

PS08.02.13 CHEMICAL AND STRUCTURAL VARIATIONS IN SERPENTINES FROM SOME METAULTRAMAFITES OF THE ROMANIAN CARPATHIANS (ROMANIA). Lucia Robu, Gabriela Stelea, I.N. Robu, Geological Institute of Romania, 1, Caransebes str., 78344-Bucuresti-32, Romania

Serpentine mineral samples come from some metaultramafic bodies included in the geological formations of the Romanian Carpathians.

For the most part of the samples mesh-texture are characteristic. Its one is determined due to the substituted processes of the olivene or/and pyroxene by chrysotile and/or lizardite in the marginal zones, and antigorite in the central ones. Sometimes, some small antigorite fringes are spread in the serpentine mass.

Crystallochemical data have been calculated according to $M_6N_4O_{10}(OH)_8$, general formula, where $M=Mg, Fe^{2+}, Ni, Fe^{3+}$, sometimes Cr and $N=Si, Al$.

However, Si and Al contents show some evident substituted processes in the tetrahedral levels, between Si and Al. A lack of silica in these levels, in the calculated formula suggests a completion of these ones by Fe^{3+} cations.

Mg, Ni, Fe^{2+} , Fe^{3+} cations were identified as filling of the octahedral chains. The exchanges between Mg and other above mentioned cations are insignificantly, so that their sum varies among 0.267-0.617. Sometimes Al cations are presented in these structural levels.

IR absorption spectra confirm these substitutions processes, registering absorption bands at the characteristic frequencies (cm^{-1}).

However the registered bands about 610 cm^{-1} varies directly proportional to the Mg substitution by Fe, Ni, Cr, at the octahedral levels. Its intensity increases when Mg content is increasing. There is no possibility to evidence the proportion in which took place this substitution, but some possible combination would be suppose, $MgMgMg, NiMgMg, NiFeMg, FeFeMg, FeMgMg$, sometimes $CrNiMg$ or $CrFeMg$.

Some of IR spectra present at the 663 cm^{-1} frequency a very low intensity peak, which could be assigned to NiNiNi combination.

These high inhomogeneous and discontinuous substitutional exchanges in the octahedral level have determined these variations of the IR absorption data.

At OH-stretching region, about the 3700 cm^{-1} domain the allures of the curves are similar to these ones characteristics for low Ni content.

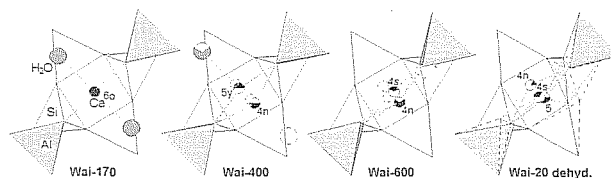
PS08.02.14 HIGH TEMPERATURE POWDER DIFFRACTION OF POLLUCITE UP TO 1073K. J. Schneider, H. L. Meyerheim, Institut fuer Kristallographie, Universitaet Muenchen, Theresienstrasse 41, D-80333 Muenchen, Germany

Framework silicates such as pollucite ($CsAlSi_2O_6 \cdot nH_2O$), leucite ($KAlSi_2O_6$) or analcite ($NaAlSi_2O_6 \cdot H_2O$) are characterized by four- and six-membered rings of corner linked (Si,Al) O_4 tetrahedra. In the cubic polymorphs this leads to formation of non-intersecting channels parallel to {100}- and {111}-directions, housing Cs- and Na-cations in the case of pollucite.

Powder diffraction of a sample from Bikita, Simbabwe (K. Rank, Bergakademie, TU Freiberg) was performed on a STOE diffractometer (MoK α 1 radiation) and a STOE stove using a rotating sample capillary. Rietveld analysis yields a distinct contraction of cell dimensions in the range between 473K and 873K, which may be ascribed to irreversible loss of crystal water. The structure model of R. M. Beger (Z. Kristallogr. 129(1968)280-302, space group Ia3d), which takes into account a significant amount of analcite, could be confirmed by refining the occupancies of the Cs, O(16b) and Na(24c) positions. Special emphasis was put onto the refinement of the temperature factors, which reach rather high values, i.e. at $T=673\text{K}$: $B(Cs)=5A^2$, $B(Na)=10A^2$. While B(Cs) shows a linear temperature dependence, B(Na) displays a change of slope at about 470K. Complementary single crystal measurements permitting anharmonic temperature factor analysis will be presented.

