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Within the NFI powder XRD is mainly used for:

1. Characterization of powders of unknown composition

In The Netherlands the number of anonymous threatening letters sent to politicians and other VIP's has increased since 9/11 and the murder of Pim Fortuyn. To aggravate the threatening effect some senders enclose cartridges or powders in the letters. The risk of such enclosed powders is assessed by means of a standard procedure. If the risk is considered negligible or absent, the powder is characterized by means of FTIR, XRF and XRD. This generally leads to a quick and clear characterization of the powder. Mostly these powders are composed of household articles, such as flour, sugar or washing powder. In some cases more particular compounds, e.g. medicines, are present, which can be important information for the criminal investigation process.

2. Comparison of materials found at a scene of crime

In a particular case threatening letters were produced on pink sheets of paper. In the house of the suspect a bundle of similar pink paper was found. A comparative investigation of pink papers from different origin was carried focussing on the characterization of fillers and the cellulose crystallinity. The result was that the questioned paper and the paper found at the suspect's house could not be distinguished from each other and that all other papers contained different fillers.

3. Characterization of pyrotechnical mixtures

In The Netherlands, strict regulations are effective with respect to the composition of consumer fireworks. The maximum allowable mass of the explosive charge depends on the chemical composition of the charge. By means of XRD the components of pyrotechnical mixtures can be identified easily and quickly.

Keywords: forensic mineralogy, paper, powder X-ray diffraction

MS06.24.4

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X-ray Chemical Analysis for Forensic Applications using Synchrotron Radiation

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A synchrotron radiation (SR) light source is one of the important technologies in the forensic science. Especially, it was expected that the use of high-energy X-rays from SPring-8 as an excitation source for X-ray fluorescence (XRF) analysis would be suitable for distinguishing the difference in the origin of the trace amount of samples. We first developed high-energy XRF utilizing 116 keV SR to conduct a scientific investigation to aid in the solving of an arsenic murder that occurred in Wakayama City on July 25, 1998 [1]. We have successfully detected the ppm levels of Sn, Sb, and Bi included in arsenic acid as the impurities. As a result, it was found that the trace heavy element compositions are distinct from each other, reflecting the different places of production. This technique has already come into routine use by the Forensic Science Laboratory of the Hyogo Prefecture Police Headquarters to solve several important criminal cases occurring all over Japan [2]. They have been beginning an analysis for various forensic samples such as gunshot residue particles, tiny glass pieces, paint chips, fluorescent powders.

In this talk, some experimental results of chemical analyses applied to the actual criminal investigations will be presented.

[1] Nakai I., *X-ray spectrometry: Recent Technological Advances*, 2004, 355.

[2] Ninomiya, T., *X-ray spectrometry: Recent Technological Advances*, 2004, 553.

Keywords: synchrotron radiation applications, forensic microanalysis, X-ray fluorescence analysis

MS07 CRYSTAL CHEMISTRY OF INORGANIC AND MINERAL COMPOUNDS

Chairpersons: Wulf Depmeier, Herta Effenberger

MS07.24.1

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The Zintl-Klemm Concept Applied to Cations in Oxides. An Alternative Interpretation of the Structures of Silicates

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The structures of ternary and quaternary silicates are reinterpreted on the basis of the Zintl-Klemm concept and the Pearson's generalised octet rule. The three-dimensional skeletons formed by the Si atoms can be interpreted as if the Si atoms were behaving as Zintl polyanions, adopting the structure of either main-group elements or Zintl polyanions showing the same connectivity. An example of this behaviour is the mineral pabstite BaSn[Si₃O₉]. In this compound, the Ba and Sn atoms donate 6 e⁻ per formula unit to the three Si atoms, converting them into Ψ-S atoms, i.e. 2-connected atoms. Thus, the Si (Ψ-S) atoms adopt the structure of the triangular S₃ molecules. The O atoms are then located close to both, the hypotheticalal 2-electron bonds and the lone pairs, giving rise to a tetrahedral coordination. In some silicates, the Si atoms clearly show an amphoteric character so that some Si atoms act as donors (bases) adopting an octahedral coordination, whereas others behave as acceptors (acid), adopting a tetrahedral coordination. Although the octahedral coordination seems to be favoured by the application of pressure, the results reported here indicate that the coordination sphere of silicon is not a function of the assumed ionic radius of the Si⁴⁺ cations but it depends on the nature of the other cations accompanying them in the structure.

