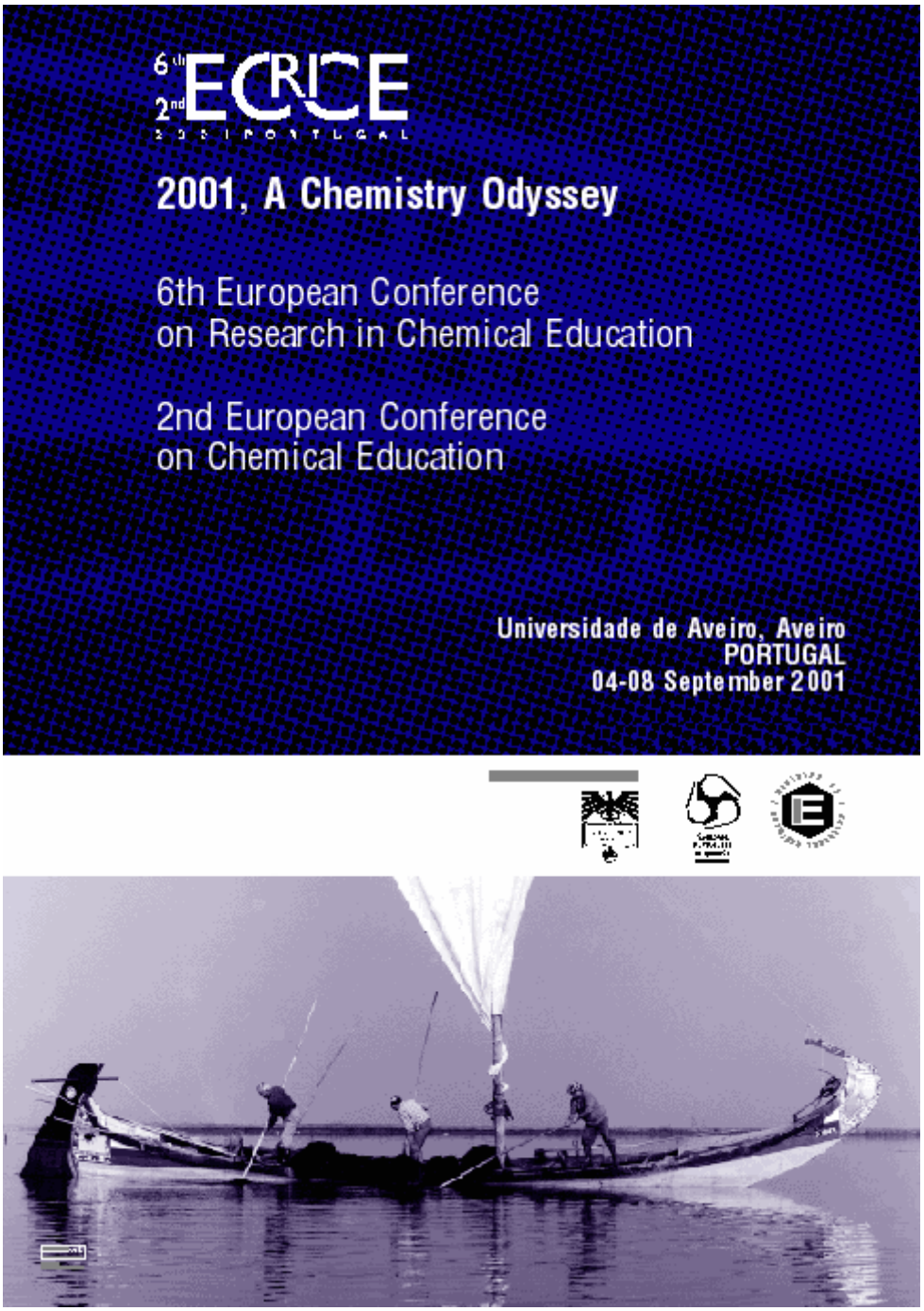


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# ABSTRACT OF POSTER 09. ECRICE 2001

## "Blues ... on the Rocks"

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Crystal growth on rocks, shells and other rough surfaces, producing large single crystals for many ionic compounds in solution can be a very attractive way to teach Inorganic Group Chemistry. Among the most popular are the preparations with different copper salts. A large variety of different formulations is presented, including:

-Simple salts and their methods of synthesis

$CuSO_4 \cdot 5H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$,

$[Cu(NH_3)_4]SO_4 \cdot H_2O$

-Double salts "schönites" $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ and $K_2Cu(SO_4)_2 \cdot 6H_2O$

- Other double salts $CaCu(CH_3COO)_4 \cdot 6H_2O$, $(NH_4)_2CuCl_4 \cdot 2H_2O$

- Solid solutions of "schönites" $M^IM^{II}(SO_4)_2 \cdot 6H_2O$, $M^{II}$= Cu, Ni, Mg, Zn; $M^I$= $NH4^+$, $K^+$

-Heterogeneous and homogeneous mixtures with other metal salts {$KAl(SO_4)_2 \cdot 12H_2O$, $CuSO_4 \cdot 5H_2O$}, {$CuSO_4 \cdot 5H_2O$, $(NH_4)Fe(SO_4)_2 \cdot 12H_2O$}, {$CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$}, etc.

