CROATICA CHEMICA ACTA CCACAA **73** (3) 869–886 (2000)

ISSN-0011-1643
CCA-2688 *Conference Paper*

Recent Contributions and Modern Perspectives in XRD Studies of Minerals*

Dmitry Yu. Pushcharovsky

Geology Department, Moscow State University,
119899 Moscow, Russia
(E-mail: dmitp@geol.msu.ru)

Received September 1, 1999; revised March 20, 2000; accepted May 26, 2000

Some exciting recent developments in the field of mineralogical crystallography are considered. The crystal chemical phenomena (*e.g.* ionic ordering, polyhedral stacking variations, microtwinning, modulation), which accompany the formation of real structures, are discussed on the basis of structural studies of a large group of minerals, recently investigated in the Moscow State University. The new approaches used for their investigation allowed extending the scientific ideas connected with: the composition and structure of the deep geospheres, structural classification of minerals, forms of concentration of chemical elements in the Earth's crust, further development of modular theory and other problems of modern structural mineralogy. The advantage of using synchrotron radiation opens the gate to a new branch of microgeochemistry (about 20% of known minerals lack structure determination, mainly because crystals are too small or imperfect for laboratory X-ray sources). Studies of the phase transitions of mantle minerals at high pressure and high temperature contribute to a better understanding of the composition, structure and geodynamics of the deep geospheres. A new model of the mantle, based on the most recent seismotomographic data and on the phase transition studies of mantle minerals, is reported. Several concentric bands are revealed in the mantle, although the previous model emphasized its subdivision only in two parts: upper and lower. New approaches to the XRD studies of

---

* Based upon the plenary lecture presented at the 8th Croatian-Slovenian Crystallographic Meeting, Rovinj, Croatia, June 17–19, 1999.

ionic ordering, structural modulation and polyhedral stacking variations are discussed.

Key words: crystal structures, mineral transformations, structure-property relationships.

INTRODUCTION

In May 1999, the European Crystallographic Association established a new special interest group – »Mineralogical Crystallography«. This paper is devoted to several modern problems and perspectives of this interdisciplinary scientific branch. It is well known that crystallography of the 18th and 19th centuries evolved from mathematics and mineralogy. However, the crystallography of the 20th century is closer to physics, chemistry and biology. Nevertheless, the mineralogical background is still, very important and the discoveries in this field significantly influence further development of modern crystallography. The episodes of this paper reflect some of the most recent achievements in the field of mineralogical crystallography based on the use of advanced techniques (diamond anvil cells, synchrotron sources, area sensitive detectors) and updated software packages.

COMPOSITION OF THE DEEP GEOSPHERES IN THE LIGHT OF RECENT CONTRIBUTIONS TO COMPARATIVE CRYSTAL CHEMISTRY

It is noteworthy that the future cannot be predicted without the past. If we look back, one of the most exciting achievements of mineralogical crystallography during the last two decades is connected with the study of the composition and structure of the deep geospheres. This problem is very important. More than 90% of the matter is under a pressure higher than 10 kbar. However, the study of compounds which are anticipated to be constituents of the deep geospheres, perhaps, is more complicated than cosmic investigations. In this connection, it is worthy emphasizing that the deepest sample from the mantle available on the Earth's surface is a nodule from the Lesoto kimberlite pipe, blasted out from a depth of 250 km. The deepest well drilled in Kola peninsula reached the depth of 12260 m. At the same time, the development of the diamond anvil techniques enabled an adequate interpretation of the main discontinuities in the velocities of seismic waves, revealed by geophysical data. Thus, crystallographic experiments are the most powerful tools for the modelling of the matter in deep geospheres.

The traditional model of the Earth's structure as compared with the new one, which considers six geospheres within the Earth's mantle,[1] is shown in

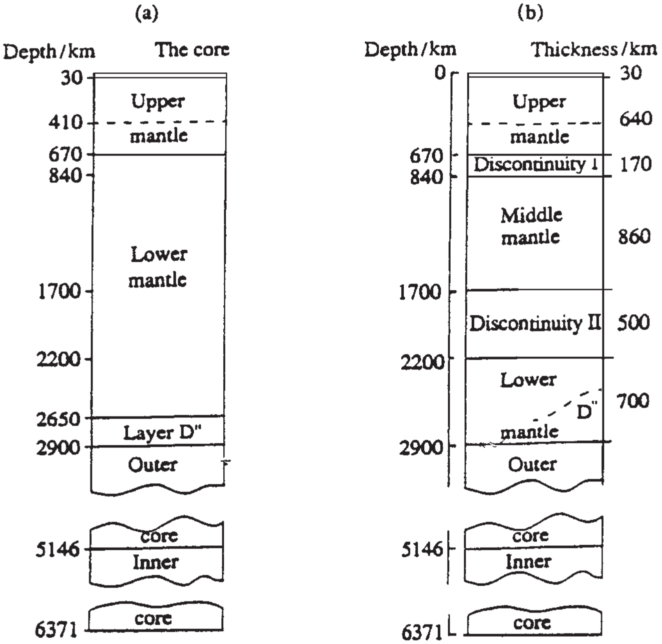


Figure 1. Models of the Earth's structure: (a) a traditional model commonly accepted at the present time, and (b) a new model based on analyses of seismotomographic maps and data on the mantle composition and seismic discontinuities. Thickness may vary within 10%.

