



Crystal chemical aspects of the classification problems of the minerals hydroxy-salts

Кристалохимични аспекти на класификационните проблеми на минералите хидрокси-соли

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The existing mineralogical classifications are based on the chemical composition with a specification of structural features (Dana and Nickel-Strunz used at www.mindat.org; Kostov, 1993). The anions (monoatomic – halogens, O^{2-} , S^{2-} , etc., polyatomic anions – NO_3^- , CO_3^{2-} , SO_4^{2-} , PO_4^{3-} , AsO_4^{3-} , VO_4^{3-} , etc.) are considered as the main component for grouping of the minerals, because they form coordinating polyhedrons; rarely hold identical positions; are more strongly influenced by the environmental changes (pH, Eh, T and P), and are less involved in ion-exchange reactions. In the presence of two or more anions in a given composition, the mineral is placed in the mineralogical class of the anion, characterized by the strongest internal bonds. In this overall picture, it remains absolutely unclear why the OH^- anion is completely ignored. Surprisingly and confusingly, the only anion that does not form its own class is the hydroxyl anion. Of course, by chemical characteristics, it differs from other anions: the OH^- with hydrogen does not make acid but water; with cations does not form salts but hydroxides. However, this cannot be a reason to eliminate the possibility of mineral hydroxides to have their own mineralogical class, but on the contrary, this fact should even be a leading one. On the other hand, the OH-group exhibits all the anion characteristics in the crystal structures: it has a negative charge and makes coordinating polyhedrons around the cations, so there is one more reason to use it for grouping the minerals containing OH^- into a separate class.

In our previous work (Stanimirova et al., 2011), it has been shown that a huge number of minerals with a single or predominant hydroxyl anion in their compositions and own their specific crystal chemical, structural, genetic, and physical and chemical properties, are improperly classified in the class “Oxide” (Nickel-Strunz’s classification system; Kostov, 1993) or in the class “Hydroxides and oxides containing OH” (Dana’s classification system), as well as the minerals com-

posed of hydroxyl groups and other anion are distributed in the classes of non-hydroxyl anion without even taking into account the quantitative relations between the two anions (the classifications used at www.mindat.org; Kostov, 1993).

The present work attempts to outline the criteria by which mineral species with the anionic part containing OH groups can be separated into a class of “Hydroxides”.

For the mineral species formed only by the cations and hydroxyl anion, naturally could be described as hydroxides. The major problems arise in determining the mineral species formed by OH groups and other anions as hydroxides with additional anions or as salts with OH groups.

To determine the boundary between hydroxides and salts, the following criteria are considered: OH^- : non-hydroxyl anion quantification; the ratio OH^- : non-hydroxyl anion charges, as well as the changes in the main coordination polyhedrons. Minerals with a basic Cu^{2+} cation were used as an example. The Cu^{2+} cation is most commonly in octahedral or pseudo-octahedral coordination.

The data from the application of the criteria (Table 1) show some important trends. The charge ratio is the most indicative criterion for determining the boundary between hydroxides and salts. In the case of equal charge ratio, the distribution of OH groups and the halogen anions or oxygen atoms of the oxo-anions in the coordination polyhedron is also equal. In this way, a mineral species with a charge ratio of 1:1 can equally be classified both in the hydroxide class and in the class defined by the non-hydroxyl anion. In the case of minerals with OH and monovalent anion A^- (where A^- is NO_3^- , halogens, etc.) the lower limit at which a mineral species should be in the class “Hydroxides” is $OH^-: A^- > 1:1$. For the minerals with divalent oxo-anions A^{2-} ($A^{2-} = CO_3^{2-}$, SO_4^{2-} , CrO_4^{2-} , etc.), the lower limit is $OH^-: A^{2-} > 2:1$, and for the trivalent oxo-anions

Table 1. Application of crystal chemical criteria for determination of the lower limit hydroxide-salt of representative Cu²⁺ minerals hydroxyl-salts