-Rochelle salt {$CuSO_4 \cdot 5H_2O$, $KNa(C_4H_4O_6) \cdot 4H_2O$} doped with copper(II) ions in different conditions, acting as habit modifiers

Granite, quartz, sandstone, arenites, marble and volcanic tuffs were used as base rocks, as well as Oyster and Murex shells and copper wires.

These examples are used to illustrate copper chemistry, the properties of the element and compounds, acid-base, precipitation and redox reactions. Solubility-temperature curves for several of these substances were used for mass balances during crystallization and calculation of initial and final concentrations. Some of the results were confirmed by UV-VIS spectra.

Our studies also include the observation of models representing the crystal lattice structure for some of these compounds, as determined by X rays diffraction data (Beevers Miniature models, 1 Angström= 1 cm).

Extension of this work to Arts, Mathematics, Mineralogy and Geology is also exploited. The method is recommended both for high school and first years graduation courses of University Chemistry.

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**Acknowledgements:** Ministério da Ciência e Tecnologia, Programa Ciência Viva, Project: "Rochas Ornamentais e Minerais Sintéticos" Rede Cristalina, P046, PII147, PIII189C; Ministério da Educação, Programa PRODEP II FOCO, 96-99.

**Key words:** crystal growth on rocks, synthetic minerals, heterogeneous nucleation, giant crystals

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## Blues... on the rocks

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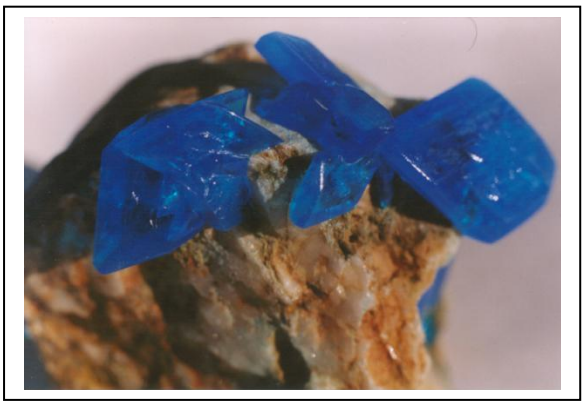
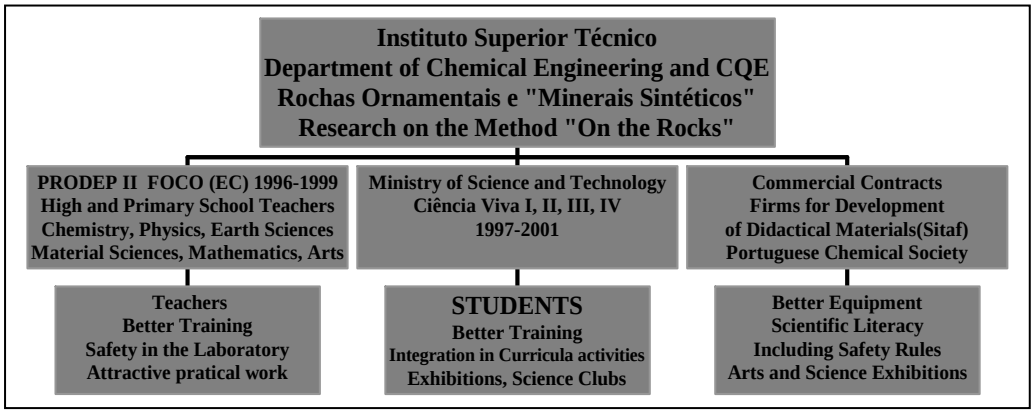


**Figure1-** Crystals of Copper (II) sulphate pentahydrate grown on quartz, an inert host [1]. Photographed by Cristina Fernandes (Art and Design High school teacher).

### Introduction

No, dear reader, you are wrong, if you think by this title we are dealing with suggestions for jazz music or cocktails! We are, as a matter of fact, offering you a very attractive approach to teach Chemistry and other Sciences that may include crystals as an important subject to study. The method of crystal growth **"On the Rocks"** is based on ***heterogeneous nucleation*** [2]: hosts with rough surfaces, such as rocks and shells, induce crystal growth of substances that can easily crystallize as giant single crystals or clusters, using common glassware and very simple and inexpensive techniques (Fig. 1). These experiments were earlier described [1] and some of them are being currently tested, quite successfully, in many Portuguese high and primary schools, in cooperation with our Research Center at Instituto Superior Técnico, CQE. The strategy of this project, also named as "Rochas Ornamentais e 'Minerais Sintéticos" (Ornamental Rocks and 'Synthetic Minerals') is resumed in Box 1, below. Our network started in 1994 at the University, searching for the best substances to test, mainly inorganic simple and double ionic salts and complexes. A rough classification of them is given in Box 2.

**Box 1- The Strategy of our Project "On the Rocks" (Rochas Ornamentais e "Minerais Sintéticos")**



During a period of four years, since 1996, the results of this preliminary research were spread to an amount of about 300 high school teachers, attending several intensive 50-hour courses financed by the FOCO Program (Ministry of Education, European Community Funds). In the beginning, the majority of them were graduated in Chemistry, Physics and Chemical Engineering. Very fast these courses were extended to Earth Sciences teachers (Mineralogy and Geology) and Material Sciences. The symmetry and shape of crystals is, however, very important in Mathematics for the study of polyhedron geometry. Furthermore, their beauty can be a strong source of inspiration to artists in their paintings and sculptures (Fig. 2). For these reasons, Mathematics and Arts teachers were finally admitted in the last two courses. These facts are showing well the important and diversified role of crystals in our surroundings and modern technology (Box 3).

