Virginia Tech Crystallography Laboratory

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2008 Annual Report

The Virginia Tech Crystallography Laboratory is a co-located facility of the Departments of Biological Sciences, Chemistry, and Geosciences, within the College of Science. The mission of VTX is three-fold:

Education – We teach crystallography courses to VT students, and we hold an annual summer crystallography workshop for faculty and students from other Universities.

Service – We provide crystallographic services (structure solution and refinement) to research groups at Virginia Tech and other universities in the region. We organize and host the Virginia Tech Structural Biology symposium.

Research - Members of VTX pursue their own research programs in crystallography and structural biology.

This year brought two major changes, together with associated challenges and opportunities, for the VT Crystallography Laboratory. In September the entire Crystallography Laboratory moved from Derring Hall in to customized laboratory space at the Integrated Life Sciences Building (shown above) on the Corporate Research Center in Blacksburg. Over the preceding year associate director Dr. Carla Slebodnick had

worked with the architects and contractors to ensure that the laboratory facilities and services in the new building were exactly what was needed. This allowed us, with the support of engineers from Oxford Diffraction to move and re-install all six diffractometers in the space of two weeks. The move locates us in the same building as many of the structural biologists at VT and provides us with the opportunity to grow the structural biology component of our operations more easily.

The move also places us immediately adjacent to the offices of our industrial partners and sponsors Oxford Diffraction, with whom we continue to develop ever-closer relations. In 2008 the company provided us with an upgrade to the Xcalibur-2 diffractometer, and we continue to work as a beta-test site for the development of their software for high-pressure work. This has the advantage for us of leveraging the productivity of their large software development team, in return for which Oxford benefit from our experience and expertise in this area of diffraction.

During the year Oxford Diffraction joined the Varian group of companies. This has provided the crystallography laboratory with a much larger group of support engineers and sales staff from Varian, and opportunities for Virginia Tech to develop similar links with the other divisions of a major instrument company. The merger has already resulted in an increase in potential customers coming to VTX. Visitors from North, Central, and South America (including Yale, U. Florida, U. Arizona, U Louisville, and Mexico, and Argentina) toured our lab and tested our instruments, helping to put Virginia Tech crystallography on the international map. In addition, in November Oxford Diffraction and VTX jointly hosted a training workshop for 12 senior and sales staff from Varian, helping to cement relations between the company and VTX.

Dr. Maureen Julian's new crystallography text book "Foundations of Crystallography with Computer Applications", which is based upon the crystallography course that she has taught in MSE for many years was published by Taylor and Francis in Spring 2008. Dr. Julian has also developed a web site to be used in association with the book, and gave three separate presentations at the international congress of the International Union of Crystallography on several aspects of her teaching methods. She continues to teach crystallography to large classes of undergraduate students in engineering, while Drs. Angel and Slebodnick teach a two-course sequence at the graduate level that is cross-listed between chemistry and geosciences. The 2008 course attracted students from the colleges of engineering and life sciences, in addition to our core departments of chemistry, geosciences and biological sciences. The sequence provides graduate students with the knowledge base and skills to be able to collect single-crystal diffraction data and to determine crystal structures that are essential for their own research projects.

The laboratory continued its regional leadership role by providing service crystallography facilities to research groups from several smaller colleges in south-west Virginia. Although the move of the laboratory to the ILSB meant that in 2008 we were only able to hold a reduced summer crystallography workshop, over the past 6 years the total number of attendees has now reached 100 participants, comprising 55 men and 45 women, of whom 8 were minority students. In addition to exposing the participants to high-tech instrumentation, the students get substantial exposure to successful female graduate

students, postdocs, and faculty, since the majority of the X-ray lab members are women. The participants are also exposed to a very international group of graduate students and postdocs who assist with the workshop--nations of origin over the past 5 years include Belgium, China, Japan, Germany, Italy, England, and Indonesia.

One of the attendees of the 2007 workshop was high-school student Laura Vogelaar who, under the guidance of Dr. Slebodnick, did her Science Fair Project on the crystal structure of chloroheme. Laura followed an extremely convoluted crystallization process to grow crystals of dimensions 0.1 x 0.02 x 0.004 mm^3 and managed to get a moderate quality structure from the data. Laura went to the 2008 International Science and Engineering Fair in Atlanta, Georgia (May 11-16) and won the "4th Award of $500" in the Biochemistry division.

Following the success of its 2006 symposium the laboratory organized and hosted the third VT Structural Biology Symposium in March 2007. The symposium attracted over 200 registrants, with the keynote lecture given by Prof. Brian Sutton, of Kings College London. Other speakers came from Virginia Tech, Virginia Commonwealth University and Wake Forest. The symposium was sponsored by Oxford Diffraction, the College of Science, the Departments of Biological Sciences, Chemistry, Geosciences and Biochemistry, as well as several biotech companies. A fourth symposium will be organized by the laboratory in March 2009.