PS08.02.15 EVOLUTION OF CALCIUM-COORDINATION IN WAIRAKITE DURING HIGH TEMPERATURE TRANSFORMATIONS. Seryotkin Yu.V.¹, Joswig W.², Bakakin V.V.³, Fursenko B.A.¹, Belitsky I.A.¹. ¹Institute of Mineralogy and Petrography, Novosibirsk, 630090, Russia; ²Institute of Kristallography, Frankfurt University, Germany; ³Institute of Inorganic Chemistry, Novosibirsk, 630090, Russia.

Single crystal X-ray structure data are obtained for wairakite (Wairakite, New Zealand) - $Ca_{0.95}Na_{0.06}[Al_{1.96}Si_{4.04}O_{12}] \cdot 2H_2O$ at temperatures 20°C (I), 170°C (II), 210°C (III), 400°C (IV), 600°C (V), and again at 20°C (I_{dh} - dehydrated at 600°C and quenched). I - monoclinic, 13.666, 13.623, 13.531 Å, $\beta = 90.50^\circ$, $I2/a$. Al-fractions in 6 various Si,Al-tetrahedra correlate with Ca(Na) positions and are (%): 2, 3, 8, 13, 84, 89. Above 140°C I transforms to tetragonal phase II ($I41/acd$) - 13.712, 13.681 Å, $\Delta V \approx +2\%$. No water loss was observed below 200°C. III - 13.713, 13.687 Å. Na sites were localized in II and III. IV - is partially dehydrated (to 0.62 H_2O per formula unit) - 13.662, 13.555 Å. V is fully dehydrated - 13.645, 13.515 Å. Phase I_{dh} has monoclinic superstructure - 27.257, 27.253, 13.432 Å, $\beta = 90.20^\circ$. Structure data for I_{dh} are presented in a subcell with 13.629, 13.627, 13.435 Å, $\beta = 90.21^\circ$, $I2/a$. Ca coordination changes as follows (Fig.): in I, II, III - octahedral [6o] $\rightarrow O_4(H_2O)_2$ (avr Ca-O = 2.39 Å); in IV - semioctahedral [5y] $\rightarrow O_4(H_2O)$ (2.36 Å) and pyramidal [4n] $\rightarrow O^4$ (2.40 Å) - statistically with the ratio 0.48/0.47); in V - [4n] (2.37 Å) and square-coplanar [4s] (2.31 Å) with the ratio 0.65/0.31; in I_{dh} - five-fold [5] $\rightarrow O_5$ (2.40 Å), [4n] (2.38 Å) and [4s] (2.33 Å) with the ratio 0.52/0.27/0.19.



PS08.02.16 THE STRUCTURAL FEATURES OF CLAY MINERALS FROM THE SUPERDEEP WELL TSG-6 OF THE WEST SIBERIAN PLATE. E.P. Solotchina, T.A. Korneva and P.A. Solotchin, United Institute of Geology, Geophysics and Mineralogy, Siberian Branch RAS, Novosibirsk, Russia

The composition as well as the structural and crystallochemical features of clay minerals of Triassic deposits lying at a depth of 6000-6500 m penetrated by the unique Tyumen superdeep well have been studied. The basic method was X-ray diffraction analysis. Optical and electron microscopy as well as thermal analysis were used in addition.

The widespread development of 7 Å berthierine as mineral with the serpentine-like structure and the composition identical to iron-rich chlorite has been established. Two polytype modifications of berthierine: orthogonal A and monoclinic B (denoted by B. Zvyagin) of different genesis have been revealed. Berthierine is the most abundant mineral of tuffs making up as much as 85 % of rock in association with kaolinite. Two modifications of mixed-layer minerals as illite/smectites with $d_{001}=10.5-11\text{Å}$ and $d_{001}=24.5\text{Å}$ in initial state are dominant in argillites and in a cement of siltstones. Berthierine, chlorite, kaolinite and mica are present in such rocks as an impurity. Illite/smectites with interplanar space 24.5 Å have been revealed in more deep horizons. These minerals contain appreciable amount of adsorbed water (7.2 %) and interlayer water (1 %) on evidence derived from thermogravimetric curves. When the specimens were saturated with ethylene glycol d_{001} was enhanced to 26.8 Å and an integral series of intense basal reflections up to ninth order was observed in the X-ray diffraction pattern. Decoding the structures of mixed-layer minerals has been performed. The content of illite and smectite

layers and motive of their interstratifications have been defined.