**Box 2- Classification of some Substances for the Method "On the Rocks"**

**a. Metals: Cu, Ag, Sn, etc., the famous "Metallic Trees" formed by Redox reactions in solution**

**b. Molecular crystals (organic compounds, elements, etc.): $S_8$,, glycine $NH_2CH_2COOH$, *salol* $C_6H_4OHCOOC_6H_5$, urea $NH_2CONH_2$, boric acid $H_3BO_3$, sucrose, tartaric acid/tartrates**

**c. Anhydrous ionic salts: $(NH_4)H_2PO_4$, $KH_2PO_4$, $NaNO_3$, $KNO_3$, $NaClO_3$, $NaBrO_3$, $K_2SO_4$, etc.**

**d. Hydrated salts, ionic: $MSO_4 \cdot 7H_2O$ (M = Mg, Ni), $NiSO_4 \cdot 6H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, etc.**

**e. Hydrated double salts, ionic**

**alums $M^{I}M^{III}(SO_4)_2 \cdot 12H_2O$ ($M^{I} = K^+, NH_4^+$, $M^{III}$=Al, Cr, Fe, V)**

**schönites $M_2^{I}M^{II}(SO_4)_2 \cdot 6H_2O$ ($M^{I} = K^+, NH_4^+$, $M^{II}$= Cu, Ni, Fe, Co, Mg, Zn, Mn)**

**f. Other hydrated ionic double salts: Rochelle or Seignette salt $KNa(C_4H_4O_6) \cdot 4H_2O$, $CaCu(CH_3COO)_4 \cdot 6H_2O$, $LiNa_3(CrO_4)_2 \cdot 6H_2O$, $(NH_4)_2CuCl_4 \cdot 2H_2O$, etc.**

**g. Solid solutions (one phase of crystallised material): solid solutions of alums $KAl_xCr_{1-x-y}Fe_y(SO_4)_2 \cdot 12H_2O$, etc., schönites $(NH_4)_2Co_xNi_{1-x}(SO_4)_2 \cdot 6H_2O$, etc.**

**h. Heterogeneous mixtures (with more than one phase of crystallised material)**

**i. Other complexes (also organometallic compounds): $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6] \cdot 3H_2O$, etc.**

Thanks to the efforts and financial support from the Ministry of Science and Technology (Ciência Viva Programs I-IV, 1996-2002) many of these teachers are now able to perform several of our experiments with their students integrated in the regular curricula programs, or at their "Science Clubs" in schools. Two years ago, a primary school (Fig.3) joined successfully our present network covering more than 60 projects related to crystal growth, all over the country. Some of the results have been presented at Science and Technology Exhibitions and Conferences but, apparently, this

approach has not yet been used for teaching purposes abroad. The co-operative interaction between both Ministries, the schools, and the University is very promising: new ideas are developing and immediately being applied, and joint research projects are emerging to solve specific questions and interesting problems arising from the application of our methodology.

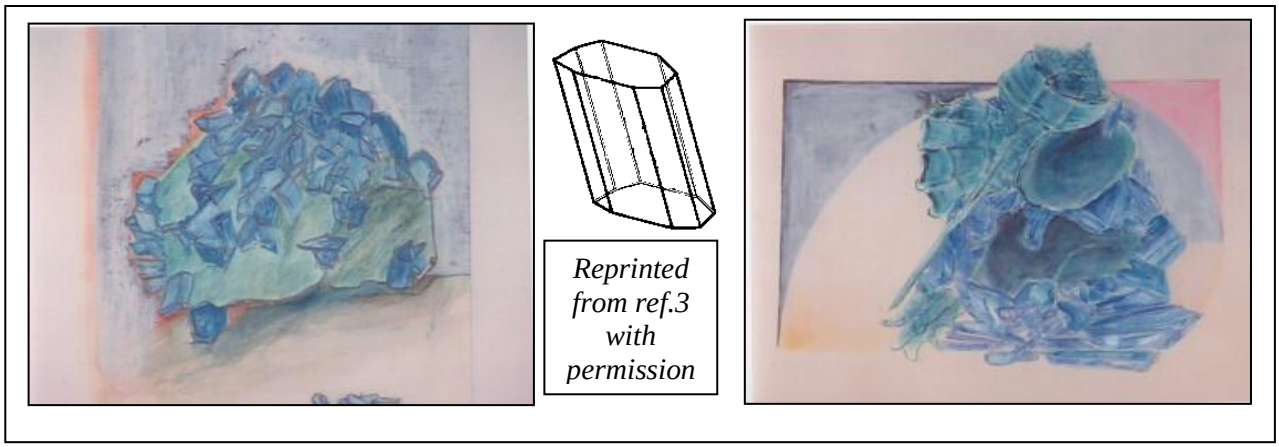



**Figure2-** Crystals of Copper (II) sulphate pentahydrate grown on limestone (left) and on a Murex (right, "Murex spiral growth and copper sulphate"). Painted by Cristina Fontoura Carvalhão (Art and Design high school teacher). The central drawing shows an ideal crystal of this compound (triclinic crystallization system) [3]. Both hosts are covered by green microcrystalline needles, formed by decomposition caused by the acidic copper ion solutions in contact with calcium carbonate.