Figure 1. The marked boundaries match the rapid increase in seismic wave velocities at the given depths. Thus, in 1909 the boundary between the Earth's Crust and the upper mantle was revealed by the Croatian seismologist Mohorovičić. In the middle of the 20th century the mantle was subdivided into the upper and lower mantle and the core into the outer and inner core. The attempts to correlate structural-mineralogical and geophysical data on the upper mantle are of great interest.[2] Figure 2 reproduces the standard seismic velocity profile. The discontinuous increases of seismic wave velocities, connected with the formation of denser phases, correlate with the phase transitions of mantle minerals shown in Figure 3, where mineral volume fractions are indicated on the vertical scale. As it was assumed in the last 20 years, the increase in seismic wave velocity at a depth of 410 km is mainly related to the structural transformation of olivine α-$(Mg,Fe)_2SiO_4$ into wadsleyite β-$(Mg,Fe)_2SiO_4$, producing a more compact phase with higher modules of elasticity. The quasiglobal seismic boundary at a depth of 520 km corresponds to the wadsleyite β-$(Mg,Fe)_2SiO_4$ transformation into ringwoodite, the γ-$(Mg,Fe)_2SiO_4$ of the spinel structure. The pyroxene

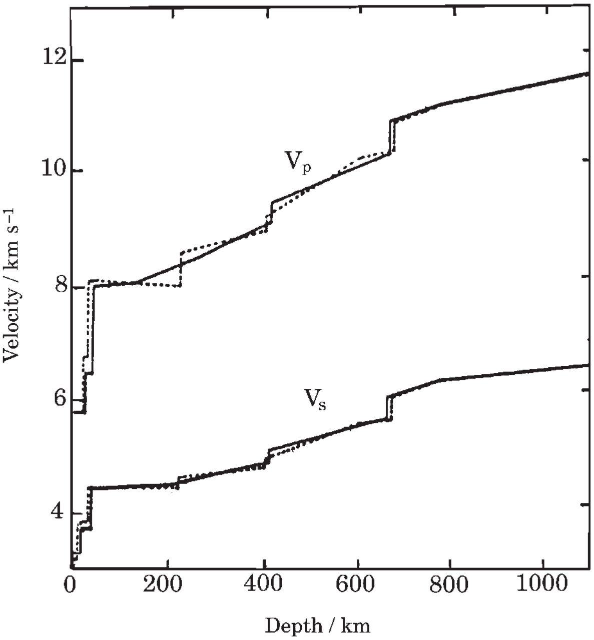


Figure 2. Standard seismic P- and S-wave velocity profile as a function of depth. Dotted and solid curves are from Refs. 3 and 4, respectively.

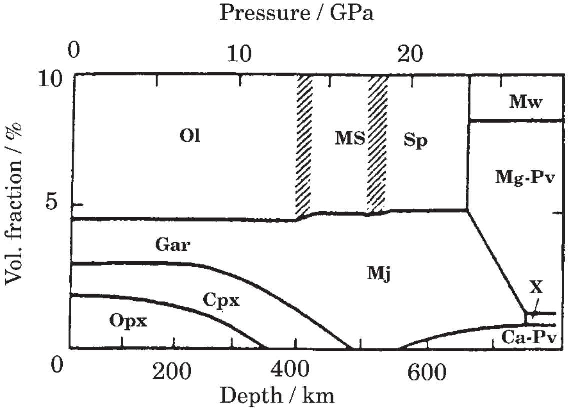


Figure 3. Volumetric proportions of minerals in pyrolite *versus* the pressure (depth), after Ref. 5: (Ol) olivine, (Gar) garnet, (Cpx) clinopyroxenes, (Opx) orthopyroxenes, (MS) »modified spinel«, or wadsleite β-$(Mg,Fe)_2SiO_4$, (Sp) spinel, (Mj) majorite $Mg_3(Fe,Al,Si)_2(SiO_4)_3$, (Mw) magnesio-wustite (Mg,Fe)O, (Mg-Pv) Mg-perovskite, (Ca-Pv) Ca-perovskite, (X) inferred Al-bearing phases with ilmenite-type, Ca-ferrite, and/or hollandite structure.

(Mg,Fe)SiO_3 → garnet $Mg_3(Fe,Al,Si)_2Si_3O_{12}$ transformation occurs within a wider depth interval in the upper mantle. Consequently, the relatively homogeneous concentric zone between 400 and 600 km consists mainly of the garnet- and spinel-type phases.

The studies of mineral phase transformations using the diamond anvils cell enabled scientists to model some features of the composition and structure of geospheres below the 670 km discontinuity. Nevertheless, many problems related to this part of the mantle, which accounts for more than half of the Earth's volume, remain unsolved. The majority of researchers agree that the deep-seated part of the mantle mainly consists of the perovskite-type phase (Mg,Fe)SiO_3, which accounts for 70% of its volume (40% of the total Earth's volume), and magnesio-wustite (Mg,Fe)O (≈20%).[6] The remaining 10% consists of stishovite and Ca, Na, K, Al, and Fe oxides, that belong to structural types of ilmenite-corundum solid solution ((Mg,Fe)SiO_3–Al_2O_3), cubic perovskite ($CaSiO_3$), or Ca-ferrite ($NaAlSiO_4$).

