

## New Approaches to the XRD Studies of Complicated Crystal Chemical Phenomena in Minerals\*

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The crystal chemical phenomena (*e.g.* polyhedral stacking variations, microtwinning, modulation, *etc.*), which accompany the formation of real structures, are considered on the basis of the most recent structural studies of a large group of silicate minerals and their synthetic analogues, *e.g.* raite, vuorijarvite, haiweeite and synthetic  $K_4(NbO)_2[Si_8O_{21}]$ . The new approaches used for their investigation allowed extension of the scientific ideas connected with the structural systematics of minerals, the forms of concentration of chemical elements in the Earth's crust, further development of modular theory and with other problems of modern structural mineralogy.

*Key words:* crystal structures, polysomatism, microtwinning, structural modulation.

### INTRODUCTION

On 8th November 1895, the German physicist W. Roentgen discovered a new type of radiation, which due to its unknown nature was named X-rays. During the 20th century this discovery has contributed significantly to the physics of condensed matter, material science, solid state chemistry, organic chemistry, protein biology, *etc.* However, one of its most productive contributions is connected with mineralogy, where X-rays play a key role in investigations of the composition and structure of minerals. Thus, X-rays extended the scientific background for crystal chemical classification of minerals, for

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\* Dedicated to Professor Boris Kamenar on the occasion of his 70<sup>th</sup> birthday.

correlations between their structures and properties, modeling of mineral transformations in deep geospheres and many other fundamental scientific problems.

This paper overviews the most recent data that demonstrate the new possibilities of XRD methods for the study of complicated crystal chemical phenomena, such as polyhedral stacking variations, microtwinning, structure modulation and some other, recently revealed in a group of natural and synthetic silicates.

## RESULTS AND DISCUSSION

### *Polyhedral Stacking Variations and Modular Aspects of Raite*

Natural processes have selected some 4 000 known mineral species and this number is increased by 40–50 new minerals discovered each year. However, about 20% of known minerals lack structure determination, mainly because crystals are too small or imperfect for laboratory X-ray sources. Determination of the crystal structure of raite,  $\text{Na}_3\text{Mn}_3\text{Ti}_{0.25}[\text{Si}_8\text{O}_{20}](\text{OH})_2 \cdot 10\text{H}_2\text{O}$ ,<sup>1</sup> using X-rays from synchrotron source ( $\lambda = 0.688 \text{ \AA}$ , crystal dimensions, exposed in the X-ray microbeam  $3 \times 3 \times 20 \text{ \mu m}$ ; effective size  $\approx 6 \text{ \mu m}$ ,  $R_{hkl} = 0.059$  for 916 reflections) opens the gate to a new field of microgeochemistry.

The crystals are characterized by monoclinic symmetry in contrast to the results of their preliminary XRD study,<sup>2</sup> when orthorhombic cell parameters were reported. The structure consists of a palygorskite-like framework, where each [001] channel is partially filled with a row of Na-octahedra (Figure 1); this row, in its turn, is weakly linked to the octahedral part of the framework through Ti-octahedra with only 1/8 occupancy. The structure comprises silicate layers with tetrahedron inversion. In raite and palygorskite,  $\text{Mg}_5[\text{Si}_2\text{O}_5]_4(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , the regions of equal spreading of the  $\text{SiO}_4$  tetrahedra are 2 *zweier* single chains,<sup>3</sup> in sepiolite,  $\text{Mg}_4[\text{Si}_2\text{O}_5]_3(\text{OH})_2 \cdot 6\text{H}_2\text{O} - 3$  *zweier* single chains. In kalifersite,  $(\text{K},\text{Na})_5(\text{Fe}^{3+})_7[\text{Si}_2\text{O}_5]_{10}(\text{OH})_6 \cdot 12\text{H}_2\text{O} -$  a new fibrous silicate,<sup>4</sup> both types of tetrahedral ribbons are characterized by tetrahedron inversion. Subsequently, this group of minerals can be described in terms of the polysomatic concept and it contributes to further development of the modular theory. On the basis of P (palygorskite module) and S (sepiolite module), kalifersite is  $\text{P}_1\text{S}_1$  member of a  $\text{P}_p\text{S}_s$  polysomatic series named palysepiol series.<sup>5</sup> In contrast to palygorskite and sepiolite, which contain interrupted octahedral layers, both raite and kalifersite comprise a (quasi, in raite) continuous octahedral sheet, which is sandwiched