## Box 3-Crystals, Technology and Society

***Crystals in our daily life***

*Nowadays we live surrounded by crystals, the basic units of most part of solid materials.*

*Snow flakes, metals, minerals, gems, and rocks composed by crystals are surely some of the most ancient examples. We cannot forget as well all the biogenic minerals such as aragonite from shells, enamel from our teeth, hydroxyapatite from our bones, etc. Many more crystals were created or manipulated by man: the sugar and salt we use in our food; the ice in the freezer; the colorful bath salts; the pills prescribed as pain killers such as aspirin and the most part of drugs used in medicine; the nice synthetic jewels for our parties, etc. As technology became more advanced, we realize our total dependency on new and sophisticated materials which have crystals in their composition: synthetic diamonds for cutting tools used by surgeons and in modern machinery; rubies for lasers; optics in many instruments; silicon wafers in electronic cards; liquid crystals in our computers and calculators, etc..*

***Crystals are studied in Crystallography. This field of Science includes many different areas. Probably the most important are:***

***a) Crystallization:*** *a classical laboratory technique for separation and purification of substances. It became an important industrial technique for large-scale production of small crystals. Some methods are resumed in Box 4.*

***b) Crystal growth****:*

***b1) Production of small single crystals*** *(~1mm) for structural characterization and identification of compounds by X-ray diffraction methods, as a complement of other instrumental methods associated to synthesis of chemicals.*

***b2) Production of large single crystals*** *in materials technology (crystal engineering, Fig.4)*

***b3) Characterization of crystals****, an important tool in studies of natural crystals in mineralogy and geology.*

***b4) Measurement of physical properties in pure crystals***

***Some examples of Crystallization and Crystal Growth in the field of Chemistry*** *are listed below [4]:*

***Industrial crystallization:***

*Polycrystalline bulk materials (NaCl, sugar, urea, zeolites) industrial production*

*Silicon single-crystals, industrial production*

***Structural analysis:*** *production of small single-crystals (less than one mm) to collect diffraction data (X rays, etc.)*

***Separation, purification, and characterisation of*** *chemicals and natural products, including the separation of racemic mixtures*

***Crystallization of macromolecules (proteins, polymers)***

***Biocrystallization in the medical field*** *(proteins, microgravity, heterogeneous nucleation)*

***Synthesis of catalysts (zeolites)***

**Figure 3-** A first approach to the study of crystals promoted by our Ciência Viva Project in a primary school (Escola do 1º Ciclo de Penamacor, Portugal). Left: silver dendrites ("metallic trees") are produced in a Petri dish and amplified by the microscope (a crystallization method based on the redox reaction between a copper coin and a silver nitrate solution:

$$Cu(s) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)\downarrow \qquad (1)$$

Right: crystals of ADP, ammonium dihydrogen phosphate, colored by a food dye [1] observed in the microscope; study and preparation of a polymer "Silly Putty" (polymers and crystals, why do they behave differently?).

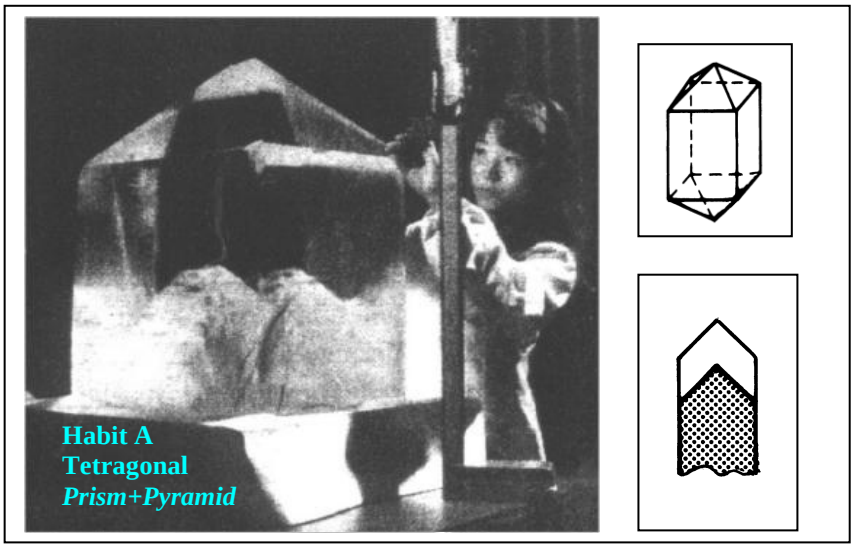



**Figure 4-** Industrial manufacture of single giant crystals of KDP [1], potassium dihydrogen phosphate, used as transducer and as a reference substance for non-linear optics [4].
*Reprinted, with permission, from*: HULLIGER, J., (1994) Chemistry and Crystal Growth, *Angew. Chem. Int. Ed. Engl.*, 33, 143-162.