Despite the interruption of moving the laboratory, in its service chemistry role, led by Dr. Slebodnick, literally many hundreds of crystals were screened, and about 150 datasets were collected to yield more than 40 publication quality structures in support of the research programs of lab members and Professors J. Barone (BSE), Berg, Brewer, Carlier, Deck, Dorn, Esker, Gibson, Hanson, T.E Long, Merola, Moore, Morris, Tissue and Yee (all Chemistry), V. Soghomonian (Physics), Daren Timmons (VMI), Erich Uffelman (W&L), Feihe Huang (Zhejiang U, China), Diego Gatta (U. Milan, Italy), T. Boffa-Ballaran (U Bayreuth, Germany). Papers containing the structures are listed below.

The new VT Crystallography Laboratory in 2050 ILSB

More information is available at www.crystal.vt.edu or by contacting Prof. Ross Angel, email: rangel@vt.edu.

People

Staff, students and faculty are appointed to the individual departments, and work together in the laboratory. Theresa Detrie successfully defended her MS thesis on the evolution of the mineral prehnite at high pressure, for which she received the College of Science Outstanding Master's Student award. She will be joining Schlumberger in the summer of 2009. Dr. Yonggang Yu joined the laboratory as a postdoctoral associate in the summer, and Ms. Lindsay Sochalski started as an MS student. Dr. Jinyuan Yan finished his work on the CEAD software project in February, and Dr. Jens Engel left in May to take up a position at DESY, the synchrotron in Hamburg. Our long-serving post-doc in biological sciences, Nancy Vogelaar, completed her work with the lab at the end of the year. A full list of affiliated staff and faculty follows:

Ross Angel	VTX Director, Professor of Crystallography in Geosciences
Mike Berg	Instructor in Chemistry
Phil Burcham	Technical staff, Geosciences
Theresa Detrie	Graduate student, Geosciences
Wang Di	Graduate student, Geosciences
Jens Engel	Postdoctoral associate, Geosciences
Carla Finkielstein	Assistant Professor, Biological Sciences
Liangming Hu	Graduate student, Chemistry
Maureen Julian	Adjunct Professor, Materials Science & Engineering
Hiro Motegi	Graduate student, Chemistry
Nancy Ross	Associate Dean, Professor of Mineralogy in Geosciences
Florian Schubot	Assistant Professor, Biological Sciences
Carla Slebodnick	VTX Associate Director, Instructor in Chemistry
Lindsay Sochalski	Graduate student, Geosciences
Elinor Spencer	Postdoctoral associate, Geosciences
Nancy Vogelaar	Postdoctoral associate, Biological Sciences
Jinyuan Yan	Postdoctoral associate, Geosciences
Yonggang Yu	Postdoctoral associate, Geosciences
Jing Zhao	Senior Research Associate, Geosciences

During the year the laboratory also hosted research visits by the following scientists:

Dr. Tiziana Boffa-Ballaran	Bayerisches Geoinstitut, Bayreuth, Germany
Bernd Maier	University of Hamburg, Germany
Dr. Daria Pasqual	University of Padua, Italy

Publications

[1] Angel R, Gatta G, Boffa-Ballaran T, Carpenter M (2008) The mechanism of coupling in the modulated structure of nepheline. *Canadian Mineralogist* 46:1465-1476.

[2] Bissel P, Khalil A, Rimoldi JM, Igarashi K, Edmondson D, Castagnoli N (2008) Stereochemical Studies on the Novel Monoamine Oxidase B Substrates (1*R*, 6*S*)- and (1*S*, 6*R*)-3-methyl-6-phenyl-3-aza-bicyclo[4.1.0]heptane. *Bioorganic and Medicinal Chemistry* 16:3557-3564.

[3] Chen Q-H, Ganesh T, Brodie P, Slebodnick C, Jiang Y, Banerjee A, Bane S, Snyder JP, Kingston DGI (2008) Design, synthesis and biological evaluation of bridged epothilone D analogues. *Organic and Biomolecular Chemistry* 6:4542-4552.

[4] Hollis WG, Poferl MG, Wolter MD, Deck PA, Slebodnick C (2008) Preparation of ferrocenes with high fluorous-phase affinities. *Journal of Fluorine Chemistry* 129:119-124.

[5] Hsu DC, Slebodnick C, Carlier PR (2008) Stopping the clock: X-ray characterization of an enantiopure silyl enol ether derivative of a dynamically chiral potassium enolate. *Angewandte Chemie International Edition* submitted.

[6] Hu L, Hanson BE, Slebodnick C, Spencer EC (2008) Metal-Organic hybrid Networks Constructed with the 4, 4'-bisimidazolylbiphenyl Ligand. *Inorganic Chemistry Communications* 11:1412-1416.

