

depicted above holds also for the $m=15$ (P) and the $m=18$ (C) polysomes.

[1] Capitani G.C., Mellini M., *Am. Mineral.*, 2004, **89**, 147. [2] Mellini M., Viti C., *Am. Mineral.*, 1994, **79**, 1194.

Keywords: antigorite, structure, polysomatism

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Two kinds of Superstructures of (Ge, Si) Wollastonite

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Two kinds of superstructures of wollastonite whose compositions were Ca(Ge_{0.55}, Si_{0.45})O₃ and Ca(Ge_{0.65}, Si_{0.35})O₃ were synthesized. The former is called 0.55Wo and the latter 0.65Wo in this abstract. The lattice constants of 0.55Wo and 0.65Wo are: (angstrom, degree) $a=2X8.016(4)$, $2X8.038(5)$, $b=7.421(1)$, $7.451(1)$, $c=7.157(2)$, $7.194(1)$, $\alpha=90.08(2)$, $89.93(1)$, $\beta=94.86(2)$, $94.85(2)$, $\gamma=103.44(2)$, $103.34(1)$, respectively. Though both of them are twice as large as the basic structure of wollastonite, those structures are different. Basically, 0.55Wo has the two units of the basic-wollastonite along a-axis and has no other partial structures in it. The largest difference between the basic wollastonite and 0.55Wo is the fact that the basic wollastonite has an inversion center but 0.55Wo has not it. Therefore, the basic wollastonite includes only 15 independent atoms but 0.55Wo includes the 60 atoms in the unit cell. The final R-value was 6% after the structure refinement of 0.55Wo. 0.65Wo has the two units of the basic-wollastonite along a-axis, too. However, the X-ray diffraction pattern of 0.65Wo was largely different from that of 0.55Wo and it showed the extinction rule of the pseudo-C lattice. The structure model having the stacking of the basic-wollastonite unit with $b/2$ displacement were tried and the R-value was 9% after the structure refinement.

Keywords: structure analysis, superstructure, wollastonite

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Light-Induced Degradation Dynamics in Realgar (As₄S₄)

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Light-induced degradation in realgar (As₄S₄) has been studied by means of four-circle XRD and XPS. Because of the alteration of realgar exposed to light, the a lattice parameter and $c \sin\beta$ value increase linearly, which leads to a continuous increase of the unit cell volume. Nevertheless, no correlation exists between the continuous increase of the unit cell volume and the bond distance variations in As₄S₄ molecules. The most pronounced change was observed in the distance between centroids in As₄S₄ cage. The spread of As₄S₄ intermolecular distances increases continuously from 5.642 Å to 5.665 Å, which directly affects the unit cell volume expansion of realgar. In addition, the O1s peak increases rapidly after light exposure. The result substantiates the reaction proposed by Bindi et al. [1]. That is, realgar is transformed into pararealgar if oxygen exists and produces As₄S₅ molecule. The additional S atom at As₄S₄ molecule contributes to anisotropic expansion for the a and c axes because the direction for the additional S atom points toward [4-14] in the unit cell. Furthermore, an S atom in the As₄S₅ molecule is released from one of equivalent As-S-As linkages in As₄S₅; it turns itself into the As₄S₄ molecular of pararealgar. The free S atom is re-attached to another As₄S₄ (realgar type) molecule, and reproduces an As₄S₅ molecule. The reproduced As₄S₅ molecule turns itself into the As₄S₄ molecular of pararealgar again. This cycle that realgar is indirectly transformed into pararealgar via As₄S₅ molecule is repeated during light exposure.

[1] Bindi L., Popova V., Bonazzi P., *Can. Mineral.*, 2003, **41**, 1463.

Keywords: single-crystal XRD, mineral physics, photochemistry

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A Revision of the Structure and Crystal-Chemistry of the Arrojadite-Group

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Arrojadite, dickinsonite and sigismundite define a group of phosphates with a very complex structure and crystal-chemistry, which has not been satisfactorily characterized so far. Previous works described the structure in the $C2/c$ space group which implies the presence of half-occupied P1 phosphate groups sharing basal faces and with the apical oxygen atoms pointing in opposite directions, and of partial occupancy at 10 out of the 49 sites in the asymmetric unit. Electron microprobe analyses suffer from severe interference problems due to the coexistence of P, Fe and F.