**Box 4- Some of the Most Common Crystallization Methods**

**PHYSICAL METHODS**

a. Without solvent - change of state:

a1. Melting/solidification ("*salol*", sulfur $S_8$, silicon, metals, etc.)

a2. Sublimation/condensation from gaseous phase (sulfur, iodine $I_2$, camphor, naphtalene (mothballs), menthol, etc.,

b. With one or more combined solvent(s):

b1. Solvent evaporation **(method "On the Rocks")**

b2. Freezing of the solvent

b3. Addition of a precipitating agent

b4. Dependence of solubility on temperature **(method "On the Rocks")**

b5. Dependence of solubility on pressure

b6. Mixed processes b1+ b4 etc., **(method "On the Rocks")**

c. Mixed processes (e.g. $NaCH_3COO{\cdot}3H_2O$, melting and dissolution in crystallization water, followed by evaporation/ decrease in temperature)

**CHEMICAL METHODS**

d. Oxidation-reduction reactions (metal trees, dendrites, combining different redox potentials

e. Double ionic exchange or metathesis reactions:

$2KI\,(aq) + Pb(NO_3)_2(aq) \rightarrow 2KNO_3(aq) + PbI_2(s)\downarrow$ (2)

f. Addition reactions (formation of double salts, alums and schönites, etc.)

g. Others, complexation, hydroxides precipitation, acid- base reactions, as those cited in Fig.2, with the formation of needles following the attack of calcium carbonate by acidic solutions, etc. $CaCO_3(s) + 2H_3O^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g/l)\uparrow + 2H_2O(l)$ (3)

**The Blues "On the Rocks"**

Among the most popular preparations "On the Rocks" are those with copper salts, many of them with wonderful blue colors. Several different formulations are presented in Table 1, together with the classification of compounds given in Box 2. Copper and transition metals salts in this Table are all complexes, but we added another classification to be able to distinguish them. The general method of preparation and type of hosts are described elsewhere [1]. Some highlights are given below for those that require a special synthesis (the pure compounds are not available in the market)

or deserve further remarks. These examples and their synthesis can include other common experiments on copper group chemistry. Granite, quartz, sandstone, arenites, marble and volcanic tuffs were used as hosts rocks, as well as Murex shells, copper and zinc wires, tissues and wood [1]. Solubility data in Appendix were used for mass calculations in the beginning and after crystallization, following the method described earlier for potassium dihydrogenphosphate [1]. The trend for $CuSO_4{\cdot}5H_2O$ in the dispersion of the concentrations of the final solutions is similar to KDP, whereas for the less soluble ammonium schönites the concentrations in the end of crystal growth clearly show that saturated solutions are obtained.

**Table 1- Major Classes of Copper Compounds, "On the Rocks"**

| **General method of synthesis from reference [1] or other** | **N$^o$ of the Sample Compound, Classification from Box 2 and Composition** |
|---|---|
| Dissolution of 56g/100 ml water; 80 g/100 ml water if metal wires are used as hosts | **1d $CuSO_4{\cdot}5H_2O$**, Hydrated ionic salt, Figs 1, 2<br>Any host. Calcium carbonate hosts are reactive (see below). |
| Dissolution of 10g/100 ml water. The addition of a few drops of acetic acid may improve the dissolution process and avoid the formation of scum. | **2d $Cu(CH_3COO)_2{\cdot}H_2O$**, Hydrated ionic salt, Fig.5. Any host. It can be prepared from CuO or $CuCO_3$ by reaction with acetic acid, followed by concentration, filtration and crystallization. |
| Dissolution of 50g of hydrated metal salts/100 ml water. The crystal | **3g {$xCuSO_4{\cdot}5H_2O$, $yNiSO_4{\cdot}6H_2O$}**, Solid solutions, Fig.5<br>**Nickel salts are human carcinogenics.** Any host. |
| system and color vary with the proportions of the two components | **4g {$xCuSO_4{\cdot}5H_2O$, $yZnSO_4{\cdot}7H_2O$},** Solid solutions. Zinc sulfate is efflorescent, high concentrations of this component are not recommended. Blue crystals. Any host. |
| Dissolution of 139g of pure tartrate in 100 ml water. A few drops of $CuSO_4{\cdot}5H_2O$ saturated solution is added. The precipitate formed is separated by filtration. The solution obtained is used to grow the crystals by the usual method. | **5f $KNa(C_4H_4O_6){\cdot}4H_2O$ doped with Cu(II) ions.** It can also be classified as a solid solution, {$CuSO_4{\cdot}5H_2O$, $KNa(C_4H_4O_6){\cdot}4H_2O$} Fig.6. Any host. Calcium carbonate hosts, together with copper(II) ions are habit modifiers of this salt. |
| The synthesis is described below. Any host can be used. | **6f Hydrated double salts $CaCu(CH_3COO)_4{\cdot}6H_2O$** Fig.7 |
| The synthesis is described below. Avoid calcium carbonates as hosts. | **7f Hydrated double salts $(NH_4)_2CuCl_4{\cdot}2H_2O$** Fig.7 |
| The same method as 9e. Any host. | **8e $K_2Cu(SO_4)_2{\cdot}6H_2O$, schönite.** The same color as ammonium schönite. |

