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Resolving Structure and Size of Amorphous Mineral Precipitates by PDF Analysis

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Amorphous, or X-ray amorphous, is a common term used to describe mineral precipitates lacking long-range order. Earth materials, such as amorphous FeS, silica, and Fe(III)-hydroxide, are abundant in natural environments and play an important role in geochemical processes and the fate of contaminants. While use this term persists in the Geosciences community, it is important to resolve the short- to medium-range structure and fundamental size of these solids to deepen our understanding of their role in geochemical processes. In this study, we report on the structure and size of so-called amorphous FeS, the first Fe-S phase formed in anoxic sediments which, over time, will convert to pyrite (FeS_2). Amorphous FeS can also sequester metals and metalloids, such as cadmium and arsenic and react with contaminants, such as Cr^{6+}. High-energy X-ray scattering data for freshly precipitated and aged FeS (7 days at 70°C) were collected at the Advanced Photon Source and analyzed using the PDF method. Results indicate that amorphous FeS has short- to medium-range order consistent with that of crystalline mackinawite. Further, the range of structural coherence (i.e., fundamental particle size) as can be obtained from PDF [1] is initially about 2 nm, but increases to 4.5 nm for the aged sample. Hence, the initial FeS precipitate is better described as a nanocrystalline material with mackinawite structure. This technique holds great promise for further study of nanocrystalline earth materials lacking long-range order.

[1] Page et al., *Chemical Physics Letters*, 2004, **393**, 385-388.

Keywords: pair distribution function, nanocrystals, particle size

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Crystal structures of $Rb_2(C_2O_4)\cdot H_2O$ and $Tl_2(C_2O_4)$: Application of Valence Matching Rule

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Crystal structures of $Rb_2(C_2O_4)\cdot H_2O$ (monoclinic, space group $C2/c$, $a = 9.617(6)$Å, $b = 6.353(5)$Å, $c = 11.010(8)$Å, $\beta = 109.46(3)^\circ$, $V = 634.2(8)$Å^3, $Z = 4$, $R1 = 0.026$, for 2646 reflections) and $Tl_2(C_2O_4)$ (triclinic, $P\bar{1}$, $a = 6.623(4)$Å, $b = 6.674(3)$Å, $c = 5.854(4)$Å, $\alpha = 90.031(35)^\circ$, $\beta = 89.967(36)^\circ$, $\gamma = 80.745(40)^\circ$, $V = 255.3(3)$Å^3, $Z = 2$, $R1 = 0.082$, for 1499 reflections) were determined using an imaging-plate diffractometer and a four-circle diffractometer, respectively (Mo$K\alpha$ radiation, graphite monochromator).

Incorporation of rubidium cations (Rb^+) with oxalic anions anions ($C_2O_4^{2-}$) establishes two-dimensional layer structure; water molecule $(H_2O)^0$ intercalates into the layers. Conformation of thallium cations (Tl^+) to seven oxygen atoms of oxalic anions sets up the two-dimensional layer structure, which is similar with that of rubidium oxalate. Except for water molecule, thallium oxalate is isotypic to rubidium oxalate (this study) and potassium oxalate $K_2(C_2O_4)\cdot H_2O$[1].

Bond valence analysis of these compounds reveals that $(H_2O)^0$ moderates the Lewis basicity of oxalic anion ($C_2O_4^{2-}$: 0.167). This moderated Lewis basicity matches the Lewis acidity of potassium and rubidium cation (K^+: 0.126, Rb^+: 0.124)[2], respectively: the valence-matching principle is satisfied.

[1] Sequeira A., Srikanta S., Chidambaram R. *Acta Cryst.*, 1970, **B26**, 77. [2] Brown I. D. *Acta Cryst.*, 1988, **B44**, 545.

Keywords: oxalate mineral, bond-valence, hydrogen bonds

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Structure and Composition Properties of Mica from Ilmen Reserve Granite Pegmatites

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Micas, picked up A) along the edges and B) from the center of five granite pegmatites were studied from Ilmen reserve (Ural, Russia), using the optical, X-ray, microprobe (SEM and TEM) and electron diffraction methods.

