



Limitations of Cu²⁺-Zn²⁺ isomorphous substitution in the Cu, Zn hydroxy-salt minerals

Ограничения на Cu²⁺-Zn²⁺ изоморфизъм в Cu, Zn минерали хидроксиди-соли

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The Cu, Zn hydroxy-salt minerals are an important part of the oxidation zones of sulfide deposits. They play an important role as protectors of the migration of both toxic ions in the environmental.

The isomorphous substitutions of Cu²⁺ ↔ Zn²⁺ cations in the structures of hydroxy-salt minerals with general formula M²⁺(OH)_{2-x}A_{x/n}ⁿ⁻·±H₂O, wherein M²⁺ is Cu²⁺ and Zn²⁺, A⁻ are SO₄²⁻, Cl⁻, CO₃²⁻ (Table 1) were investigated. The structures of all studied minerals are built of positively charged hydroxide layers or chains and charge-balancing anions, located in the interlayer space or connecting different chains. Despite of the similar ionic radii and equal valence the two cations Cu²⁺ (3d⁹) and Zn²⁺ (3d¹⁰) show different crystal chemical behavior in a strong ligand field. The copper cations form hydroxide layers or chains represented as a pseudo-octahedral, made up of Cu(OH)₄

square frames due to Jahn-Teller’s effect (Eby, Hawthorne, 1993; Stanimirova et al., 2013), while the zinc cations cause formation of octahedral-tetrahedral ([^{oh}Zn_x□^{td}Zn_{x/4}(OH)_{2-x}]²⁺) (Bevins et al., 1982) hydroxide layers as result of their ability to realize both octahedral and tetrahedral coordination.

In the structures of all studied hydroxy-salt minerals, the Cu²⁺ ↔ Zn²⁺ cationic substitution occurs only in structures with average bond length between the M²⁺ and four nearest located OH groups equal from 2.02 to 2.08 Å (Fig. 1). In the structures of copper hydroxy-salt minerals – brochantite, poznjakite, botallackite, atacamite, malachite and azurite, the isomorphous substitution of Cu²⁺ with Zn²⁺ cations was not observed due to the very short distances between Cu cations and coordinating hydroxyl groups (1.94–2.00 Å). In the structures of atacamite and ktenasite a Cu²⁺ ↔ Zn²⁺ mu-

Table 1. Minerals Cu, Zn hydroxy-salts

Mineral	Formulae	Symbol	Mineral	Formulae	Symbol
copper hydroxy-salt minerals			zinc hydroxy salt minerals		
Posnjakite	Cu ₄ (OH) ₆ SO ₄ ·H ₂ O	<u>Pos</u>	<i>Namuwite-type structures</i>		
Brochantite	Cu ₄ (OH) ₆ SO ₄	<u>Bro</u>	Namuwite	Zn ₄ (OH) ₆ SO ₄ ·4H ₂ O	<u>Nam</u>
<i>Ktenasite-type structure</i>			Osakaite	Zn ₄ (OH) ₆ SO ₄ ·5H ₂ O	<u>Osa</u>
Ktenasite	Cu ₄ Zn(OH) ₆ (SO ₄) ₂ ·6H ₂ O	<u>Kten</u>	Lahnsteinite	Zn ₄ (OH) ₆ SO ₄ ·3H ₂ O	<u>Lahn</u>
Kobayashevite	Cu ₅ (OH) ₆ (SO ₄) ₂ ·4H ₂ O	<u>Kob</u>	Gordaite	NaZn ₄ (OH) ₆ SO ₄ Cl·5H ₂ O	<u>Gor</u>
Christelite	Zn ₃ Cu ₂ (OH) ₆ (SO ₄) ₂ ·4H ₂ O	<u>Chri</u>	Ca-gordaite	CaZn ₈ (OH) ₁₂ (SO ₄) ₂ Cl ₂ ·9H ₂ O	<u>Ca-Gor</u>
Botallackite	Cu ₄ (OH) ₆ Cl ₂	Bot	Simoncolleite	Zn ₅ (OH) ₈ Cl ₂ ·H ₂ O	Sim
Atacamite	Cu ₄ (OH) ₆ Cl ₂	Ata	Guarinoite	(Zn,Co,Ni) ₆ (OH,Cl) ₁₀ SO ₄ ·5H ₂ O	
Paratacamite	Cu ₃ (Cu,Zn)(OH) ₆ Cl ₂	Parata	Schulenbergite	(Cu,Zn) ₇ (OH) ₁₀ (SO ₄ CO ₃) ₂ ·3H ₂ O	Schu
Malachite	Cu ₂ (OH) ₂ (CO ₃) ₂	Mal	Hydrozincite	Zn ₅ (OH) ₆ (CO ₃) ₂	HyZt
Azurite	Cu ₂ (OH) ₂ (CO ₃) ₂	Azu	Behererite	(Cu,Zn) ₆ Zn ₂ (OH) ₁₂ (SO ₄ HSiO ₄) ₂	