Recognition of intermediate seismic boundaries below the 670 km level correlates with the data on the structural transformations of mantle minerals, whose forms may be rather diverse, including changes in chemical bonds and electronic structure of transitional metals (transition from a high-spin (HS) to low-spin (LS) state). According to Knittle and Jeanloz,[7] at the depth 1700 km the ionic-covalent bonds of magnesio-wustite can be replaced by the bonds in which metallic component dominates. The boundary of 1200 km may correspond to the transformation of SiO_2 with the stishovite structure into the $CaCl_2$ structural type (orthorhombic equivalent of rutile TiO_2), first predicted by quantum mechanism calculations and then modelled under a pressure of 45 GPa and at a temperature of 2000 K. The 2000 km boundary may represent its further transformation into a phase with the structure that is transitional between α-PbO_2 and ZrO_2, and corresponds to a more compact packing of silicon-oxygen octahedra.[8] Also beginning from this depth (2000 km) and at a pressure of 80–90 GPa, the perovskite-type $MgSiO_3$ may dissociate, leading to enrichment in periclase MgO and free silica. In addition, the Mossbauer spectroscopy under a pressure of 90 GPa indicates the beginning of a transition from the high-spin to the low-spin state of Fe atoms incorporated into the magnesio-wustite crystal structure.[9] Under a somewhat higher pressure (96 GPa) and at a temperature of 800 K, FeO polytypism has been established. This phenomenon is related to the formation of niccolite-type (NiAs) structural fragments (B8) alternating with antiniccolite domains where Fe atoms are located in the positions of As atoms, and O atoms in the positions of Ni atoms.[10] In this connection, it should be noted that the wustite structure exhibits at high pressure a nonstoichiometric composition, lattice defects, polytypism, and changes in magnetic ordering related to the changes in the electronic structure of Fe atoms (HS → LS transition). These features imply that wustite is one of the most complicated minerals with unusual properties, which control the specific features of deep mantle zones. The transformation of Al_2O_3 with the corundum structure into the phase with an orthorhombic structure Rh_2O_3 is also possible here. Such a transformation has been modelled under 100 GPa and at a temperature of 1000 K, *i.e.* at a depth of 2200–2300 km.[11]

Thus, the new data on structural transformations of mineral phases at a great depth will provide an adequate interpretation of other important geophysical boundaries identified in the Earth's interior. The general conclusion is that global seismic boundaries, such as those at 410 and 670 km levels, are related to substantial changes in the mineral composition of mantle rocks. Phase transformations have been also reported at depths of 850, 1200, 1700, 2000 and 2200–2300 km, that is, within the lower mantle. This important fact allows us now to discard the argument asserting its homogeneous structure. Apparently, the problems of comparative crystal chemistry and composition of the deep geospheres will be in the focus of mineralogical crystallography during the next decade.

DISCOVERY OF NEW MINERALS AND ITS IMPACT ON THE DEVELOPMENT OF THE CLASSIFICATION OF MINERALS

Another exciting area where crystallography intersects with geology is the discovery of new minerals, which extends scientific ideas about the forms of concentration of chemical elements in the geospheres and contributes to further development of the systematics of minerals. The latter is very important because systematics provokes imagination and helps find out the parameters that control the formation of different structural types. The discovery of minerals is closely connected with the development of XRD techniques. Natural processes have selected some 4000 known mineral species and this number is increased every year by 40–50 new minerals. The increase of the amount of known minerals during the last two centuries is shown in Figure 4. However, about 20% of known minerals lack structure determination, mainly because crystals are too small or imperfect for laboratory X-ray sources.

Historically, crystal chemistry began with the determination of the atomic packing in centimetre to millimetre crystals of minerals, such as rocksalt or diamond, about 80 years ago during the so called Bragg era. In the twenties and thirties, during the era of Taylor and Pauling, it moved on to more complex structures studied on the basis of submillimeter crystals as the hot-cathode X-ray machine became available. By 1960, the progress in

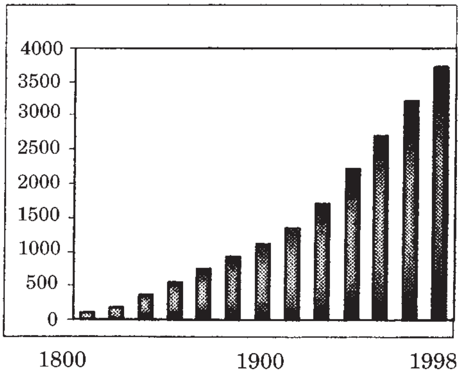


Figure 4. The increase of discoveries of new minerals the 19th and 20th centuries.

software coupled with more intense X-ray sources allowed structure determination of single crystals of a size of 0.05 mm. Since 1970, the X-ray intensity began to increase dramatically as synchrotron radiation started to be used for structure determination and now the size of the crystals is measured in microns. Thus, we are just before new discoveries in the chemistry and physics of minerals.

The application of synchrotron radiation (SR) to the XRD study of the 6 micron crystal of Na,Mn-silicate raite was reported by Pluth *et al.*[12] Raite belongs to the family, comprising palygorskite $Mg_5[Si_2O_5]_4(OH)_2 \cdot 8H_2O$, sepiolite $Mg_4[Si_2O_5]_3(OH)_2 \cdot 6H2O$, kalifersite $(K,Na)_5Fe^{III}{}_7[Si_2O_5]_{10}(OH)_6 \cdot 12H_2O$, and some other minerals, and its structure can be used as an illustration of modern crystal chemical concepts, namely modular theory, which enables predicting the possible new structural types and which promotes the classification of minerals with very complex atomic arrangements.

The influence of octahedral cations on the topology of silicate layers in chemically related and recently studied Na,Mn-silicates varennesite, intersilite and raite is shown in Figure 5. Liebau emphasised the role of the two main parameters that control the formation of silicate sheets with specific configuration.[13] One is the average radius of octahedral cations (r_M) and the other is the ratio of octahedral to tetrahedral co-ordinated cations (r_M/r_T). An increase of these values is accompanied by the formation of sheets with larger rings in the range raite → intersilite → varennesite. Topological relationships similar to the modular theory are also very productive for the prediction of possible structural types.