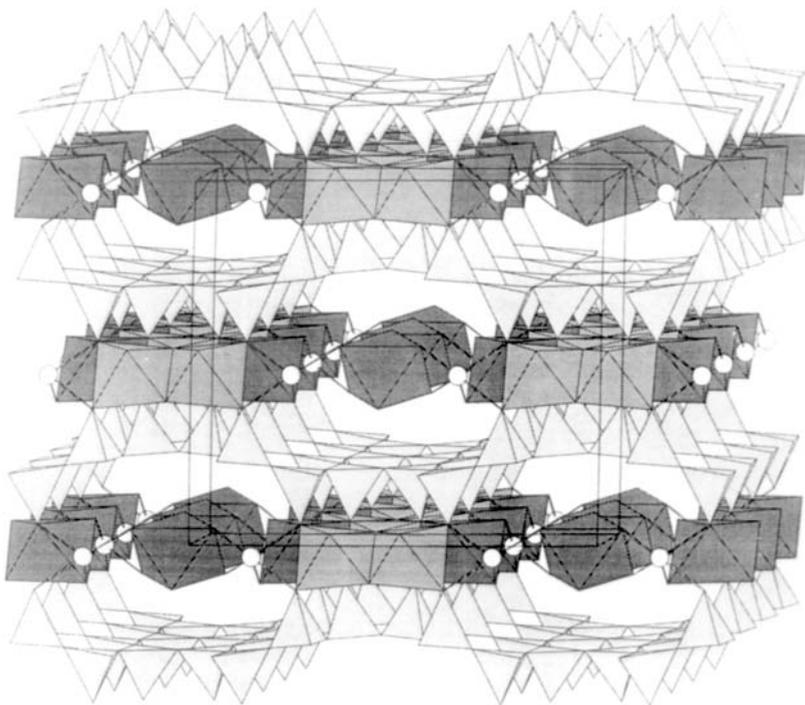


Figure 1. The structure of raitite (view along [001]).  $\text{MnO}_6$  octahedra are grey,  $\text{NaO}_6$  octahedra are dark grey. The statistical positions of Ti atoms are marked by white circles.

between two inverted tetrahedral sheets. Thus, raitite and kalifersite can be considered as bridges between the structures of the »true« phyllosilicates and the structures with interrupted octahedral layers.

### *Microtwinning*

We studied this phenomenon in the process of structure investigation of K-rich nenadkevichite,<sup>6</sup> which in 1995 was recognized as a new mineral by CNMMN under the name vuorijarvite. The family of rare Nb,Ti-silicates, nenadkevichite-labuntsovite, includes orthorhombic and monoclinic members. The crystals of K-rich nenadkevichite are characterized by an X-ray powder diffraction pattern, similar to that of orthorhombic nenadkevichite. However, XRD and electron microprobe data demonstrated that it is definitively distinct not only from nenadkevichite, because of its monoclinic symmetry (sp.gr. *Cm*) and an excess of K over Na, but also from labuntsovite,