The established crystallochemical features and the regularities in distribution of clay minerals allowed decompaction zones at significant depths to be found out and the character as well as the degree of epigenetic transformations of Triassic rocks of West Siberian Plate penetrated by TCG-6 well to be refined.

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PS08.02.17 CRYSTAL-CHEMICAL STUDY OF KAISi_3O_8 - KFeSi_3O_8 SOLID SOLUTION SERIES. V.K. Taroev¹, V.L. Tauson¹, H. Kroll², J. Gottlicher³. ¹Institute of Geochemistry, Irkutsk, 664033, Russia; ²Institute of Experimental Mineralogy, Munster Univ., D-48149, Germany; ³Institute of Technical Mineralogy, Karlsruhe, D-76021, Germany

The monoclinic mixed crystals $\text{K}(\text{Fe,Al})\text{Si}_3\text{O}_8$ are synthesized under hydrothermal conditions from pure oxides in KOH solution at temperatures 500 and 600°C and pressure ca. 100 MPa. The mixed crystals up to 2 mm were obtained. An extensive formation of solid solution was observed only under sufficiently high oxygen fugacities corresponding to Cu-Cu₂O buffer assemblage (up to 60 mole per cent of KFeSi_3O_8). The unit cell edges vs. mole fraction graphs are close to linearity, their extrapolation to monoclinic end member agrees well with the data available from the literature. Both the Mossbauer spectroscopy and X-ray structure refinement studies indicate the absence of Fe²⁺ species, and preferential occupancy of T1 position by Fe³⁺ and Al³⁺ in the proportion of their bulk concentrations. The data obtained are in poor agreement with the well-known Eberhard's solvus for monoclinic Al-Fe - potassium feldspar (Eberhard, 1965). The discrepancy may be explained by the dispersed state of phases in Eberhard's experiments, and so, the possibility of crystallite size effect (Tauson & Akimov, 1993) or the absence of oxygen fugacity control.

References:

Eberhard, E. (1965) *Tschermaks. Min. Petr. Mitt.* 10, 400-408. Tauson, V.L. & Akimov, V.V. (1993) *Chem. Geol.* 109, 113-118.

PS08.02.18 TRANSFORMATIONS OF CUBIC LAZURITE WITH INCOMMENSURATE-MODULATED STRUCTURE. V.L. Tauson, A.N. Sapozhnikov, K.E. Kuznetsov, and V.V. Akimov, Institute of Geochemistry, Irkutsk, 664033, Russia

The sodalite-like minerals are the convenient object for studying different types of structure modulations, especially that ones which can be considered as the result of forced equilibria attainment (Tauson & Akimov, 1993;1994). The set of experiments is performed using lazurite sample of composition $(\text{Na,Ca})_{7-8}\text{Si}_6\text{Al}_6\text{O}_{24}(\text{SO}_4,\text{S,Cl})_2$ from the Baikal region deposit. The sample is characterized with the three-dimensional incommensurate modulation of structure with the modulation parameter $n=0.217$. When annealed in air, the sample changes the initial modulation to the commensurate one with $n=0.168$ via an intermediate state without superstructure. The diagrams of lazurite stability on coordinates temperature-gas fugacity (T - $f\text{O}_2$, T - $f\text{S}_2$, T - $f\text{SO}_2$) are obtained. Lazurite is unstable under $f\text{O}_2 > 10^{-14}$ - 10^{-12} bars and decomposes with the formation of complex sulphates of Ca, Na and Al which are qualitatively similar to the clusters observed in lazurite and hauyne structures. However, the actual reason of lazurite instability lies in the high $f\text{SO}_2$, not high $f\text{O}_2$ value. Under a sufficiently low $f\text{SO}_2$, lazurite undergoes the transformation to the sulfide sodalite because the SO_4 - ion loses its stability. This is accompanied by a strong contraction of the lazurite lattice. Under very low $f\text{SO}_2$ ($< 10^{-14}$ bar) at 550°C, a new phase with incommensurate modulation $n=0.136$ is observed in addition to S-sodalite. For moderate $f\text{SO}_2$ values, the ordering and condensation of clusters occur before lazurite decomposition. As a result, a persistent density modulation is formed which originates from the balance of cluster ordering energy and Na-Ca mixing energy because the formation of cluster condensates needs

a local change in solid solution composition for its accommodation to the clusters stoichiometry. This state is recognized as metastable forced equilibrium of type II.