| | |
|---|---|
| 55g (0.22 mol) $CuSO_4 \cdot 5H_2O$ is added to the same amount of the ammonium salt 29g (0.22 mol), primarily dissolved in the minimum amount of water. The total volume for the solution should be 250 ml. | **9e $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$, schönite.** The anmmonium salt is easier than the potassium one for obtaining larger crystals. Any host. See Fig.7. |
| The same method as 9e. a total amount of 0.22 mol of hydrated metal salts should be used. | **10g $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$, M= $Cu_xNi_yMg_zZn_{(1-x-y-z)}$** Cobalt should be excluded in the presence of copper. Solid solutions of schönites of different colors. Any host. |
| A variable amount of copper sulfate is dissolved in a solution of potassium alum (30g/100 ml water). | **11g {$KAl(SO_4)_2 \cdot 12H_2O$, $CuSO_4 \cdot 5H_2O$}.** This solid solution has a very light blue color. The solubility of the copper compound is very low. |
| A variable amount of copper sulfate is dissolved in a solution of ferric alum (50g/ 150 ml solution). | **12h {$CuSO_4 \cdot 5H_2O$, $(NH_4)Fe(SO_4)_2 \cdot 12H_2O$}.** Efflorescent green and light yellow.crystals. |
| The color and number of different phases changes with the composition. | **13h {$KAl(SO_4)_2 \cdot 12H_2O$, $KCr(SO_4)_2 \cdot 12H_2O$, $CuSO_4 \cdot 5H_2O$}** |
| Dissolution of $CuSO_4 \cdot 5H_2O$ 56g/100ml water, followed by crystal growth of the same compound. Addition of ammonium sulfate to the saturated solution for co-precipitation of the double salt. | **14h {$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$}** Fig.7. There are alternative methods for preparation. This one is better, as long as some of the copper sulfate remains in solution, after the growth of $CuSO_4 \cdot 5H_2O$. The double salt is rather less soluble (see Appendix). Any host. |
| Only microcrystalline samples were obtained.on basalt. | **15i $[Cu(NH_3)_4]SO_4 \cdot H_2O$.** Dark blue crystals. |

**Notes to Table 1, compounds and methods of synthesis/crystal growth**

**1d- Copper (II) sulphate pentahydrate $CuSO_4 \cdot 5H_2O$**

Most of the copper salts aqueous solutions have low pH (-2, 3) due to the acid character of $[M(H_2O)_6]^{n+}$ ions, Brönsted acids (4). Carbonated hosts will decompose, with bubbling of carbon dioxide (reaction 3, Box 4, Fig.2):

$$[Cu(H_2O)_6]^{n+}(aq) + H_2O(l) \leftrightarrow [Cu(H_2O)_5(OH)]^{(n-1)+}(aq) + H_3O^+(aq) \qquad (4)$$

Crystal growth on zinc or metals with lower redox potentials than copper ($E^o$ ($Cu^{2+}$/ Cu) = 0.34 V and $E^o$ ($Zn^{2+}$/ Zn) = -0.76 V) will compete with redox reactions, producing metallic copper crystals:

$$Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)\downarrow \qquad (5)$$

During this reaction the solution turns green, the zinc wires are covered with metallic copper and blue $CuSO_4 \cdot 5H_2O$ crystals are also formed.

It is also very interesting to combine as a side experiment the redox reaction from Fig.3 ($E^o$ ($Ag^+$/ Ag) = 0.90 V).

The compound $CuSO_4 \cdot 5H_2O$ can be produced from the reaction of concentrated sulfuric acid with copper, or by the reaction of the diluted acid on copper oxide, copper carbonate or copper hydroxide**.** Again the redox potentials should be discussed after these experiments.

$$Cu(s) + 2H_2SO_4\ (conc) \rightarrow CuSO_4\ (c) + SO_2(g) + 2H_2O(l) \qquad (6)$$

$$CuSO_4\ (c) + 5H_2O(l) \rightarrow CuSO_4 \cdot 5H_2O\ (c) \qquad (7)$$

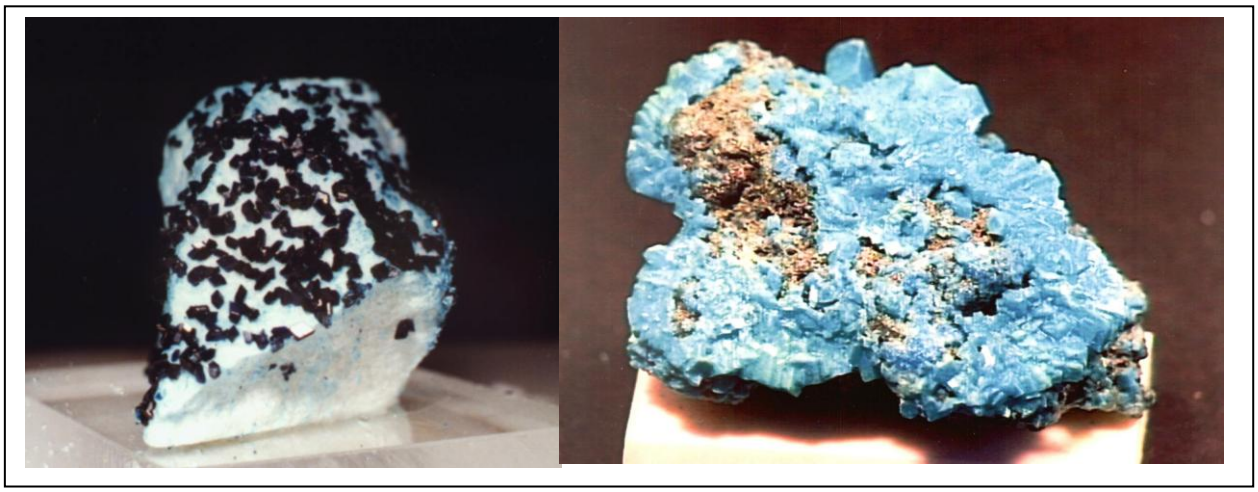


**Figure 5-** $Cu(CH_3COO)_2 \cdot H_2O$ on white marble (left). {$CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$} solid solution (right).

