

[1] <http://www.diamond.ac.uk/Home/Beamlines/MX.html>

Keywords: microbeam, macromolecular crystallography, beamline

MS37.P10

Acta Cryst. (2011) A67, C484

The new neutron single crystal diffractometer "BioDiff" for proteins at FRM II

Andreas Ostermann,^a Tobias E. Schrader,^b Michael Monkenbusch,^c Bernhard Laatsch,^d Philipp Jüttner,^a Winfried Petry,^a Dieter Richter,^{c,b} ^aForschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), Technische Universität München, D-85747 Garching. ^bForschungszentrum Jülich GmbH, Jülich Centre for Neutron Science – FRM II, D-85747 Garching. ^cForschungszentrum Jülich GmbH, Institute for Complex Systems, D-52425 Jülich. ^dForschungszentrum Jülich GmbH, Zentralabteilung Technologie, D-52425 Jülich. E-mail: Andreas.Ostermann@frm2.tum.de

Hydrogen atoms play an important role in many biological processes. Especially hydrogen atoms in polarized bonds are often involved in enzymatic catalysis. These hydrogen atoms take part in the substrate binding process and are essential for proton transfer reactions during the catalysis. Therefore the knowledge about the protonation states of amino acid residues in the active centre of proteins is crucial for the understanding of their reaction mechanisms. However, hydrogen atoms, especially rather flexible ones, are often barely detectable in X-ray structure determinations of proteins. On the other hand, hydrogen atoms are clearly visible in neutron crystallography experiments even at moderate resolutions ($d_{\min} < 2.0 \text{ \AA}$).

The new neutron single crystal diffractometer "BioDiff" has finished its final construction phase. The instrument is a joint project of the Forschungszentrum Jülich (FZJ/JCNS) and the Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II). "BioDiff" is especially designed to collect data from crystals with large unit cells. The main field of application is the structure analysis of proteins, especially the determination of hydrogen atom positions.

By using a highly orientated pyrolytic graphite monochromator the diffractometer is able to operate in the wavelength range of 2.4 Å to about 5.6 Å. Higher order wavelength contaminations are removed by a neutron velocity selector. To cover a large solid angle and thus to minimize the data collection time the main detector of "BioDiff" consists of a neutron imaging plate system in a cylindrical geometry. A Li/ZnS scintillator CCD camera is available for additional detection abilities. The main advantage of this instrument is the possibility to adapt the wavelength to the size of the unit cell of the sample crystal while operating with a clean monochromatic beam that keeps the background level low. First user operation of the instrument is anticipated to start around autumn 2011.

Keywords: neutron, diffractometer, protein

MS37.P11

Acta Cryst. (2011) A67, C484

XRD analysis of human dental tissues using synchrotron radiation

M. V. Colaco,^a R.C. Barroso,^a I.M. Porto,^c R.F. Gerlach,^d F.N. Costa,^b D. Braz,^b R. Droppa Jr.,^c ^aPhysics Institute, State University of Rio de Janeiro, Brazil, ^bNuclear Instrumentation Laboratory/COPPE, ^cDepartment of Morphology, State University of Campinas, ^dDepartment of Morphology, Stomatology and Physiology, University

of São Paulo, ^eNatural and Human Sciences Center, Federal University of the ABC Region. E-mail: mvcolaco@gmail.com

The mineral phase of human tooth enamel and dentin was identified as a calcium phosphate with an apatite structure as early as 1926 using X-ray diffraction, namely as hydroxylapatite (HAp - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). The discussions on details of the apatite and tooth problems have induced continuous studies employing new and more refined instruments in an endeavor to find specific phases and to answer specific questions on the apatite problem [1-3]. In the present work, the crystallinity and average crystallite size of enamel, dentin and circumpulpal dentin from five healthy human third molar teeth were analysed using synchrotron X-ray powder diffraction. All the measurements were carried out at D12A-XRD1 beamline in the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil. This study was approved by the Committee of Ethics in Research (FORP/USP 2003.1.1329.58.2), according to the Resolution 196/96 of the National Commission of Ethics in Research.

The powder diffraction patterns were collected over an angular range from 20° to 52° in 2θ with statistical uncertainty smaller than 2% for the scattering count. In order to allow an estimation of the wavelength and zero shift of each experiment, SRM 676a (alumina powder) reference sample was also run. The diffraction patterns were analysed using the Rietveld method, in which the structural parameters describing the dominant crystalline phase, HAp, were refined (ICSD CIF 9011092). The Rietveld refinements were carried out for the five specimens using GSAS software ($R_{\text{wp}} < 10\%$). The peak profiles were fitted with pseudo-Voigt functions and the background was described by the Chebyshev function of the first kind.