Recently, a crystal structure of a new Cu-arsenate pushcharovskite, ideally $CuAsO_3(OH) \cdot 1.5H_2O$, was also studied with the use of SR.[14] The struc-

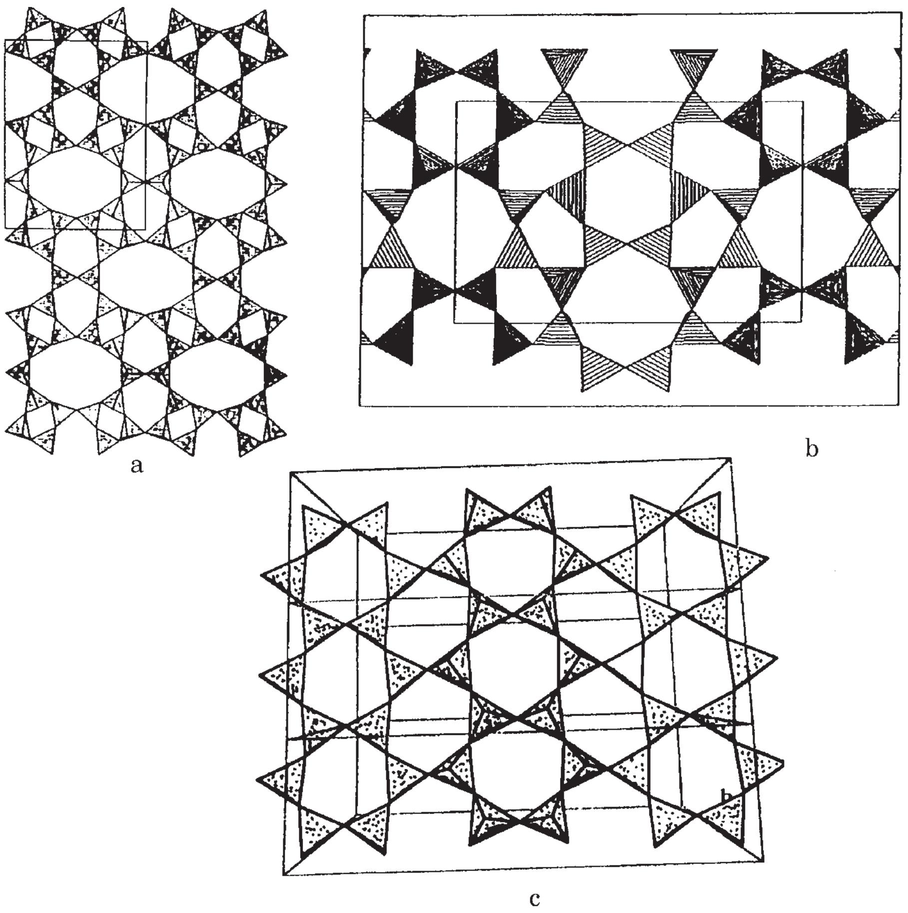


Figure 5. Silicate sheets in: varennesite, $Na_8Mn_2[Si_{10}O_{25}](OH,Cl)_2 \cdot 12H_2O$ (a); intersilite, $(Na,K)Na_5Mn(Ti,Nb)[Si_{10}O_{24}(OH)](OH)_3 \cdot 4H_2O$ (b); and raite $Na_3Mn_3Ti[Si_8O_{20}](OH)_2 \cdot 10H_2O$ (c).

ture is very complicated and it contains more than 120 crystallographically independent atoms. The complex sheets formed by Cu-polyhedra and by As-tetrahedra are its most specific features (Figure 6). The structure contains 3 types of As tetrahedra, in particular mono- and biprotonated ones. Thus, pushcharovskite is the second mineral (after iron arsenate kaatialaite) that contains $AsO_2(OH)_2$ tetrahedra. The layered constitution of this structure is in agreement with the structures of two chemically related Cu-arsenates, geminite and yvonite, discovered at the same locality. However, the degree of condensation of Cu-polyhedra increases in the range geminite → ivonite → pushcharovskite and the partial volume per one O atom also

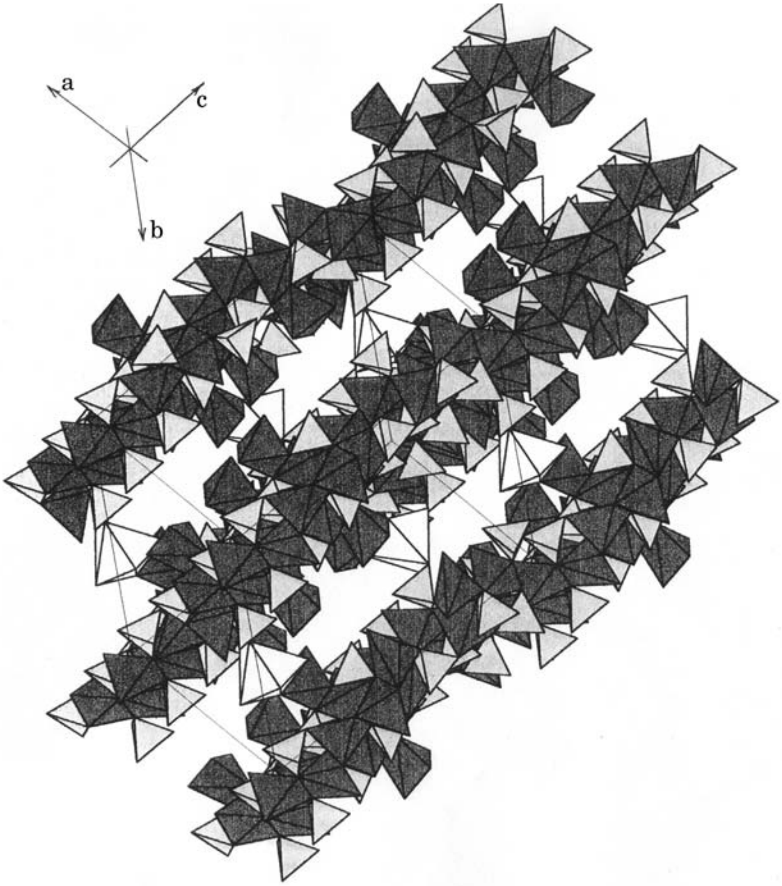


Figure 6. A general view of the structure of pushcharovskite. Cu,O polyhedra and AsO_3OH tetrahedra are shown in dark and light grey color, respectively. Big white octahedra between heteropolyhedral layers are filled with K atoms with partial occupancies.

increases. These crystal chemical parameters are in accord with the evolutional trend that comprises these minerals and allows us to consider pushcharovskite as the latest mineral in this series.