Keywords: silicate structures, Zintl-Klemm concept, cation arrays

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Uranyl Selenates: From Finite Clusters to Nanotubules

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Structural chemistry of uranyl selenates with over than 50 compounds first characterized by the authors is described on the basis of graph theory adapted to the description of heteropolyhedral structures [1]. Structural motifs in uranyl selenates are based upon corner-sharing UO₇ pentagonal bipyramids and SeO₄ tetrahedra. Structural diversity of these motifs range from finite clusters and chains to complex sheets and nanotubules [2, 3]. It is shown that most of the 0-D, 1-D and 2-D graphs corresponding to the uranyl selenate motifs can be considered as derivatives of highly regular {3.6.3.6} graph consisting of 3-connected white and 6-connected black vertices. Structural and geometrical isomerism induced by tetrahedra orientation and selective hydration of UO₇ polyhedra will be described. The model of nanotubule formation in uranyl selenate systems based upon the rolling of 2-D sheets is discussed. Self-assembly of organic amines governing by competitive hydrophobic/hydrophilic interactions and structure of organic/inorganic interfaces in uranyl selenates will be discussed.

[1] Krivovichev S.V., *Crystallogr. Rev.*, 2004, **10**, 185. [2] Krivovichev S.V., Kahlenberg V., Kaindl R., Mersdorf E., Tananaev I.G., Myasoedov B.F., *Angew. Chem. Int. Ed.*, 2005, **44**, 1134. [3] Krivovichev S.V., Kahlenberg V., Tananaev I.G., Kaindl R., Mersdorf E., Myasoedov B.F., *J. Amer. Chem. Soc.*, 2005, **127**, 1072.

Keywords: uranium compounds, structural motifs, nanochemistry

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Molecule-Mineral Inner-Surface Interactions in Nanoporous Silicates

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We have carried out single-crystal and powder Raman studies of zeolites, SiO₂-clathrates and other silicate structure types with small nanopores (beryl, cordierite) to investigate the nature of inner-surface molecule-crystal interactions and the role of hydrogen bonding.

Bikitaite has an H-bonded H₂O chain along [010] termed 'one-dimensional ice'. The molecules are ordered, whereby one H atom per molecule is unbonded and the other is H-bonded. With increasing temperature, the H-bonding weakens continuously until the chain 'breaks' and isolated H₂O molecules are present.

Melanophlogite has quasi-free N₂, CO₂ and CH₄ molecules, but no H₂O, which partition between the [5¹²] and [5¹²6²] cages. The molecules are orientationally disordered in the cavities and they have only weak dispersion interactions with the SiO₂-crystal framework. However, the incorporation of molecules is necessary to allow the SiO₂ framework to condense.

Cordierite and beryl contain quasi-free CO₂ molecules, as well as H₂O, in small cavities. The CO₂ molecules are orientated parallel to the crystallographic *x*-axis. The H₂O molecules have their H-H vector parallel to the *z*-axis in alkali-free crystals and are dynamically disordered about the *z*-axis. They show weak H-bonding with their frameworks.

Keywords: nanopores, H-bonding, vibrational spectroscopy

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TEM and XPS Evidences of O/F Ordering in NbO₂F

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NbO₂F is a member of a relatively small group of MO_{3-x}F_x (*M* = Nb, Ta, Ti, Mo, W) oxyfluorides with the cubic ReO₃ structure type. They have been of interest in recent years as host compounds for Li-insertion in battery electrolytes [1] and also because of a pressure-induced phase transition from cubic (*Pm3m*) to rhombohedral (*R3c*) [2]. The average structure consists of corner-sharing *M*(O,F)₆ octahedra, as in undistorted *ABO*₃ perovskite, with the *A* sites being empty. Oxyfluorides are reported to exhibit a statistical distribution of O and F, generally attributed to their similar ionic radii (1.35 and 1.285 Å, respectively). Bond-length/bond-strength calculations, however, suggest there should be a strong driving force for ordering. Evidence for one-dimensional O/F ordered columns along $\langle 001 \rangle$, but with no lateral correlation from one column to the next has already been recognized from transmission electron diffraction [4]. In the present work, coupled HRTEM and electron diffraction revealed the presence of characteristic transverse planes of diffuse intensity running through $G \pm (hk/2)^*$ regions (*i.e.* existence of O/F-ordering), and XPS confirmed the existence of two distinct atomic positions for O and F and just one for Nb. These data are consistent with three-dimensional O/F ordering within NbO₂F structure.