The lattice parameters were refined and the best peak shape was found to be a Lorentzian with slight asymmetry. In enamel the hexagonal lattice parameters were found $a = 9.4463(39) \text{ \AA}$ and $c = 6.8848(51) \text{ \AA}$. Atom positions and bond lengths also were refined. The average crystallite size measured by the diffracting planes was calculated using the Debye-Scherrer equation. For the enamel, the crystallite size was 28 nm. For dentin and circumpulpal dentin, the values found were 21 nm and 16 nm, respectively. These data suggest that average crystallite size increases from circumpulpal dentin to enamel.

It is well-known that the shape of the profiles of diffraction depends on the spectral contribution of X-ray source, geometric parameters of the experimental setup and the characteristics of the material microstructure (crystallite size and microstrain effects). The influence of the first two factors in the broadening of diffraction peaks could be minimized through the use of synchrotron radiation and the adoption of high-precision diffractometer. Therefore, in this work, the instrumental effects were minimized and the broadening of the peaks is predominantly due to microstructural characteristics of the dental tissues.

[1] P. Anderson, J.C. Elliott, U. Boze, S.J. Jones *Archives of Oral Biology* **1996**, *41*, 281-290. [2] R.M. Wilson, J.C. Elliott and S.E.P. Dowker *American Mineralogist* **1999**, *84*, 1406-1414. [3] M. Al-Jawada, A. Steuwer, S.H. Kilcoyne, R.C. Shore, R. Cywinski, D.J. Wood *Biomaterials*, **2007**, *28*, 2908-2914.

Keywords: tooth, diffraction, rietveld

MS37.P12

Acta Cryst. (2011) A67, C484-C485

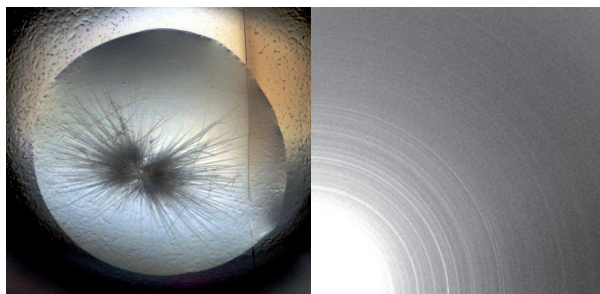
Mayaro virus non structural protein 3 macro domain, via powder diffraction on a single urchin like crystal

Yves Watier^a, Nicolas Papageorgiou,^b Coutard Bruno,^b Lantez Violaine,^b Gould Ernest A.,^b Fitch Andrew N.,^a Wright Jonathan P.,^b ; Canard Bruno,^b Margiolaki Irene,^c ^aEuropean Synchrotron Radiation Facility, ESRF, BP-220, 38043 Grenoble, FRANCE, ^bArchitecture et Fonction des Macromolécules Biologiques, CNRS and Universités

d'Aix-Marseille I et II, UMR 6098, ESIL Case 925, 13288 Marseille, FRANCE, ^c*Department of Biology, Section of Genetics, Cell Biology and Development, University of Patras, GRECE* E-mail: yves.watier@esrf.fr

Measuring on a single urchin like crystal at room temperature used to be unrealistic due to the absence of a reliable available setup. In air, the samples were dehydrated, and measuring a small amount of protein powder sample in a capillary is also difficult. Also, for fragile samples, the centrifuging of microcrystals in a capillary may be fatal for diffraction. We have seen that the design of the humidity control device available at the ESRF allowed us to collect high quality powder diffraction pattern on a PX beamline on a single urchin like crystal. The possibility to preserve small protein powder samples at room temperature without losing diffraction properties is a new step for protein powder diffraction. This allows several possibilities, first, to screen very easily and routinely crystalline precipitates in order to determine their diffraction quality, on any PX beamline; second, to get reliable intensities at low to medium resolution, suitable to solve a structure by molecular replacement; third, to build and refine a preliminary model using these extracted intensities or via a Rietveld refinement.

Data acquisition and preliminary analysis on the non structural protein 3 macro domain of the Mayaro virus will be presented, following previous studies[1] done on a larger amount of sample.