### 6f- Hydrated double salt $CaCu(CH_3COO)_4 \cdot 6H_2O$

Obtained by synthesis:

CaO powder, 11.3g, after grinding, are added to 100 $cm^3$ water in a 400 $cm^3$ beaker.

$$CaO\ (s) + H_2O(l) \rightarrow Ca(OH)_2(aq) \qquad (8)$$

Concentrated acetic acid is added to this suspension and stirred. Filtration may be required to obtain a transparent solution.

$$Ca(OH)_2\,(aq) + 2CH_3COOH(aq) \rightarrow Ca(CH_3COO)_2(aq) + 2H_2O(l) \qquad (9)$$

$Cu(CH_3COO)_2{\cdot}H_2O$, 10 g, are dissolved in water, 150 ml, heated and stirred. The two solutions are mixed. The general method for crystal growth is followed.

$$Ca(CH_3COO)_2(aq.) + Cu(CH_3COO)_2(aq) + 6H_2O(l) \rightarrow CaCu(CH_3COO)_4{\cdot}\,6H_2O\,(c) \qquad (10)$$

### 7f- Hydrated double salt $(NH_4)_2CuCl_4{\cdot}2H_2O$

Prepared from the addition reaction of ammonium chloride (0.2 mol) to dihydrated copper chloride (0.1 mol) in 65 ml water. Only inert hosts can be used (basalt, quartz).

### 9e- Ammonium copper schönite $(NH_4)_2Cu(SO_4)_2{\cdot}6H_2O$

Addition reaction:

$$CuSO_4{\cdot}5H_2O\,(aq) + (NH_4)_2SO_4\,(aq) + H_2O\,(l)$$
$$\downarrow\downarrow$$
$$(NH_4)_2\,Cu\,(SO_4)_2{\cdot}6H_2O(s) \qquad (11)$$

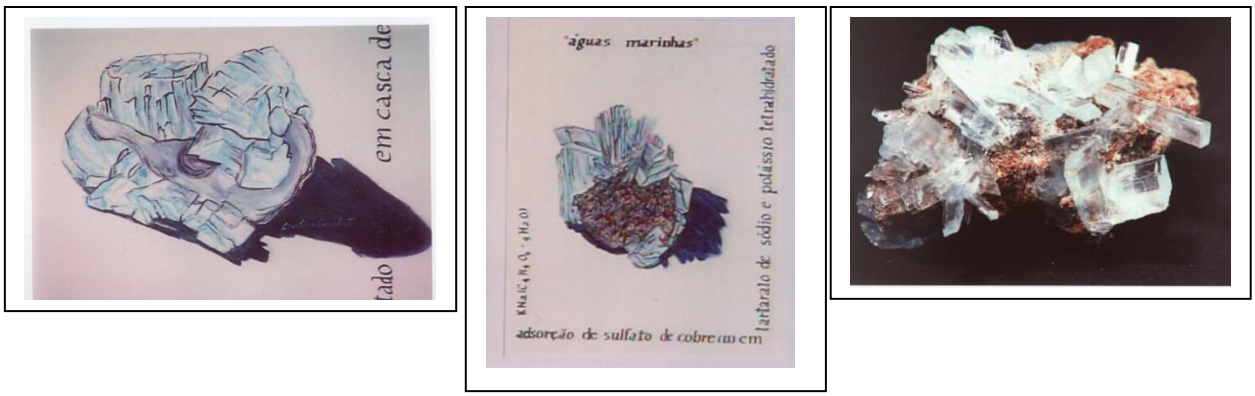



**Figure 6-** Potassium sodium tartrate $KNa(C_4H_4O_6){\cdot}4H_2O$ modified by Cu(II) ions: a few drops of copper sulfate (aq) are added to the solution. Left: crystals grown on shells or "basic" hosts (calcium carbonates: marble, limestone, etc.) are more "tabular" than those of the pure compound. Right and center: on basalt crystals grow like columns. Drawings made by Cristina Fontoura Carvalhão.

### 10g- Solid Solutions $(NH_4)_2M(SO_4)_2{\cdot}6H_2O$, M= $Cu_xNi_yMg_zZn_{(1-x-y-z)}$

The different solid solutions of schönites are easily obtained recycling the solutions used to prepare the pure double salts. After collecting the crystals formed in the first step, the mother liquid is filtrated and ammonium sulphate (or potassium sulphate) and another metal hydrated salt is added

[3]. There are many different possibilities because all the compounds from the same family are isostructural. The variety of colours is very large.