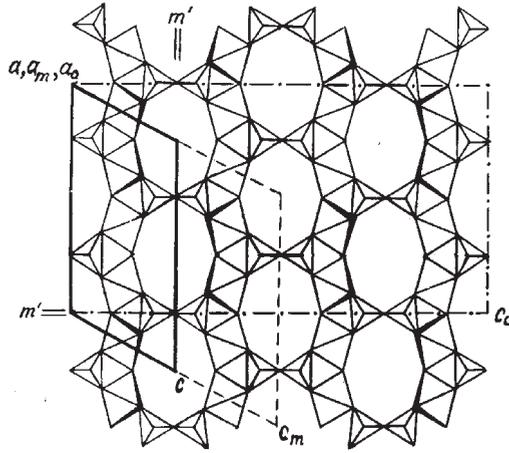


Figure 2. Octahedral and tetrahedral mixed framework of the K-nenadkevichite structure;  $\mathbf{a}$  and  $\mathbf{c}$ : vectors of the monoclinic C-centred unit cell;  $\mathbf{a}_0$  and  $\mathbf{c}_0$ : vectors of the orthorhombic twinned F-centred unit cell;  $\mathbf{a}_m$  and  $\mathbf{c}_m$  – vectors of the monoclinic twinned C-centred unit cell, similar to the unit cell of labuntsovite. Twinning planes are marked by the letter »m«.

because of the excess of Nb over Ti. The chemical formula of K-rich nenadkevichite, obtained on the basis of structure refinement ( $R = 0.055$  for 1443 reflections) is in good agreement with the data of microprobe analysis:

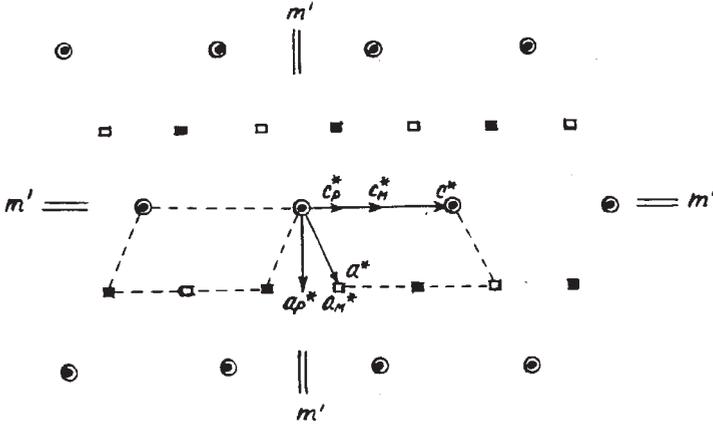


Figure 3. Projection of the reciprocal lattice of vuorjarvite. Black and white colours correspond to the reflections of twinning crystals. The reflections with  $k = 2n$  are marked by circles.

$(\text{Na,K})_2(\text{Nb}_{1.1}\text{Ti}_{0.9})[\text{Si}_4\text{O}_{12}](\text{O,OH})_2 \cdot 1.6\text{H}_2\text{O}$ . The structures of all members of this family contain columns, formed by  $\text{TiO}_6$  octahedra with shared vertices, which are linked by 4-membered silicate rings. Thus, a mixed framework is formed (Figure 2). In contrast to nenadkevichite, the structure of monoclinic labuntsovite is characterized by the presence of an additional  $\text{TiO}_6$  octahedron, which connects the octahedral columns into layers. The absence of this additional (Nb,Ti)-octahedron, typical of labuntsovite, brings the studied crystals closer to nenadkevichite. The last stage of structural refinement was accompanied by a change of the primary chosen F-cell for C-cell, because there were absences with  $h + l = 4n + 2$  for  $k$  even in the 3-dimensional set of reflections (Figure 3), which allowed to consider the diffraction pattern as a superposition of two sets of reflections from two parts of the twinned crystal. This model led to the reduction of  $R_{hkl}$  from 0.24 down to 0.055.<sup>6</sup> The ratio of intensities of split reflections allowed to estimate the volume coefficients of twin (0.52 and 0.48). The indexes of the twinning planes are (001) and  $(-4\ 0\ 1)$  (Figure 2).

