

P.10.05.6*Acta Cryst.* (2005). **A61**, C377**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 of 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 (FeS₂). Amorphous FeS can also sequester metals and metalloids, such as cadmium and arsenic and react with contaminants, such as Cr⁶⁺. 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

P.10.05.7*Acta Cryst.* (2005). **A61**, C377**Crystal structures of Rb₂(C₂O₄)·H₂O and Tl₂(C₂O₄): Application of Valence Matching Rule**

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Crystal structures of Rb₂(C₂O₄)·H₂O (monoclinic, space group C2/c, *a* = 9.617(6)Å, *b* = 6.353(5)Å, *c* = 11.010(8)Å, β = 109.46(3)°, *V* = 634.2(8)Å³, *Z* = 4, *R*1 = 0.026, for 2646 reflections) and Tl₂(C₂O₄) (triclinic, *P* 1̄, *a* = 6.623(4)Å, *b* = 6.674(3)Å, *c* = 5.854(4)Å, α = 90.031(35)°, β = 89.967(36)°, γ = 80.745(40)°, *V* = 255.3(3)Å³, *Z* = 2, *R*1 = 0.082, for 1499 reflections) were determined using an imaging-plate diffractometer and a four-circle diffractometer, respectively (MoKα radiation, graphite monochromator).

Incorporation of rubidium cations (Rb⁺) with oxalic anions (C₂O₄²⁻) establishes two-dimensional layer structure; water molecule (H₂O)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 isotopic to rubidium oxalate (this study) and potassium oxalate K₂(C₂O₄)·H₂O[1].

Bond valence analysis of these compounds reveals that (H₂O)⁰ moderates the Lewis basicity of oxalic anion (C₂O₄²⁻: 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

P.10.05.8*Acta Cryst.* (2005). **A61**, C377**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 homogeneity 2V distribution on all area of one crystal B) heterogeneous 2V distribution, which is also showed by X-ray and microprobing analyses. Some fluctuations in Ng' and Nm' significance are caused by heightened content of F, Fe and Li. слюды 2M₁, 1M, 3T and M_d polytypes were detected by X-ray powder diffraction. For all that optical homogeneity of micas were 2M₁ 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 111 and 021 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 trillionite.

As a result the homogenous 2M₁ mica with utmost di- or trioctahedral composition on board and heterogeneous 1M and 3T polytypes with heightened content Li, F and Fe on center of pegmatites were exposed.

Prescribed specialities of homogeneity 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

P.10.05.9*Acta Cryst.* (2005). **A61**, C377-C378**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*/2*m* 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