Mineral name	Chemical formula	Number OH:A ⁻	Charge balance OH:A ⁻	Number in polyhedron OH:A ⁻	Offered class
Beloite	Cu(OH)Cl	1:1	1:1	3:3	halides; hydroxides
Azurite	Cu ₃ (OH) ₂ (CO ₃) ₂	1:1	1:2 (2:4)	2:4	carbonates
Linerite	Cu ₃ (OH) ₂ (MoO ₄) ₂	1:1	1:2 (2:4)	2:4	molybdates
Olivenite	Cu ₂ (OH)(AsO ₄)	1:1	1:3	2:4; 1:4	arsenates
Liberthenite	Cu ₂ (OH)(PO ₄)	1:1	1:3	2:4; 1:4	phosphates
Versingite	Cu ₃ Ba(OH) ₂ (VO ₄) ₂	1:1	1:3 (2:6)	2:4	vanadates
Diaboleite	CuPb ₂ (OH) ₄ Cl ₂	2:1	2:1 (4:2)	4:2	hydroxides
Linarite	CuPb(OH) ₂ Cl	2:1	2:1	4:2	hydroxides
Malachite	Cu ₂ (OH) ₂ (CO ₃)	2:1	1:1 (2:2)	50% 2:4; 50% 4:2	carbonates
Cornwallite	Cu ₅ (OH) ₄ (AsO ₄) ₂	2:1	1:2 (4:8)	40% 4:2; 60% 2:4	arsenates
Turanite	Cu ₂ (OH) ₄ (VO ₄) ₂	2:1	1:2 (4:8)	40% 4:2; 60% 2:4	vanadates
Atacamite	Cu ₂ (OH) ₃ Cl	3:1	3:1	66% 4:2; 33% 6:0	hydroxides
Rouaite	Cu ₂ (OH) ₃ (NO ₃)	3:1	3:1	50% 4:2; 50% 5:1	hydroxides
Ktenasite group	Cu ₄ M ²⁺ (OH) ₆ (SO ₄) ₂ ·3–6H ₂ O M ²⁺ – Zn, Cu, Mn, Cd, Ca	3:1	3:2 (6:4)	33% 4:2; 55% 5:1	hydroxides
Sbelliite	Cu ₂ Zn(OH) ₃ (AsO ₄)	3:1	1:1 (3:3)	3:3	arsenates
Veszeliite	Cu ₂ Zn(OH) ₃ (PO ₄)	3:1	1:1 (3:3)	50% 4:2; 50% 2:4	phosphates

A³⁻ (A³⁻ = PO₄³⁻, AsO₄³⁻, VO₄³⁻, MoO₄³⁻, etc.) the limit ratio is OH⁻: A³⁻ > 3:1 (Table 1).

In terms of OH⁻ to non-hydroxyl anions larger ratio, the minerals exhibit properties that are predetermined by the specific nature of OH group as anion – chains, ribbons or layers of cation-hydroxide polyhedrons, ion exchange of the non-hydroxyl anion, an alkaline reaction of their solutions, etc.

The bipolar character of the OH-group determines the bi-dimensional character of the hydroxide structural unit by allowing polymerization of the cation-hydroxyl polyhedron in two crystallographic directions and limiting it in the third direction (Hawthorne, 1992). In turn, the type of cation-hydroxide units (chains, ribbons or layers) depends on the non-hydroxyl anion since its occupation of the OH⁻ position in the polyhedron disturbs the polymerization. In cases where a small number of OH⁻ positions are occupied by non-hydroxyl anions, the layered character of the hydroxide unit is most often retained. With the increase in the number of non-hydroxyl anions coordinating cations, 2–4 chain ribbons or simple chains are formed. In this aspect, the character of the anion is of great importance for the number of non-hydroxyl anions around the cations. For monoatomic anions (halides), all anions could be in direct coordination with the cation. The maximum number of directly cation-coordinated halogen anions at the lower hydroxide-salt boundary is half of all anions in the polyhedron. In the case of oxo-anions, however, the charge of each oxygen atom in the anion is of a particular importance. For example, for the NO₃⁻, each O atom has 1/3 valent units (v.u.) negative charge, therefore, at most 1 of the O atoms can be included in the cationic polyhedron. The larger charge of each O, e.g. in CO₃²⁻ (-2/3 v.u.) or PO₄³⁻ (-3/4 v.u.) predetermines a greater “competitiveness”

of O atoms to occupy OH positions around the cations. For this reason, for the most minerals containing high valent anions (>-0.5 v.u. per O atom), all O atoms are involved in coordinating polyhedrons. In the oxo-anions where each O atom has -1/2 v.u. (SO₄²⁻-type), the greatest diversity in the number of O atoms involved in the hydroxide polyhedrons is observed – from 1 to 4, depending on the specificity of the individual cation-hydroxide construction. This aspect of the structural distribution of O atoms of the oxo-anions directly effects on the anion-exchange properties, which are very typical for this type of compounds. The anion-exchange properties increase with an increase in the ratio of OH⁻: Aⁿ⁻ and hence with a reduction in the number of directly cation-coordinated O atoms of oxo-anions.

In conclusion, from a crystal chemical point of view, the mineral hydroxy-salts having the ratio OH⁻: Aⁿ⁻ > n (where Aⁿ⁻ is non-hydroxyl anion), together with pure hydroxides are appropriate to be combined into a class of “Hydroxides”. For hydroxides with additional oxo-anion, the charge of each O atoms in the oxo-anions plays an important role for mineral’s ion-exchange properties, for the number of mineral species as well as for the prediction of new mineral species and the conditions of their formation.

References

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