### Structural Modulation

This phenomenon, connected with small displacements of atoms, which lead to an increase of the unit cell parameters, was recently discovered in the structures of many rock-forming minerals. More than three vectors in reciprocal space are necessary for the description of their diffraction patterns. Crystals  $\text{K}_4(\text{NbO})_2[\text{Si}_8\text{O}_{21}]$ , synthesized in the hydrothermal system  $\text{K}_2\text{O}-\text{Nb}_2\text{O}_5-\text{SiO}_2-\text{H}_2\text{O}$ , can be regarded as an interesting example of modu-

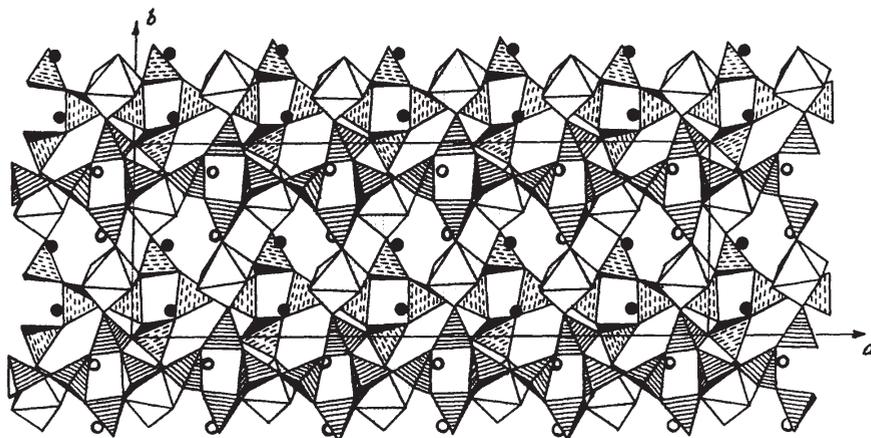


Figure 4. Structure of  $\text{K}_4(\text{NbO})_2[\text{Si}_8\text{O}_{21}]$  in (001) projection. The circles represent K atoms on two levels ( $z \approx 0.25$  and  $\approx 0.75$ ).

lated structures. The triclinic structure of this compound (Figure 4) was established from X-ray single-crystal diffraction ( $R = 0.042$  for 8855 reflections).<sup>7</sup> This phase is isotypic with  $\text{Cs}_4(\text{NbO})_2[\text{Si}_8\text{O}_{21}]$ , where the new type of silicate chains, which F. Liebau called the »loop branched dreier chains«, were recently revealed.<sup>8</sup> However, the main structural distinction of  $\text{K}_4\text{Nb}$ -silicate is connected with one-dimensional commensurable structural modulation along the  $a$ -axis:  $0.2a$  of  $\text{K}_4\text{Nb}$ -silicate is approximately equal to the  $a$ -axis of  $\text{Cs}_4\text{Nb}$ -silicate. The diffraction pattern of  $\text{K}_4\text{Nb}$ -silicate can be described with the help of 4 indices with modulation vector  $\mathbf{q} = 0.4\mathbf{a}^*$  (Figure 5). Thus, besides the reflections of basic structure, there are two sets of satellites: i) relatively strong satellites with 4-th index odd; ii) weak satellites with 4-th index even. This description allowed us to use the special software program JANA for modulated structures.<sup>9</sup>

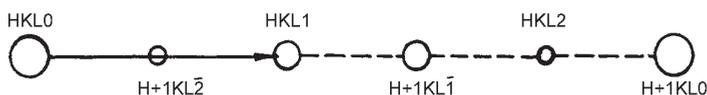


Figure 5. The  $\mathbf{a}^*$  axis in reciprocal lattice of  $\text{K}_4(\text{NbO})_2[\text{Si}_8\text{O}_{21}]$ .