The 2V measurements showed two different types of mica: A) with homogeny 2V distribution on all area of one crystal B) heterogeneous 2V distribution, witch is also showed by X-ray and microprobing analyses. Somme fluctuations in Ng' and Nm' significance are caused by heightened content of F, Fe and Li. слюды $2M_1$, 1M, 3T and M_d polytypes were detected by X-ray powder diffraction. For all that optical homogeneity of micas were $2M_1$ polytype, while the heterogeneous micas with intermediate *a* and *b* sense between di- and trioctahedral structures are presented in 1M and 3T polytypes. Fe-micas were an Md modification. Diagnostic and division of 1M and 3T modification in powder samples were made on intensity and position of 11l and 02l peaks.

Crystal formula was calculated on bulk chemical composition, SEM and TEM analyses, taking into account X-ray and optical data. Blocks with different composition possess so hard as smooth edges in one crystal, were detected for heterogeneous samples using the TEM and electron diffraction data. Interesting is, that two neighbor area have different ultimate mineral members. This complex of analyses allows the dioctahedral mica with heightened Fe content carry on muscovite and celadonite, trioctahedral mica – on flogopyte and annite and the Li-Fe mica on trilitionite.

As a result the homogenous $2M_1$ mica with utmost di- or trioktahedral composition on board and heterogeneous 1M and 3T polytypes with heightened content Li, F and Fe on center of pegmatites were exposured.

Prescribed ecpecialites of homogeny and heterogeneous structure and composition in mica can be used as typomorphic indicators of granite pegmatites crystallization conditions.

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Keywords: X-ray, mica, granite pegmatites

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XRD and HRTEM Structural Analyses of Antigorite Polysomes

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The modulated crystal structure of two common antigorite polysomes, the "odd" m=17 and the "even" m=16 polysomes (m being the number of tetrahedral modules in a wave), have been recently refined by XRD using single crystals from the Val Malenco Italian Alps. The m=17 polysome [1] has Pm symmetry, cell constants a=43.505(6), b=9.251(1), c=7.263(1) Å, β=91.32(1)°, and consists of a wavy 1:1 layer, curled on the b-axis and modulated along [100]. Sixteen **O**-modules form a continuous **O**-sheet. Seventeen **T**-modules link the **O**-sheet at the concave sides, forming a "short" half-wave, and "long" half-wave with opposite polarities. The **T**-sheet shows 6-membered tetrahedral rings, like in lizardite, which reverse polarity via alternating 6-reversals (6-membered tetrahedral rings) and 8-reversals (8- and 4-membered tetrahedral rings, coupled along **b**).

The "even" m=16 polysome has $C/2m$ symmetry, cell constants a=81.664(10), b=9.255(5), c=7.261(5) Å, β=91.41(5)°, and the same structural configuration of the m=17 polysome, but for the even number of **T**-modules, which makes the halfwaves symmetric, and the periodic **b**/2 shifting of the 8-reversal position, which makes the cell double and C-centered. First neighbors interactions are very similar in the two polysomes, and similar to lizardite [2].

HRTEM investigations carried on the same batch of crystals, confirm the presence of P and C structures, and show that the scheme 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(Ge0.55, Si0.45)O3 and Ca(Ge0.65, Si0.35)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 unite 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 diffracrion 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 (As_4S_4)

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Light-induced degradation in realgar (As_4S_4) 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* sinβ 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 As_4S_4 molecules. The most pronounced change was observed in the distance between centroids in As_4S_4 cage. The spread of As_4S_4 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 As_4S_5 molecule. The additional S atom at As_4S_4 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 As_4S_5 molecule is released from one of equivalent As-S-As linkages in As_4S_5; it turns itself into the As_4S_4 molecular of pararealgar. The free S atom is re-attached to another As_4S_4 (realgar type) molecule, and reproduces an As_4S_5 molecule. The reproduced As_4S_5 molecule turns itself into the As_4S_4 molecular of pararealgar again. This cycle that realgar is indirectly transformed into pararealgar via As_4S_5 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 *C*2/*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 PO_4 groups. The correct number of OH groups *pfu* is 3 and not 2 (2 OH are bonded to octahedral sites and 1 to a PO_4 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 *C*2/*c* derives from the presence in some samples of *Cc* domains related by a diad along *b* plus a ½ 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 Organiphilic Clays

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Studies of mixted systems using clays and tensioactive molecules (TA) are of particular importance in many fields such as medecine, 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 caracterisation of two different purified and organoplilic 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 benzyltétradécyldiméthylammonium (BTDMA) and the benzyldodécyldiméthylammonium (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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