[1] Perm er L., Lundberg M., *J. Solid State Chem.*, 1989, **81**, 21. [2] Carlson S., et al., *Acta Cryst. B*, 2000, **56**, 189. [3] Vogt T., et al., *J. Solid State Chem.*, 1999, **144**, 228. [4] Brink F.J., et al., *J. Solid State Chem.*, 2002, **166**, 73.

Keywords: O/F ordering, electron diffraction, XPS

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Crystal Structures and Topology of New and Rare Arsenates

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The crystal chemical phenomena (e.g. polyhedral stacking variations, microtwinning etc.) which accompany the formation of real structures are considered on the basis of the results of structural study of a large group of new and rare natural arsenates (pushcharovskite, tillmannsite, zdenekite and mahnertite). The use of synchrotron radiation allowed to perform the crystal structure investigation of these four new and rare minerals and to reveal their structural peculiarities and topology.

The structure of pushcharovskite is characterized by some

structural disorder and contains heteropolyhedral sheets formed by Cu-polyhedra and As-tetrahedra and linked by hydrogen bonds.

The main peculiarity of tillmannsite structure is connected with unique tetrahedral clusters (Ag₃Hg)³⁺ revealed in this mineral in which mercury is characterized by the low-valence state.

Mahnertite and zdenekite have close chemical composition but different symmetry. These minerals contain a new type of mixed polyhedral sheets, which are characterized by the different mode of stacking.

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Keywords: arsenates, crystal structures, topology

MS08 MEMBRANE PROTEIN STRUCTURE AND FUNCTION

Chairpersons: Jacqueline M. Gulbis, Michael R. Garavito

MS08.24.1

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Does the Crystal Structure of Ammonium Transporter Tell us its Function?

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Ammonium is one of the most important nitrogen sources for bacteria, fungi and plants but it is toxic to animals. The ammonium transport proteins (Mep/Amt/Rh) are present in all domains of life, but the chemical identity of their substrate was uncertain. We have solved the structure of wild type AmtB from *E. coli* in two crystal forms at 1.8 and 2.1 Å resolution, respectively. Substrate transport occurs through a narrow, mainly hydrophobic pore located at the centre of each monomer of the trimeric AmtB. At the periplasmic entry, a binding site for NH₄⁺ is observed. Two phenylalanine side chains (F107 and F215) block access into the pore from the periplasmic side. Further into the pore, the side chains of two highly conserved histidine residues (H168 and H318) bridged by a H-bond, lie adjacent with their edges pointing into the cavity. These histidine residues may facilitate the deprotonation of an ammonium ion entering the pore. Adiabatic free energy calculations support that an electrostatic barrier between H168 and H318 hinders the permeation of cations but not that of the uncharged NH₃. The structural data and energetic considerations strongly indicate that the Mep/Amt/Rh proteins are ammonia gas channels [1]. Interestingly at the cytoplasmic exit of the pore, two different conformational states are observed which might be related to the inactivation mechanism by its regulatory partner.

[1] Zheng L., Kostrewa D., Bern eche S., Winkler F.K., Li X.D., *Proc. Natl. Acad. Sci. USA*, 2004, **101**, 17090.

Keywords: ammonia transport, conformational change, X-ray structure

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Two OMPs: Autotranslocation and LPS-Deacylation

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The outer membrane proteins (OMPs) of Gram-negative bacteria are often involved in pathogenesis. Their exposure to the extracellular environment make them potential targets for antimicrobial treatments. We present recent crystal structures of two outer membrane proteins, NalP [1] and PagL.

NalP belongs to the autotransporter family. Autotransporters secrete their own N-terminal passenger domain with their C-terminal translocator domain. The crystal structure of the translocator domain of NalP from *Neisseria meningitidis* reveals an N-terminal helix inside