The refinement procedure making use of this program has definite advantages because the total number of the refined parameters in this particular case is 388 (including the scale factor), and the standard process of anisotropic refinement of 93 atoms in the superstructure includes calcula-

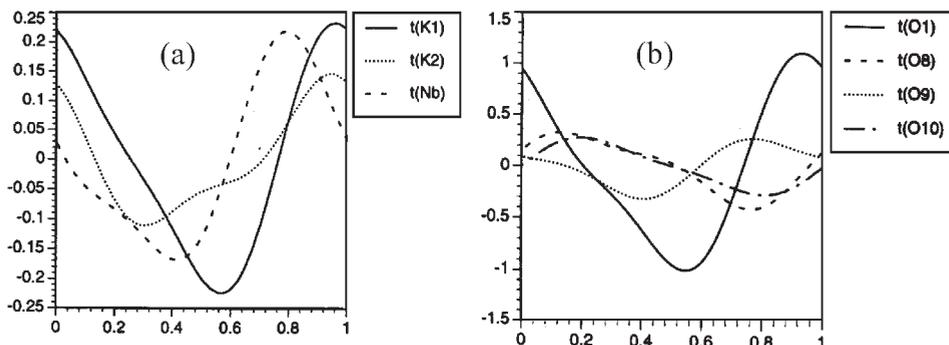


Figure 6. Modulation waves along  $z$ -axis for cations (a) and O-atoms (b) in  $\text{K}_4(\text{NbO})_2[\text{Si}_8\text{O}_{21}]$ . The vertical scale represents atomic shifts (in  $\text{\AA}$ ) along  $c$ -edge (horizontal scale).

tion of 831 parameters. The calculation of modulated waves for each type of atoms revealed higher displacements of O-atoms, which are on the contacts of two parts of the double bands of  $\text{SiO}_4$ -tetrahedra, as well as shifts of K-atoms (Figure 6).

The crystals of K,Nb-silicate belong to the family of compounds with covalent networks, built of tetrahedra and octahedra, which often exhibit technologically important properties, *e.g.* ionic conductivity, non-linear optical effects, *etc.* However, they are characterized by a relatively low non-linear polarization, as compared with the other alkaline niobates. This peculiarity of the studied crystals is apparently due to the low concentration of the isolated  $\text{NbO}_6$  octahedra in their structure, since in crystals that exhibit a strong non-linear effect, for example, in  $\text{K}_2(\text{NbO})_2[\text{Si}_4\text{O}_{12}]$ ,<sup>10</sup>  $\text{NbO}_6$  octahedra are linked in columns.

### *New Subdivision of Silicate Structural Systematics*

The double bands revealed in the structure of K,Nb-silicate are formed by 4-membered rings (Figure 7a). Another new type of silicate tetrahedral bands with 4-membered rings was discovered in 1997 in the structure of haiweeite,  $\text{Ca}(\text{UO}_2)_2[\text{Si}_5\text{O}_{12}(\text{OH})_2] \cdot 5\text{H}_2\text{O}$ .<sup>11</sup> This mineral belongs to the family of uranyl-silicates, whose systematics is based on the U/Si ratio. Lack of structural data for compounds with  $\text{U/Si} \approx 1 : 3$  stimulated the structural study of haiweeite. The complex layers formed by the columns of pentagonal U bipyramids connected with silicate bands are the most specific feature of

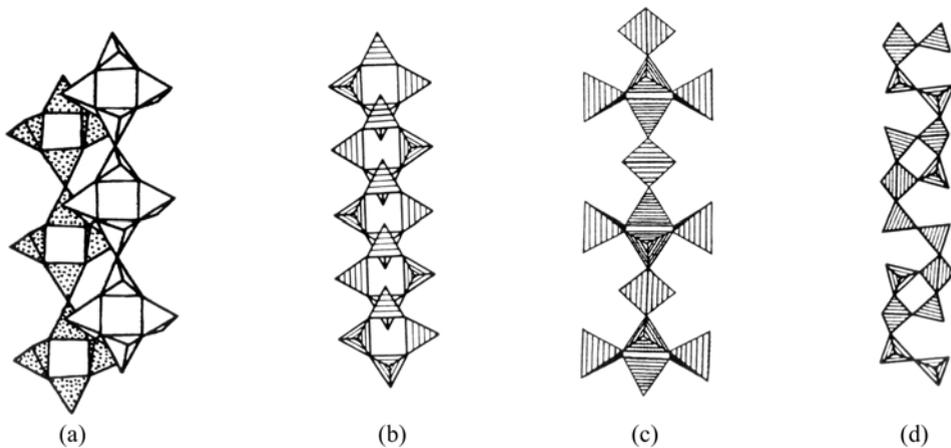


Figure 7. The loop-branched Si,O bands in structures of  $\text{K}_4(\text{NbO})_2[\text{Si}_8\text{O}_{21}]$  (a), vlasovite (b), haiweeite (c) and nordite (d).