As it was mentioned above, the discovery and characterization of minerals are closely connected with their systematics. The last few years were marked by the elaboration of new approaches to the solution of this problem. The chemical-structural classification of H. Strunz has gone through a number of editions, and is currently in the process of being refined in the light of recent crystal-structure determinations. In the current system,[15] minerals are divided into 10 major compositional classes (1. elements, 2. sulphides, 3. halides, 4. oxides, 5. nitrates, carbonates, 6. borates, 7. sulphates, 8. phosphates, 9. silicates, 10. organic compounds), which are subdivided into divisions, families and groups on the basis of their chemical composition and crystal structure.

Lima de Faria has developed a different approach, which he applies to the pure structural classification.[16] It is based on the analysis of the strength distribution and of the directional character of bonds. In 1994, he successfully applied this approach for the classification of the most common minerals. He emphasized that the spatial distribution of bonds can be either homogeneous or heterogeneous. If it is heterogeneous, there are atoms that are more tightly bonded. These assemblages are considered to be structural units. Structural units are characterized by 5 main categories, according to the kind of bond strength distribution (atomic, group, chain, sheet, framework) and by 4 kinds of dimensionality (0-, 1-, 2-, 3-). The structural systematics of sulphates, based on the same principles, was reported in 1998.[17] Similarly to the general structural systematics of minerals, it contains five main categories of structures.

In contrast to this study, the first category, which comprises the so-called atomic structures, was not considered in any precursory systematics of sulphate minerals. The structures included into this subdivision occur mostly when individual large atoms form either the closest packing or their arrangement is close to it. In this subdivision the packing of large atoms, which should be considered as structural units, is characterized by the predominance of nondirectional forces. The smaller atoms occupy the intersti-

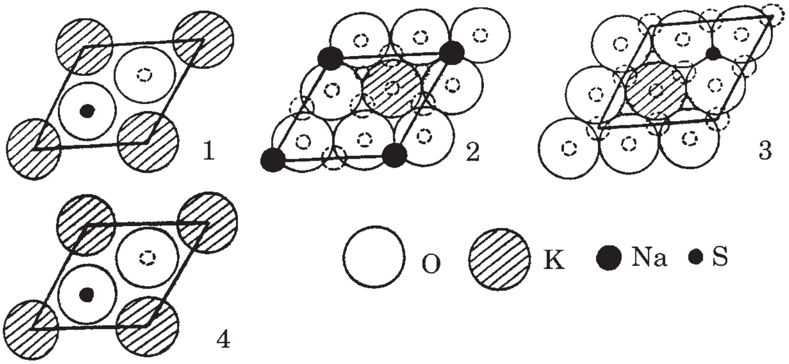


Figure 7. Schematic representation of the condensed model of aphthitalite (glaserite) $(K,Na)_3Na(SO_4)_2$; numbers 1–4 refer to the adjacent sheets formed by O and K packing atoms.

ces in these packings. Aphthitalite (glaserite), $Na^{o}S^{t}{}_{2}\,[K^{[10]}{}_{2}K^{[12]}\,O_{8}]^{T3/2T4}$, is one of the members of this group. The period along [001] contains 3 sheets formed by O and K atoms (Figure 7).

The next four categories comprising the structures formed by SO_4 tetrahedra and by cationic polyhedra with the bond strengths between central cation and oxygen are comparable with those of the bonds between S and O. These SO_4 tetrahedra and cationic polyhedra can be isolated or form complex structural units, whose diversity (about 50 types) is compared with tetrahedral complexes in silicates.

The bond strength distribution in a structure is in many cases difficult to define, due to the lack of quantitative measure. It is therefore natural that, at this initial stage of structural classifications some differences in structural systematics will arise. However, this approach can apparently be used in the future to reveal new correlations between the composition, structure and properties of minerals.

NEW APPROACHES TO THE XRD STUDY OF COMPLEX CRYSTAL CHEMICAL PHENOMENA

The history of XRD studies during the 20th century was connected with the search for perfect crystals. However, it was found out during the last decades that extremely important information can be obtained on the basis of the study of imperfect crystals. In this connection, one of the main aims of modern crystallography is related with the study of complex crystal chemical phenomena that accompany the formation of real crystal structures. The new approaches to the XRD studies of structural modulation, microtwinning and polyhedral stacking variations were discussed by Pushcharovsky.[18] The problems related to the investigation of cationic ordering are considered below on the basis of the crystal structure of lewisite, $(Ca,Sb^{III},Fe^{III},Al,Na,Mn,\ \ )_2(Sb^{V},Ti)_2O_6(OH)$.

Lewisite was originally discovered more than 100 years ago in the gravel of the cinnabar mine of Fazenda Tres Cruzes, Tripui (formerly Tripuhy), Ouro Preto, Minas Gerais, Brazil, and was related to the pyrochlore group of the general formula $A_2B_2O_7$. However, the crystal structure of lewisite had not been reported when we began its XRD study. This investigation was practically finished when Rouse *et al*. published the results of their work on the crystal structure determination of lewisite.[19] They showed that there is a splitting of the A-position and that there is ordering of Sb^{3+} in the A'-sites with a separation $A–A' \approx 0.5$ Å. Moreover, two symmetry-forbidden reflections allowed them to reject the *Fd*-3*m* symmetry and to prefer the *F*-43*m* space group. However, our results did not confirm these data and the crystal chemical discussion of the atomic arrangement of lewisite in different space groups[19] still left some doubts. Therefore, we decided to complete our structural study for the type specimen of lewisite stored in The Natural History Museum, London (B.M. 80141). The use of the anharmonic refinement of the structure resulted in a different approach to the description of its model, which will be discussed below.