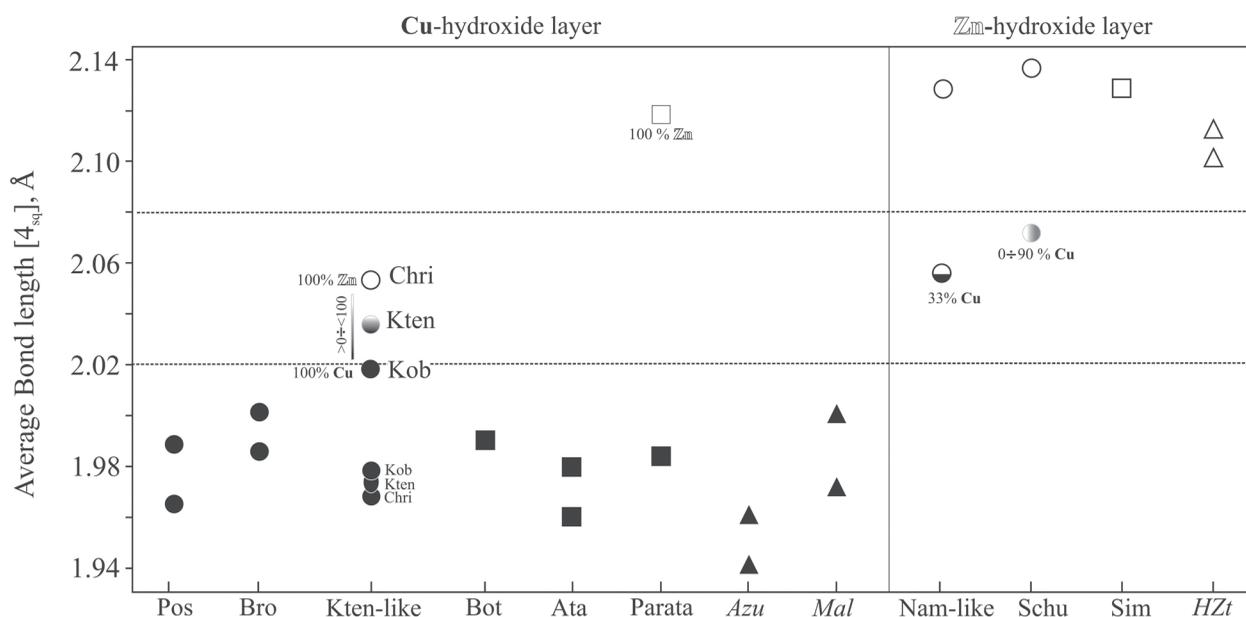


Fig. 1. Cationic Cu-Zn isomorphous relationships depending on the average bond lengths between cations and 4 nearest anions (○, sulfate hydroxy minerals; □, chloride hydroxy minerals; △, carbonate hydroxy minerals)

tual isomorphous substitution was observed. However, this complete isomorphism occurs only in one of the octahedral positions which is characterized by average bond length equal to 2.04–2.8 Å. The end members of isomorphous series with ktenasite-type structure are known as minerals kobyashevite and christelita (Table 1). The occupation of the entire isomorphous octahedral position by Cu^{2+} cations in the kobyashevite structure leads to an increase of the average bond length of the non isomorphous octahedral position (Fig. 1). Conversely, the settlement of isomorphous position by Zn^{2+} cations causes a contraction of the size of the second octahedral position (Fig. 1). This elasticity of the structure allows the realization of the $\text{Cu}^{2+} \leftrightarrow \text{Zn}^{2+}$ isomorphism in minerals with ktenasite-type structure.

In the structures of Zn hydroxy-salt minerals (Table 1), the isomorphous substitutions can be expected only in the octahedral part of the structures, because the Cu^{2+} cations have never found in tetrahedral coordination. Indeed, the analysis of the chemical composition of natural specimens and the structural features of minerals with namuwite-type structure showed that an isomorphism in octahedral positions is occurred. The isomorphous substitution is limited only in the octahedral positions with the average bond length equal to 2.07 Å, as only 1/3 of the atoms can be replaced. Substitution of more

than 1/3 of Zn^{2+} cations by Cu^{2+} would cause tearing of the layer and destruction of the structures, due to the Jahn-Teller's contraction of the octahedra. In the structures of simoncolleite and hydrozincite, the larger sizes of the octahedra and a larger number of tetrahedra (ratio of octahedral and tetrahedral positions is 3:2, while for namuwite type it is 3:1) lead to full limitation of isomorphous substitution of Zn^{2+} by Cu^{2+} cations in these structures.

In conclusion, the main crystal-structure feature that controls the implementation and the degree of isomorphism is the size of coordination polyhedron which the two cations form. It was found that $\text{Cu}^{2+} \leftrightarrow \text{Zn}^{2+}$ isomorphous substitution is limited in the polyhedra (octahedra or squares) with average bond length of 2.03–2.08 Å.

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