Single-crystal refinement, Raman spectroscopy and well-controlled *in situ* microchemical analysis of selected samples allowed a better interpretation of the structure and crystal-chemistry of the arrojadite group. The correct space group is Cc , and the lowering in symmetry implies recognition of strong cation ordering among the 21 cationic sites besides the 12 PO₄ groups. The correct number of OH groups pfu is 3 and not 2 (2 OH are bonded to octahedral sites and 1 to a PO₄ group), and a selectivity is shown for F incorporation at one of these sites. The active exchange vectors were identified, and a new nomenclature has been proposed on crystal-chemical basis.

The $C2/c$ derives from the presence in some samples of Cc domains related by a diad along b plus a $1/2$ shift along c . This feature cannot be treated by X-ray structure refinement, and may be related to growth defects occurring during high- T crystallisation (in pegmatites).

Keywords: phosphate crystal-chemistry, mineralogy, crystal-structure

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Supramolecular Arrangement of Tensioactive Molecules in Interlayer Spaces of Two Organophilic Clays

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Studies of mixed systems using clays and tensioactive molecules (TA) are of particular importance in many fields such as medicine, pharmacy and cosmetics. The substitution of the initial cations and intercalation of cationic organic molecules in the interlayer spaces of the clay structure lattice provide new physicochemical properties. The aim of the present study consist in a structural characterisation of two different purified and organophilic clays, mainly made of smectite with a marked montmorillonitic nature, as a function of the inserted TA quantity using high-resolution X-ray powder diffraction. Two different TA are used, the benzyltétradécyltriméthylammonium (BTDMA) and the benzyldodécyltriméthylammonium (BDDMA).

Keywords: organomineral materials, powder X-ray diffraction, supramolecular assemblies

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Ti-investigation by XPS of Biotite from Metapelites of El Joyazo (Spain)

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The Ti-rich biotite from graphite-bearing metapelitic xenoliths (El Joyazo – Spain) have been recently studied through a multitechnical approach [1]. The study, combining several techniques, showed TiO₂ content ranging from 4.5 to 4.9 wt% and a constant X_{Fe} = 0.67. According to the results of their investigations, Cesare *et al.* [1], suggest that titanium (as Ti⁴⁺) is logged only in octahedral site. The aim of the present work is the investigation both the oxidation state and the site partition of titanium accepting the main crystal chemical conclusion achieved by [1]. The following Ti-coordination polyhedra have been considered during XPS analysis: 4-fold coordination (tetrahedral), 5+1 coordination (distorted octahedral), 6-fold coordination (regular octahedral). In order to obtain the best fitting, the BE of the Ti⁴⁺ for the octahedral and tetrahedral coordination have been determined following the procedure in [2]. While the BE for Ti⁴⁺ in distorted octahedron (5+1) has been obtained by means of *ab initio* calculations [3]. The result of XPS investigation shows that Ti⁴⁺ populates both tetrahedral and octahedral sites. Taking in account the structural formula proposed by [1], we note that the entrance of Ti⁴⁺ in the tetrahedral site and of Al³⁺ in octahedral site, in the same amount, results in a both better balance of the substitution mechanisms and in a better m. a. n.'s agreement between EPMA and SCXRD data.

[1] Cesare B., Cruciali G., Russo U., *Am. Mineral.*, 2003, **88**, 583-595. [2] Malitesta C., Losito I., Scordari F., Schingaro E., *Eur. J. Mineral.*, 1995, **7**, 847-858. [3] Saunders V.R. *et al.*, *CRYSTAL'03 User Manual*, Turin, University of Torino, 1999.