References

Tauson V.L. & Akimov V.V. *Geologia i Geofizika* 34,103 (1993), 35,57 (1994).

PS08.02.19 THE INFLUENCE OF COMPOSITION AND EXTERNAL ACTIONS ON MICA CRYSTALS STRUCTURE. V. V. Voyna, V.A. Liopo, Phys. & Engin. Dept., Grodno State University, Grodno, BELARUS. 230023

Structural variations of the mica crystals with different degrees of hydration (G) in the processes of heating and mechanical deformations were studied. The G-values of phlogopite (Ph) crystals, their interplanar distances [$d=d(00l)$], the relative K-maximum altitude on Z-projection of electron density (Z), the IR-absorption factor for 3550 cm^{-1} (A), concentrations of 14 Å layer (W), microhardnesses (H) are bounded by relations $G \sim d \sim Z^1 A \sim W \sim H^1$. Symmetries of the thermal expansion tensor and the tensor of elasticity for trioctahedral Ph and dioctahedral muscovite (M) were ∞/mmm and mmm respectively. The ratios of major axes of these tensors are determined. The scheme of the thermic destruction for different mica crystals was investigated. The measure of crystal defectivity is a ratio of structural deformation to the macro ones when external forces are the same. The structural variations in the heating and strain processes for mica crystals with different hydration degrees are the biggest ones in the interlayer interval. The changes of geometrical sizes of the structural polyhedrons and their turnings at heating depend on the crystal composition and external forces. The principal differences between the tri- and dioctahedral micas (Ph and M in our case) crystals structural variations in the processes of heating and strain are determined by possibility of trioctahedral mica to form mixed-layer structures.

PR08.02.20 THE CRYSTAL STRUCTURE OF SCOMIOKITE-(Y), $\text{Na}_3\text{Y}(\text{CO}_3)_3\text{3H}_2\text{O}$. Pushcharovsky, Dmitry Yu.¹, Rastsvetneva, Ramisa K², Pekov, I.V.¹, ¹Department of Geology, Moscow State University, 119899 Moscow, Russia; ²Institute of Crystallography RAN, 117333 Moscow, Russia

Among 11 carbonate minerals, which contain Y atoms in the individual positions, schomiokite-(Y), $\text{Na}_3\text{Y}(\text{CO}_3)_3\text{3H}_2\text{O}$, is chemically related to orthorhombic tengerite $\text{Y}_2(\text{CO}_3)_3\text{2-3H}_2\text{O}$, kimuraite $\text{CaY}_2(\text{CO}_3)_4\text{6H}_2\text{O}$, lokkaite $\text{CaY}_4(\text{CO}_3)_7\text{9H}_2\text{O}$ and tetragonal kamphaugite-(Y) $\text{CaY}(\text{CO}_3)_2(\text{OH})\text{H}_2\text{O}$. The aim of the present study is to determine the position of schomiokite inside of this crystal chemical family.

The parameters of the orthorhombic cell are: $a=17.358$, $b=10.034$, $c=5.946\text{Å}$, sp. gr. $\text{Pha}2_1$. The structure was refined up to $R_{\text{hkl}} 0.059$ for 1973 observed reflections. The structure contains isolated mixed complexes, formed by YO_9 polyhedra, which share their three edges with CO_3 groups. YO_9 polyhedra can be considered as 3-caped pseudotrigonal antiprisms, where one base is formed by three H_2O molecules. Three CO_3 groups are characterized by pyramidal distortion with the deviations of C atoms from the planes, formed by O atoms, 0.006, 0.003 and 0.01Å respectively.

The mixed complexes are considered as relicts of the corrugated polyhedral layers, described in tengerite, kimuraite and lokkaite, and are connected by Na octahedra and 5-fold polyhedra as well as by a system of H-bonds. The interpretation of the structure in terms of the interrupted layers is confirmed by the values of its lattice parameters ~ 6 and 10Å , which are parallel to the plane of the sheet and are close to the corresponding values of tengerite, kimuraite and lokkaite.