**15i- $[Cu(NH_3)_4]SO_4 \cdot H_2O$**

A concentrated ammonia solution (25%, reaction 12) is slowly added to a copper sulphate aqueous solution (2g, minimum of water), until a blue precipitate is formed (reaction 13). Excess of ammonium solution is added, until a dark blue colour is formed and the precipitate $Cu(OH)_2$ (s) is completely dissolved (14). The complex precipitates by addition of ethanol (15):

$$NH_3\,(aq) + H_2O \leftrightarrow NH4^+(aq) + OH^-(aq) \qquad (12)$$

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2\,(s)\downarrow \qquad (13)$$

$$Cu(OH)_2\,(s) + 4NH_3\,(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 2\,OH^-(aq) \qquad (14)$$

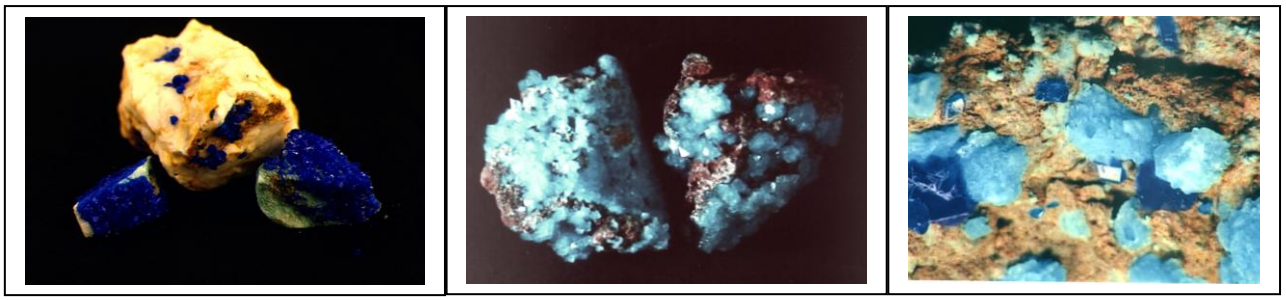


**Figure 7-** Copper double salts. Left: $CaCu(CH_3COO)_4 \cdot 6H_2O$ on marble. Centre: $(NH_4)_2CuCl_4 \cdot 2H_2O$ on basalt. Right: heterogeneous mixture of copper schönite $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$.

$$[Cu(NH_3)_4]^{2+}(aq) + SO_4^{2-}\,(aq) + H_2O\,(l) \rightarrow [\,Cu(NH_3)_4]\,SO_4 \cdot H_2O\,(s)\downarrow \qquad (15)$$

A side reaction (16) may also occur (16):

$$[Cu(NH_3)_4]^{2+}(aq) + 2\,OH^-(aq) + H_2O\,(l) \rightarrow [Cu(NH_3)_4](OH)_2 \cdot H_2O\,(s)\downarrow \qquad (16)$$

**Safety rules**

**Always wear a lab coat, goggles, and gloves. Toxic substances should be handled in a fume hood. If not available (depending on the toxicity of the substances) work in a well ventilated room and wear at least a powder mask for grind up the solid substances. Avoid breathing the vapors. Copper and transition metal salts are nocive. Safety rules for these compounds were published elsewhere [5-7].**

**References:**

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7-OHS Material safety data sheet.

**Key words:** crystal growth on rocks, synthetic "minerals", heterogeneous nucleation, giant crystals, Copper group chemistry

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## Appendix

**Table 2 -Solubility Data for Pentahydrated Copper Sulfate [3]**

| **t/$^{o}$C** | **Mass (g) of $CuSO_4 \cdot 5H_2O$ per 100 g of total water; M=249.54** | **$CuSO_4 \cdot 5H_2O$ Moles** | **Mass (g) of anhydrous* $CuSO_4$ per 100 g of total water; M=159.5** |
|---|---|---|---|
| 0 | 22.4 | 0.089765 | 14.3 |
| 10 | 27.2 | 0.109001 | 17.4 |
| 20 | 32.3 | 0.129438 | 20.7 |
| 30 | 39.1 | 0.156688 | 25.0 |
| 40 | 44.6 | 0.178729 | 28.5 |
| 50 | 52.0 | 0.208383 | 33.3 |
| 60 | 62.6 | 0.250862 | 40.0 |
| 80 | 86.0 | 0.344634 | 55.0 |
| 100 | 117.9 | 0.472469 | 75.4 |

* Solid phase, $CuSO_4 \cdot 5H_2O$: mass of anhydrous salt obtained by calculation. The total amount of water is the one added as a solvent plus the crystallization water liberated by the salt dissolution.

**Table 3- Solubility Data for Copper Schönites [3]**

| t/$^{o}$C | Mass (g) of anhydrous $K_2Cu(SO_4)_2$ per 100 g of saturated solution | Mass (g) of anhydrous $(NH_4)_2Cu(SO_4)_2$ per 100 g of saturated solution |
|---|---|---|
| 0 | 4.84 | 10.27 |
| 10 | 6.71 | 13.10 |
| 20 | 9.09 | 16.22 |
| 30 | 11.97 | 19.64 |
| 40 | 15.37 | 23.34 |
| 50 | | 27.34 |
| 60 | | 31.63 |
| 70 | | 36.21 |
| 80 | | 41.08 |

* Solid phase: hydrated salt, $6H_2O$. Anhydrous salt mass obtained by calculation.



**This work was published in 2001, in a CDROM of the Proceedings of a Conference in Aveiro, Portugal. It is a review concerning crystal growth on rough surfaces, the method "On the Rocks" published for the first time in 1994. It comprehends the preparation of blue compounds in the Laboratory, and a resumé of the method "On the Rocks" for copper compounds, the essence of the Blues… Minor corrections were added, and a few side experiments are indicated in the field of Chemical Microscopy (following chemical reactions and crystallization processes under the stereomicroscope).**

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