Keywords: Ti-bearing micas, XPS analysis, Ti speciation

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Mg, Al, Si, Ca -Bearing Magnetite from Korshunovskoe, East Siberia

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The crystal chemistry of magnetite crystals from Korshunovskoe iron ore deposit were investigated by means of single-crystal X-ray diffraction and electron microprobe analyses. The crystals were picked from two rock samples and show significant Mg, Al, Si and Ca content. The cell parameters are close to 8.392 Å, slightly smaller than for pure magnetite, and the oxygen positional parameters are close to 0.2550. After refinement, weak residual peaks were systematically founded in position 48f; possibly an indication of interstitial atoms [1]. Introducing an atom in the suggested position led to significant improvement in the refinement disagreement factors [2]. Refined site occupancies led to an estimate of about 25 electrons both in the T and M sites, consistent with the substitution in both sites of some elements lighter than iron. However the number of electrons calculated from the microprobe analyses is significantly lower, therefore some of the detected cations could not be part of the magnetite structure, however no other phases were detected from the powder diffraction profile.

[1] Fleet M.E., *Acta Cryst.*, 1982, **B38**, 1718. [2] Hamilton W.C., *Acta Cryst.*, 1965, **18**, 502.

Keywords: magnetite, structure analysis, interstitial atoms

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Analysis of Structure Factors of 2D-connected Crystal Structures
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The solution of complex inorganic structures from powder diffraction data is much easier when dominant scatterers are present.

Due to the small X-ray scattering contrast between Si and O, solution of complex zeolitic materials is still difficult. One characteristic of the latter is their 3D connectivity and the known tetrahedral coordination that means that once the positions of the Si are located, the positions of the O atoms can be interpolated. In other words, the positions of the O atoms are not independent from the Si positions. The ideal situation for solving crystal structures from powder data at moderate resolution ($d > 2\text{Å}$) by direct methods would be to have at one's disposal structure factor moduli with the contributions of the O atoms removed [1], [2].

In order to better analyse this possibility, the modulus C and the phase angle δ of group structure factor of one triangular O polyhedron around a central Si atom have been plotted as a function of its orientation. The respective variation coefficients of C are 9.1 and 21.5% at 2 and at 1.85 Å resolution, respectively, while the corresponding standard deviations of δ are 27° and 12°. These values are used to estimate the accuracy of the structure factors of an hypothetical planar 2D connected model built of such triangular polyhedra after removal of the average O contribution.

[1] Rius J., *Acta Cryst.*, 1993, **A49**, 406. [2] Rius J., *Z. Kristallogr.*, 2004, **219**, 826.

Keywords: powder structure solution, complex compounds crystal structure, inorganic materials

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The Spinel Unit Cell Parameter as Diamond Potentiality Indicator

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The Russia (Yakut and Archangel kimberlite provinces), South Africa, North America and Australia spinels grains (about 500) content from different types deep rocks was discovered. The spinels are characterised by two types of substitutions: 1) Cr⁽³⁺⁾-Al⁽³⁺⁾, 2) Cr⁽³⁺⁾-Fe⁽³⁺⁾+Ti⁽⁴⁺⁾.

The clear lineal dependance between unit cell parameter (a_0) and oxides contents was not observed. The obtained data are testified the limitations of using the diagram based on the Yakut and Archangel regions spinels X-ray data. The lineal dependance can be observed within the samples with Cr⁽³⁺⁾-Al⁽³⁺⁾ or Cr⁽³⁺⁾-Fe⁽³⁺⁾ isomorphism. The realisation both substitutions schemes and also enough amount of titanium (more than 2 mas.%) in spinel structure and the wide substitutions between Mg⁽²⁺⁾-Fe⁽²⁺⁾ disturb the lineal dependance between oxide contents and a_0 : decreasing a_0 is held by decreasing Al₂O₃, and increasing a_0 depends not only from chrome (III) oxide, but from Cr₂O₃, Fe₂O₃ and TiO₂, MgO and FeO together influence. Therefore during first steps searching spinels upon X-ray data one can get higherferrous and titanious varieties.

The two lines have been identified between a_0 and IR-spectra absorbance maximum within spinels from kimberlites which indicates on a crystallization consequence and a fluid-magmatic differentiation on the first mantle magmas.

This approach also can be used as a guide by Geological Enterprises to search spinels as mineral-indicators on diamondiferous rocks.

Keywords: spinels, unit cell parameter, IR-spectra absorbance maximum

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Variations in the Morphologies and Magnetic Properties of Magnetite Crystals in Bacteria

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