[1] Papageorgiou, N. and Watier, Y. and Saunders, L. and Coutard, B. and Lantéz, V. and Gould, E.A. and Fitch, A.N. and Wright, J.P. and Canard, B. and Margiolaki, I. Preliminary insights into the non structural protein 3 macro domain of the Mayaro virus by powder diffraction *Z. Kristallogr* **2010**, *225*, 576-580

Keywords: protein, virus, powder

MS38.P01

Acta Cryst. (2011) **A67**, C485

Solid state reactivity and solvent mobility in crystals of a cubane polymer

Elena Forcén-Vázquez,^a Javier Campo,^a Larry R. Falvello,^{a,b} Fernando Palacio,^a Milagros Tomás,^c ^a*Aragón Materials Science Institute (ICMA), CSIC, University of Zaragoza (Spain).* ^b*Department of Inorganic Chemistry, University of Zaragoza (Spain).* ^c*Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC, Universidad de Zaragoza (Spain).* E-mail: elenafv@unizar.es

Solids that accommodate small molecules in structural voids are of interest for applications as diverse as catalysis or gas storage and purification. Most systems studied to date in this area are 2- and 3-D polymers with frameworks that maintain open voids. In contrast, 1-D polymers give structures without rigidity in three dimensions, so removal of small molecules that might be present leads to the collapse of the crystal structure. Moreover, solids formed by 1-D polymers usually have a lesser amount of void space to house solvent and other small molecules.

To understand the storage of small molecules in solids, it is necessary to characterize the geometries of the pores or voids involved, and also their chemical nature. The study of solid-state reactions provides insight into both the chemical and physical natures of the substances and processes involved. [2]

Quadruply deprotonated citrate forms transition metal complexes with a topologically cubic M_4O_4 core and 12 peripheral oxygen atoms that can bind transition metals or form non-covalent interactions with interstitial small molecules. The cubane units are structural building blocks for polymers of varying dimensionality; their hydrophilic periphery confers exceptional qualities on the solids, including structural variability, water solubility and solid-state chemical reactivity. [4,5]

We have previously reported an unprecedented solid-state crosslinking in which a 1-D polymer of cobalt citrate cubanes fuses under mild conditions to produce a 2D polymer. [5] This quasi-topotactic process demonstrates the structural flexibility and solid-state reactivity typical of these compounds and suggests the possibility of studying the reaction mechanisms of the solid state transformations.

We present here a new family of non-porous 1-D and 2-D manganese citrate cubane polymers whose flexible structural natures permit the reversible desorption of water in SCSC transformations at room temperature. Both species have mobile interstitial water molecules. There are no clearly defined voids or channels for water mobility, so the structural framework must yield in order for water egress and reuptake to take place. In addition, if the dehydrated derivative of the 1-D polymer is exposed to a methanol atmosphere, one molecule of methanol substitutes an aqua ligand on a non-cubane manganese(II) unit present in the structure, through a possible associative mechanism. This reversible transformation preserves the crystallinity of the polymer. There is evidence that one more molecule of methanol enters the polymer through a physisorption process.

[1] M. García-Castro, A. Martín, M. Mena, C. Yélamos, *Organometallics* **2007**, *26*, 408-416. [2] S. Libri, M. Mahler, G. Mínguez Espallargas, D.C.N.G. Singh, J. Soleimannejad, H. Adams, M.D. Burgard, N.P. Rath, M. Brunelli, L. Brammer *Angew. Chem., Int. Ed.* **2008**, *47*, 1693-1697. [3] T.A. Hudson, K.J. Berry, B. Moubaraki, K.S. Murray, R. Robson, *Inorg. Chem.* **2006**, *45*, 3549-3556. [4] E. Burzurí, J. Campo, L.R. Falvello, E. Forcén-Vázquez, F. Luis, I. Mayoral, F. Palacio, C. Sáenz de Pipaón, M. Tomás, *Chemistry: A European Journal* **2011**, *17*, 2818-2822. [5] J. Campo, L.R. Falvello, I. Mayoral, F. Palacio, T. Soler, M. Tomas, *J. Am. Chem. Soc.* **2008**, *130*, 2932-2933.

Keywords: crystalline, polymer, chemisorption

MS38.P02

Acta Cryst. (2011) **A67**, C485-C486

Flexibility found in silica-like metal-organic frameworks

I.E. Collings,^a A.L. Goodwin,^a A.L. Thompson,^a M. Dove,^b L. Rimmer,^b ^a*Department of Inorganic Chemistry, University of Oxford, Oxford (UK).* ^b*Department of Earth Sciences, University of Cambridge, Cambridge (UK).* E-mail: ines.collings@chem.ox.ac.uk

Throughout the last decade, the study of metal-organic frameworks (MOFs) has remained one of the most topical fields in solid-state chemistry, due to the extensive and unique range of structural and functional properties they exhibit [1].

In recent years, studies on MOFs have revealed unusual mechanical properties, such as negative thermal expansion in MOF-5 [2], and amorphisation of zeolitic imidazolate frameworks at high temperature [3].

This poster will be focused on mechanical properties of some MOFs whose structures resemble those of silicate frameworks. For example, cadmium and mercury imidazolates (with a topological resemblance to α -cristobalite), have shown unusual thermal expansion