its structure. The bands  $[\text{Si}_5\text{O}_{12}(\text{OH})_2]$ , formed by 4-membered rings, linked by additional Si-tetrahedra, represent a new type of loop branched silicate chains<sup>3</sup> and occupy the intermediate position between the bands described in the crystal structures of vlasovite and nordite (Figure 7).

### *Lone-pair Electrons in U-oxide*

The new complex oxide deloryite,  $\text{Cu}_4(\text{UO}_2)[\text{Mo}_2\text{O}_8](\text{OH})_6$  was recently discovered in the Cap Garonne mine (Var, France). Its monoclinic (sp.gr.  $C2/m$ ) structure was refined to  $R = 0.064$  for 402 reflections.<sup>12</sup> Similarly to the synthetic analogue of deloryite<sup>13</sup> and to chemically and crystallographically related derriksite  $\text{Cu}_4(\text{UO}_2)(\text{SeO}_3)_2(\text{OH})_6$ ,<sup>14</sup> it contains layers formed by distorted  $[\text{Cu}(\text{O},\text{OH})_6]$  octahedra with shared edges. The octahedral layers are linked by columns, built up of alternating pseudotetragonal  $\text{U}^{[2+4]}\text{O}_6$  bipyramids and pseudotrigonal  $\text{Mo}^{[4+1]}\text{O}_5$  bipyramids. The five-fold coordination of Mo leads to a different description of the structural model of deloryite with respect to the earlier XRD study of its synthetic analogue.  $\text{Mo}^{[4+1]}\text{O}_8$  dimers in deloryite replace the pairs of tetrahedra  $\text{SeO}_3\text{E}$  (E = lone-pair electrons) in derriksite (Figure 8).

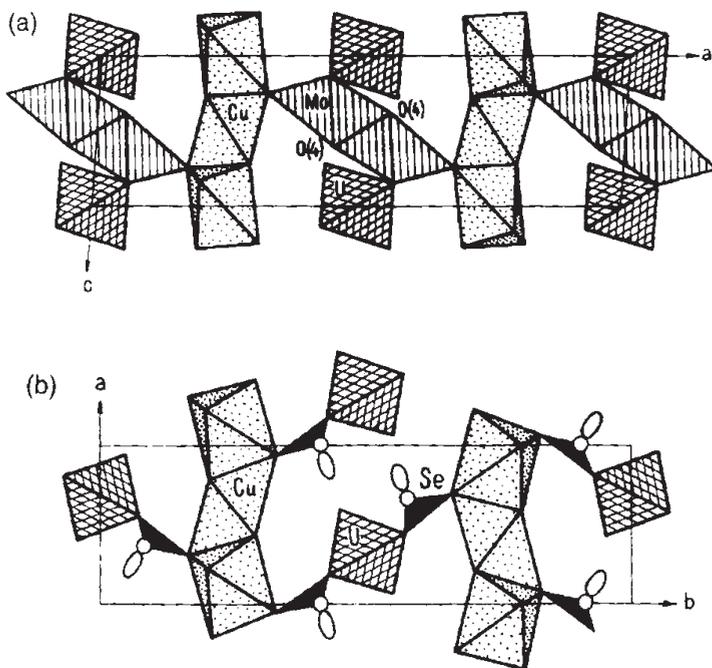


Figure 8. Projections of (a) deloryite on (010) and (b) derriksite on (001).