In the first stage, an isomorphous mixture of atoms in both A and B sites in pyrochlore structure was accepted in accordance with the values of occupancy, isotropic displacement parameters of cations and the chemical analyses (model I). Any other distribution of cations at either A- or B-site led to an increase of the R_{hkl} value and to inferior values of the atomic thermal parameters. Conversion to anisotropic displacement factors reduced the residual R_{hkl} to 0.0282. A difference Fourier analysis (Figure 8a) revealed a set of symmetry equivalent peaks at (0.48, 0.48, 0.53) around the A-site, where, according to Rouse *et al.,*[19] Sb^{3+} cations are located. To check this idea, we decided to eliminate Sb^{3+} cations from the refinement and to obtain the electron density map using the anharmonic thermal displacement factors (Gram-Charlier expansion to tensors ***F(ijklmn)***) for B-atoms. Figure 8b shows that the calculated difference electron density around both A- and B-sites significantly decreases in this model II. Two assumptions were used

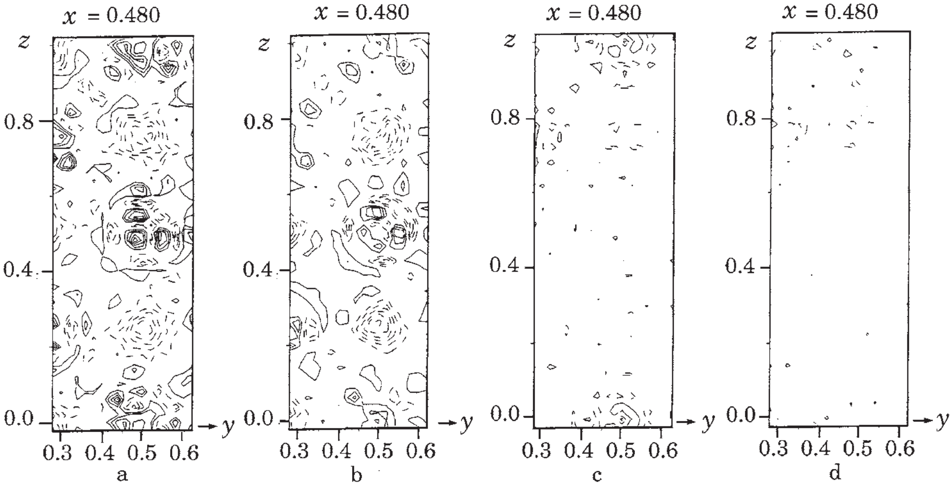


Figure 8. Difference Fourier maps through A'-site of lewisite, space group *Fd*-3*m* (96 g positions: 0.48, 0.48, 0.54) on $x = 0.480$. The step between solid (positive area) and dashed (negative area) lines is 0.2 e/Å^3. Maps (a), (b), (c) and (d) correspond to models I, II, III and IV, respectively.

for further refinement of the structure: i) Sb^{3+} cations are located at A'-sites with partial occupancies (static model III as accepted by Rouse *et al.*);[19] ii) Sb^{3+} cations are located at A-sites and the peaks around them were considered as a result of their anharmonic thermal displacements (model IV). The latter two models were tested by refinement using 128 reflection with $\sin \theta/\lambda > 0.7$ Å^{-1} . Figures 8c and 8d reproduce the difference Fourier maps for models III and IV, respectively. Their comparison allowed us to prefer the dynamic model IV to model III because of the lower values of residual R_{hkl} and of $\Delta\rho$.

STRUCTURE–PROPERTY RELATIONSHIPS

In the mineralogical kingdom, silicates are characterized by the largest scale of industrial application. From this point of view, zeolites are certainly one of the most prominent group, which comprises 47 minerals and more than 120 synthetic compounds.

They are produced commercially because of their structural properties, which allow them to be used as molecular sieves, ion exchangers and in the selective shape catalysis. Zeolite tetrahedral frameworks are characterized by low density (d_f). Here $d_f = 1000\ n_T/V$, where: V, volume of the unit cell; n_T, number of T-atoms in the unit cell. The values of d_f change from 12.7 (Al+Si) in faujasite $(NaCa_{0.5})Al_2Si_5O_{14} \cdot 10H_2O$ up to 29.3 in coesite (high-pressure form of SiO_2). Low density means that there are big voids and channels (3.5–15 Å) in zeolite structures, which accommodate different cations and water molecules, weakly connected with the framework. These weak bonds determine the capability of zeolites as ion exchangers. For example, it is worth mentioning the water softening by zeolites that incorporate Na^+ as the process in which $2Na^+$ cations can be replaced by $Ca^{2+}(Mg^{2+})$. Another example is the extraction of radioactive elements from the nuclear waste by clinoptilolite $K_2Na_2Ca[AlSi_5O_{12}] \cdot 8H_2O$.

The voids in zeolite structures permit them to be used as molecular sieves. For example, the Ca-form of Linde A, $Na_{12}[Al_{12}Si_{12}O_{48}] \cdot 27H_2O$, (Figure 9) with rather small voids removes from natural petroleum undesirable hydrocarbons having straight molecular chains that burn with explosion. Thus, the presence of cyclic or branched hydrocarbon molecules increases the petroleum quality.

Zeolites participate in many processes (selective shape catalysis) which take place at high temperatures. Therefore, the thermal stability of zeolites is important. This stability increases with the increase of Si/Al ratio in their composition. Hence the interest in the synthesis of high-silica zeolites is justified.

