



## Crystal chemical preconditions for the species diversity of minerals-hydroxy-salts

### Кристалохимични предпоставки за видовото разнообразие на минералите хидрокси-соли

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The minerals hydroxy-salts form an essential part of the mineralogical nomenclature. Typically, they are stable in a small range of external conditions (such as Eh, pH, T, solution concentration, component ratio, impurities, etc.) and often associated with many other minerals with similar compositions in the same paragenesis. Unlike stable rock-forming minerals, the hydroxy-salt minerals react to changes in the environment through changes in the crystal structure forming new minerals. This leads to a great mineral diversity of the mineral hydroxy-salts.

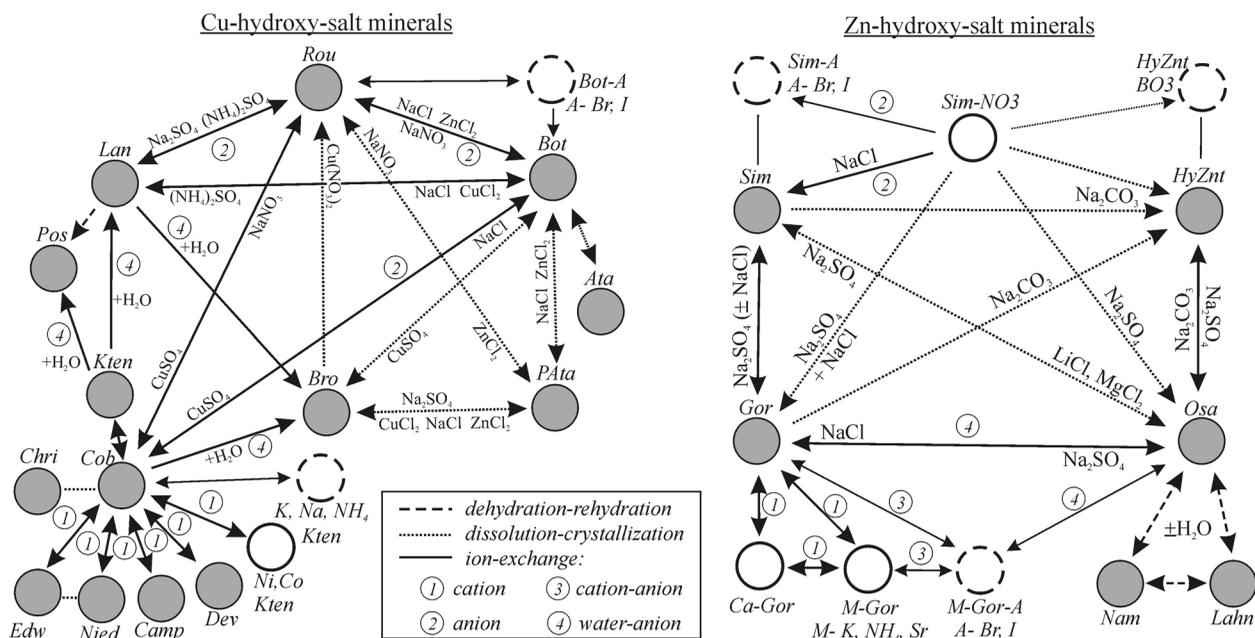
The main reason for the diversity of these mineral species is the binary nature of their structures, i.e. they are built up of structural units (SUs) linked by intersectional complexes (ICs) (Hawthorne, Schindler, 2008). The SU is characterized by strong and relatively homogeneous bonds between the components. The bipolar character of the dominant anion ( $\text{OH}^-$ ) in the hydroxy salts predisposes the polymerization of cation-OH polyhedrons (octahedra, tetrahedra, squares) in one or more often two directions, forming hydroxide layers or single or coupled ribbons of metal-OH polyhedrons. The components of the IC are weakly connected and easy to move. The wide variety of IC components (water molecules, cation-water complexes and/or anions), their different role and their interaction with each other as well as with the SUs are the main factors for the multiplicity of hydroxyl-salt mineral species.

Based on the study of the different mechanisms of their mutual transformations, their specific properties can be determined, as well as to synthesize and predict new crystalline compounds. Two major mechanisms of transformation of layered minerals have been discussed in the literature: solid state and dissolution-crystallization (Cuadros, 2012). The complexity of the IC and the variety of its interaction with the SUs (the hydroxide layers of the minerals hydroxy-

salts), provoked the study of the mechanisms of their transformations.