*Chemical Reactions Registered by X-rays or »Never Wash  
Cu-minerals with Detergents«*

The study of minerals sometimes leads to unpredictable results. One of such episodes is considered below. The mineralogical collection of the Geneva Museum of Natural History was recently supplemented by a sample, which contained essentially azurite,  $\text{Cu}_3[\text{CO}_3]_2(\text{OH})_2$ , associated with another mineral, dark blue in colour. All attempts to identify this mineral using optical and XRD studies failed and did not reveal any similarities with any natural or synthetic compounds known so far. The qualitative chemical analysis proved the presence of copper and carbon as the main elements. These results led to the conclusion that these crystals can be considered as an unknown copper carbonate hydrate. However, their structural investigation revealed that the crystals are in fact a hydrated copper salt of succinic acid  $\text{Cu}(\text{C}_4\text{H}_4\text{O}_4) \cdot \text{H}_2\text{O}$ .<sup>15</sup> The crystals are characterized by a layered structure, which consists of Cu-square pyramids, connected by bridges formed by four C atoms (Figure 9). It is closely related with the earlier known monoclinic salt of copper maleate hydrate,  $\text{Cu}(\text{C}_4\text{H}_2\text{O}_4) \cdot \text{H}_2\text{O}$ .

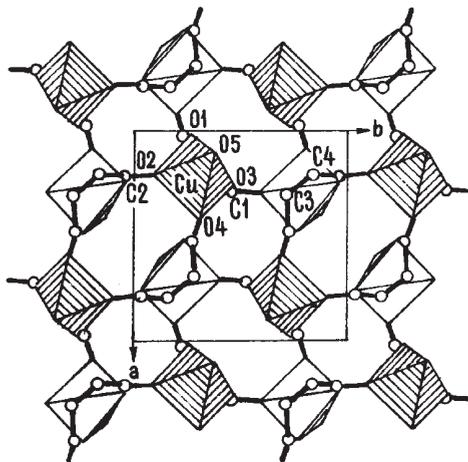


Figure 9. Layers, formed by Cu square pyramids and by carbon chains in the structure of Cu(II) succinate hydrate. The circles represent C atoms.

The crystallization of copper succinate, untypical of the world of minerals, is due to the fact that Mrs. Casanova from Toulon, France, who collected the sample, had previously cleaned it with detergent W5, produced by the LIDL company in Strasbourg. We were informed by this company that the chemical composition of W5 detergent is confidential, however we sup-

pose that it contains succinic acid,  $H_2[OOCCH_2CH_2COO]$ , which determined the final composition of the studied copper salt. This assumption can be attributed to the fact that organic acids, as constituents of many detergents, reinforce their hydrotrophy. Use of succinic acid in detergent production seems reasonable as it is easily soluble in contrast with other acids, which contain more carbon atoms. Moreover, it is relatively cheap and its single bond between two methylene groups  $CH_2$  makes it less aggressive than other organic acids. Thus, a practical piece of advice to professional and amateur collectors of minerals resulting from this study can be formulated as »never wash copper minerals with detergents«.

## CONCLUSION

The petrological significance and technological application of minerals are based on the detailed study of their structure, composition and physical properties. The examples discussed in this paper illustrate some correlations between these characteristics. It is evident that the fundamental solution of this problem should be based on joint efforts of researches, from different branches of modern science.

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## SAŽETAK

### Novi pristupi XRD izučavanjima složenih kristalokemijskih pojava u mineralima

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Kristalokemijske pojave, poput raznolikosti u slaganjima poliedara, mikrosraštanja, modulacija itd., kojima je popraćeno nastajanje prostorne građe minerala, razmatrane su na temelju najnovijih strukturnih istraživanja velike skupine silikatnih minerala i njihovih sintetskih analoga, npr. raita, vuorijarvita, haiweeita i sintetskog  $K_4(NbO)_2[Si_8O_{21}]$ . Novi pristupi korišteni u ovom istraživanju proširili su znanstvene zamisli u svezi sa strukturnom sistematikom minerala, sa stanjem koncentracije kemijskih elemenata u Zemljinoj kori te s daljnjim razvojem modularne teorije i ostalim pitanjima moderne strukturne mineralogije.