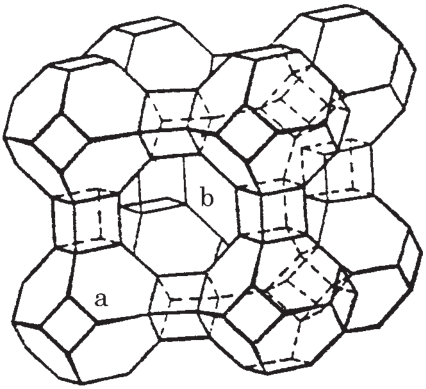
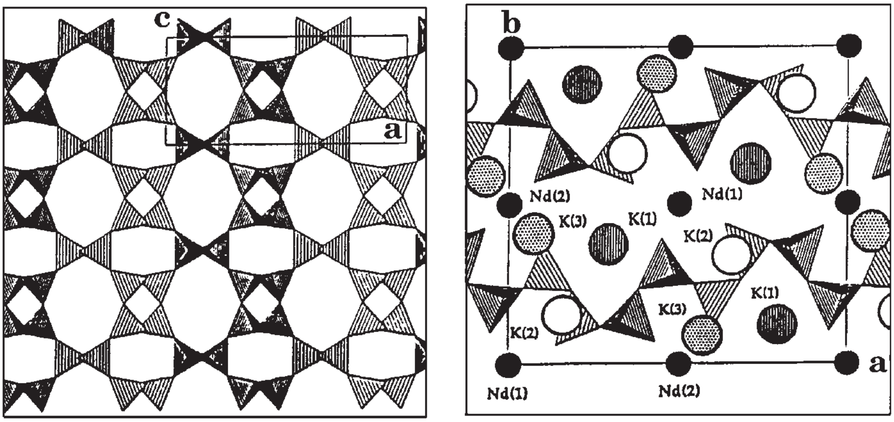


Figure 9. Schematic presentation of the crystal structure of zeolite Linde A: each vertex corresponds to the centre of SiO_4 tetrahedron.

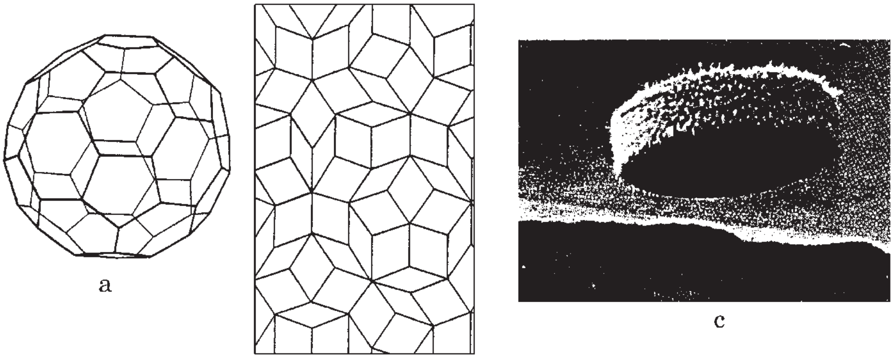
As it was mentioned earlier, cations can completely leave the low density framework of zeolites. However, there are structures, where cations can migrate only inside the framework, that contain smaller voids. These are mainly mixed frameworks built of octahedra and tetrahedra. The compounds in which the transfer of charges is realized by the migration of ions are called ionic conductors. The presence of 2- or 3-dimensional channels linked by the voids of appropriate size, as revealed by structural analysis, is considered as an important peculiarity, which determines the search for possible new ionic conductors. Another indicator is the presence of unusually large thermal-vibration amplitudes for some atoms, suggesting that these ions reside in a shallow minimum of potential energy. The crystal structure of K-rare earth silicate, $K_3NdSi_6O_{15}$, studied by our group as an exercise in silicate crystal chemistry, confirms this statement. It was synthesized hydrothermally in the system K_2O–Nd_2O_3–SiO_2–H_2O at $T = 500$ °C and $P = 825$ bar. The structure comprises unusually corrugated Si_2O_5 tetrahedral layers with 4-, 6- and 8-membered rings (Figure 10a). The alkali and rare earth cations are located between these layers. In our publication,[20] it was mentioned that K-atoms are characterized by relatively high thermal parameters ($B_{iso} = 3.90$–5.46 Å^2) and this fact attracted attention of the researchers from MIT, who succeeded in completing our results with new data connected with the characterization of the physical properties of this compound.[21] The projection along *c*-axis (Figure 10b) shows the continuous channel in which K1 ion resides and which is regarded as a potential path for high ionic mobility. The large temperature factors for this ion ($U_{11} = 0.059$, $U_{22} = 0.054$, $U_{33} = 0.104$ Å^2) indicate that K1 indeed resides in a shallow potential minimum and that the well is especially soft along [001]. Its conduc-



a b

Figure 10. The structure of $K_3NdSi_6O_{15}$: silicate sheet $[Si_2O_5]$ (a); projection along *c* of one-half of the cell contents ($0 < z < 0.5$) (b). The edge-on view shows the marked corrugation of silicate sheets and the open channel along *c* in which K(1) resides (after Ref. 26).

tivity was measured approximately at 550 °C and the pre-exponential factors $\sigma_{11}T = 2.6 \times 10^3$, $\sigma_{22}T = 5.3 \times 10^4$, $\sigma_{33}T = 1.1 \times 10^6$ indicate a really high mobility of K1 along [001].



a b c

Figure 11. Three most prominent discoveries in inorganic crystal chemistry during the decade 1980–90: a) fullerenes – 1984; b) Penrous mosaique, which represents a 2-dimensional model of quasicrystals – 1985; c) Meissener effect, observed with HT-superconductors – 1986.