In the present study the mineral salts of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  are investigated. They are an important part of the oxidation zones of sulphide deposits. Depending on the nature of the slurry solutions, these minerals are mostly crystallized as hydroxy sulphates, hydroxy-chlorides and hydroxy-carbonates, but are also associated with similar hydroxy-phosphate, hydroxy-arsenate minerals. The different electronic structure of the two cations  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  determines formation of different hydroxide layer. In the structures of copper hydroxides with general formula  $[\text{Cu}^{2+}(\text{OH})_{2-x}\text{A}_{x/n}^{n-}] [\pm\text{H}_2\text{O}]$ , the charge is generated by the hydroxyl vacancies in  $\text{M}^{2+}(\text{OH})_2$  layer, which are occupied by non hydroxyl anion. In the case of zinc hydroxy-salt minerals with the general formula  $\text{Zu}^{2+}(\text{OH})_{2-x}\text{A}_{x/n}^{n-} \cdot \pm\text{H}_2\text{O}$ , the layer has a composition  $[\text{Zn}_x\text{Zn}_{x/4}(\text{OH})_{2-x}]^{2+}$ , where  $^{\text{oh}}\text{Zn}$  and  $^{\text{td}}\text{Zn}$  are octahedral and tetrahedral coordinated cations, respectively and  $\square$  is an octahedral vacancy. The positive charge is balanced by an anion, and the tetrahedron is completed by a water molecule.

The results of the experimental study show several mechanisms of transformation in the two mineral systems (Fig. 1). Similar to clay minerals, the hydroxy salt minerals are transformed through two main mechanisms: dissolution-crystallization and solid state transformation. In this case, however, solid state transformation involves several particular mechanisms: ion exchange (cationic and/or anionic); dehydration-rehydration; import/export of ion pair. Depending on the interaction strength of non-hydroxyl anions with the layer, the different type of transformation mechanism is predetermined. In cases where the anion is part of the SU (hydroxide layer) (atacamite, paratacamite, brochantite and simoncolleite, hydrozincite), the mutual transformations proceed by dissolution-crystallization. In cases where non-hydroxyl anions are part



**Fig. 1.** Schemes of mutual transformations in the systems of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  hydroxy salt minerals. Symbols: *Circles*: bolded – natural minerals; non-bolded – synthetic compounds; dashed – predicted samples; *Rou* – rouaite;  $\text{Cu}_4(\text{OH})_6(\text{NO}_3)_2$ ; *Bot* – bottallackite  $\text{Cu}_4(\text{OH})_6\text{Cl}_2$ ; *Ata* – atacamite  $\text{Cu}_4(\text{OH})_6\text{Cl}_2$ ; *PAta* – paratacamite  $\text{Cu}_4(\text{OH})_6\text{Cl}_2$ ;  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot n\text{H}_2\text{O}$ : *Lan* – langite ( $n=2$ ); *Pos* – posnjakite ( $n=1$ ); *Bro* – brochantite ( $n=0$ );  $\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot M^{2+}\text{SO}_4 \cdot 6\text{H}_2\text{O}$ : *Kten* – Ktenasite ( $M\text{-Zn}$ ); *Cob* – cobyashevite ( $M\text{-Cu}$ ); *Nie* – niedermayrite ( $M\text{-Cd}$ ); camplingite ( $M\text{-Mn}$ );  $\text{Cu}_3\text{M}_2(\text{OH})_6(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ : *Cri* – christelite ( $M\text{-Zn}$ ); *Edw* – edwardsite ( $M\text{-Cd}$ ); *Sim* – simoncolleite  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ ; *HyZnt* – hydrozincite  $\text{Zn}_2(\text{OH})_6(\text{CO}_3)_2$ ;  $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot n\text{H}_2\text{O}$ : *Osa* – osakaite ( $n=5$ ); *Nam* – namuwite ( $n=4$ ); *Lahn* – lahshteinite ( $n=3$ ); *Gor* – godaite  $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot \text{NaCl} \cdot 6\text{H}_2\text{O}$ .

of IC (rouaite, bottallackite, langite) or are equally energetically related to SU and IC (gordaite, simoncolleite), a typical reversible anion exchange (rouaite, bottallackite, langite, simoncolleite) or simultaneous cation-anion exchange (gordaite) are occurred. The replacement of the interstitial cation in both types of hydroxide layers (ktenasite and godraite) is a typical reversible ion-exchange process. There is also an isomorphic cationic substitution in the hydroxide layer, which proceeds through dissolution-crystallization (ktenasite-christelite; niedermayrite-edwardsite, paratacamite, namuwite). This type of transformation has limitations predetermined by the structural features of the two types of hydroxide layers (Stanimirova, Delcheva, 2015). In the zinc system, a specific exchange between water molecules that are equally energy-related to CE and IC and halides (namuwite-gordaite) is occurred. This process involves the import/export of a cation-anion pair. For minerals with water molecules as the only interstitial component (osakaite, namuwite and lahshteinite) a classical dehydration-rehydration also proceeds.

In conclusion, the variety of components in the IC, their different crystal-chemical roles that they perform (charge balancing, charge distribution, charge transfer, space filling, and ion hydration), and the strength of interactions predetermine a wide range of transformations and formation of different types of structures and minerals, respectively. On the other hand, knowing the specificity of the structures and mechanisms of transformation makes it possible to predict possible new minerals as well as to synthesize new materials with similar structures and specific properties.

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