CONCLUSION

A few problems of modern mineralogical crystallography, which reflect the level of the studies in this branch only to some extent, have been considered in this paper. Figure 11 reminds of three, perhaps, most important achievements in the XRD studies of inorganic compounds and minerals during the last decade, namely the synthesis of fullerenes, discovery of quasicrystals and characterization of high-temperature superconductors. Both sciences are closely connected because inorganic chemistry evoled from mineralogy and certainly the actual discoveries in the former influence further development of the latter. All these examples allow the conclusion that mineralogical crystallography is very much alive and the nearest future will see many new discoveries which will be accepted by future generations with gratitude and respect.

Acknowledgements. – This work was supported in part by the Russian Scientific Foundation (grants 00–05–65399, 00–15–96633), by The Russian Universities program and by a grant in Geology (MGGA).

REFERENCES

1. Yu. M. Pushcharovsky and D. Yu. Pushcharovsky, *Geotectonics* **33** (1999) 1–11.
2. A. Ross, *Nature* **385** (1997) 490.
3. A. M. Dziewonski and D. L. Anderson, *Phys. Earth Planet. Inter.* **25** (1981) 297–356.
4. B. L. N. Kennett and E. R. Engdahi, *Geophys. J. Int.* **105** (1991) 429–465.
5. T. Irifune and A. E. Ringwood, *Phase Transformations in Primitive MORB and Pyrolite Compositions to 25 GPa and Some Geophysical Implications,* in: M. H. Manghan and Y. Soyono (Eds.), *High-Pressure Research in Mineral Physics*, Terrapub-Washington: Am. Geophys. Union, Tokyo, 1987, pp. 231–242.
6. L-G. Liu, *Phase Transformations and the Constitution of the Deep Mantle*, in: M. W. Mc Elhinni (Ed.), *The Earth, Its Origin, Structure and Evolution*, Academic, 1979, pp. 117–202.
7. E. Knittle and R. Jeanloz, *Geophys. Res. Lett.* **13** (1986) 1541–1544.
8. L. S. Dubrovinsky, S. K. Saxena, P. Lazor, R. Ahuja, O. Eriksson, J. M. Wills, and B. Johansson, *Nature* **388** (1997) 362–365.
9. M. P. Pasternak, R. D. Taylor, R. Jeanloz, X. Li, J. H. Nguyen, and C. A. Mc Cammon, *Phys. Rev. Lett.* **79** (1997) 5046–5049.
10. I. I. Mazin, Y. Fei, R. Downs, and R. Cohen, *Am. Mineral.* **83** (1998) 451–457.
11. N. Funamori and R. Jeanloz, *Science* **278** (1997) 1109–1111.
12. J. J. Pluth, J. V. Smith, D. Yu. Pushcharovsky, E. I. Semenov, A. Bram, Ch. Ruickel, H-P. Weber, and H.-P. Broach, *Proc. Natl. Acad. Sci. USA* **94** (1997) 12263–12267.
13. F. Liebau, *Structural Chemistry of Silicates*, Springer, Berlin, 1985, p. 347.
14. D. Yu. Pushcharovsky, S. Teat, V. N. Zaitsev, N. V. Zubkova, and H. Sarp, *Eur. J. Mineral.* **12** (2000) 95–104.

15. H. Strunz, *Neues Jahrb. Mineral. Monatsh.* (1996) 435–445.
16. J. Lima-de-Faria, *Structural Mineralogy, an Introduction*, Kluwer Academic Publishers, Dordrecht, 1994, p. 346.
17. D. Yu. Pushcharovsky, J. Lima-de-Faria, and R. K. Rastsvetaeva, *Z. Kristallogr.* **213** (1998) 141–150.
18. D. Yu. Pushcharovsky, *Croat. Chem. Acta* **72** (1999) 135–145.
19. R. C. Rouse, P. J. Dunn, D. R. Peacor, and L. Wang, *J. Solid State Chem.* **141** (1998) 562–569.
20. D. Yu. Pushcharovsky, O. G. Karpov, E. A. Pobedimskaya, and N. V. Belov, *Sov. Phys. Dokl.* **234** (1977) 1323–1325.
21. S. M. Haile, B. J. Wuensch, R. A. Laudise, R. Opila, and Th. Siegrist, *Trans. ACA* **27** (1991) 77–94.

SAŽETAK

Noviji prinosi i moderne perspektive u proučavanju minerala difrakcijom X-zraka

Dmitry Yu. Pushcharovsky

Razmotrena su neka nedavna uzbudljiva otkrića u polju mineraloške kristalografije. Na temelju strukturnih proučavanja velike skupine minerala nedavno istraživanih na Državnom sveučilištu u Moskvi, diskutira se o kristalokemijskim fenomenima, koji prate stvaranje realnih struktura (na pr. ionsko sređivanje, varijacije poliedarskog slaganja, mikrosraštanje, modulacija). Novi pristupi istraživanjima omogućili su proširenje znanstvenih nazora o sastavu i strukturi dubokih geosfera, o strukturnoj klasifikaciji minerala, kemijskim oblicima i koncentracijama kemijskih elemenata u Zemljinoj kori, te o daljnjem razvoju modularne teorije. Prednost uporabe sinkrotronskog zračenja otvara vrata novoj grani mikrogeokemije (za oko 20% poznatih minerala nedostaje određivanje strukture, uglavnom zato jer su kristali premaleni ili nedovoljno savršeni za laboratorijski dobivene X-zrake). Proučavanja faznih prijelaza pokrovnih minerala pod visokim tlakom i pri visokoj temperaturi pridonose boljem razumijevanju sastava, strukture i geodinamike dubokih geosfera. Opisan je novi model pokrova temeljen na najnovijim seizmotomografskim podacima i na proučavanjima faznih prijelaza pokrovnih minerala. Otkriveno je nekoliko koncentričnih slojeva u pokrovu, iako je prijašnji model naglašavao njegovu podijeljenost na samo dva: gornji i donji. Diskutira se o novim pristupima proučavanju ionskog sređivanja, strukturne modulacije i varijacija poliedarskog slaganja.