[7] Hu L, Slebodnick C, Gandour RD, Hanson BE (2008) The Role of 4,4'-Trimethylene-Dipyridine Flexibility in the Construction of Hybrid Networks Templated on Aromatic Alcohols. *Inorganica Chimica Acta* 361:2439-2446.

[8] Hu L, Spencer EC, Wang GB, Yee GT, Slebodnick C, Hanson BE (2008) Novel Cationic Copper Coordination Frameworks Constructed from Copper Phosphate 8-Rings and 4,4'-Bisimidazolylbiphenyl as a Bridging Ligand. *Inorganic Chemistry Communications* 11:982-984.

[9] Jain A, Slebodnick C, Winkel BSJ, Brewer KJ (2008) Enhanced DNA Photocleavage Properties of Ru(II) Terpyridine Complexes Upon Incorporation of Methylphenyl Substituted Terpyridine and/or the Polyazine Bridging Ligand dpp (2,3-bis(2-pyridyl)pyrazine). *Journal of Inorganic Biochemistry* 102:1854-1861.

[10] Jani D, Nagarkatti R, Beatty W, Angel RJ, Slebodnick C, Andersen J, Kumar S, Rathore D (2008) HDP—A Novel Heme Detoxification Protein from the Malaria Parasite. *PLoS Pathogens* 4:e1000053.

[11] Mihailova B, Angel R, Welsch A-M, Zhao J, Engel J, Paulmann C, Gospodinov M, Ashbahs H, Stosch R, Guettler B, Bismayer U (2008) Pressure-induced phase transition in $PbSc_{0.5}Ta_{0.5}O_3$ as a model Pb-based perovksite-type relaxor ferroelectric. *Physical Review Letters* 101:017602.

[12] Motegi H, Hu L, Slebodnick C, Hanson BE (2008) Synthesis and Structure of Two Novel Cobalt(II) and Zinc(II) Crystalline Coordination Networks Constructed with 1,3,5-Benzene Tricarboxylate and 9,10-Bis(imidazol-1-ylmethyl) Anthracene. *Microporous and Mesoporous Materials*, submitted:

[13] Murphy BT, Brodie P, Slebodnick C, Miller JS, Birkinshaw C, Randrianjanaka LM, Andriantsiferana R, Rasamison VE, TenDyke K, Suh EM, Kingston DGI (2008) Antiproliferative Limonoids of *Malleastrum* sp. from the Madagascar Rainforest. *Journal of Natural Products* 71:325-329.

[14] Nestola F, Curetti N, Benna P, Ivaldi G, Angel RJ, Bruno E (2008) Compressibility and high-pressure behaviour of $Ab_{63}Or_{27}An_{10}$ anorthoclase. *Canadian Mineralogist* 46:1433-1454.

[15] Nestola F, Nemeth P, Angel R, Buseck P (2008) Equation of state and crystal structure of the new germanate post-titanite phase. . *American Mineralogist* 93:1424-1428.

[16] Pederson AM-P, Vetor RC, Rouser MA, Huang FH, Slebodnick C, Schoonover DV, Gibson HW (2008) A New Functional Bis(*m*-phenylene)-32-Crown-10-Based Cryptand Host For Paraquats *Journal of Organic Chemistry* 73:5570-5573.

[17] Pederson AM-P, Ward EM, Schoonover DV, Slebodnick C, Gibson HW (2008) High-Yielding, Regiospecific Synthesis of cis(4,4 ')-Di(carbomethoxybenzo)-30-crown-10, Its Conversion to a Pyridyl Cryptand and Strong Complexation of 2,2 '- and 4,4 '-Bipyridinium Derivatives. *Journal of Organic Chemistry* 73:9094-9101.

[18] Ross NL, Spencer EC, Levchenko AA, Kolesnikov AI, Wesolowski DJ, Cole DR, mamontov E, Vlcek L (2008) Neutron Scattering Studies of Surface Water on Metal Oxide Nanoparticles. In L Liang, R Rinaldi, and H Schober (eds.), *Neutron applications in Earth, Energy, and Environmental Sciences.*, Springer-Verlag, vol.

[19] Sen S, Deck PA, Slebodnick C (2008) Structural characterization of 2,3,5,6-tetrafluoro-4-hydroxypyridine. *personal communication to Cambridge Structural Database*

[20] Shit S, Chakraborty J, Howard JAK, Spencer EC, Desplanches C, Mitra S (2008) A New Mixed Ligand Coordination Polymer of Mn(II): Structural Aspect and Cryomagnetic study. *Structural Chemistry* 19:553-558.

[21] Shu C, Slebodnick C, Xu L, Champion H, Fuhrer T, Cai T, Reid JE, Fu W, Harich K, Dorn HC, Gibson HW (2008) Highly Regioselective Derivatization of Trimetallic Nitride Templated Endohedral Metallofullerenes via a Facile Photochemical Reaction. *Journal of the American Chemical Society* 130:17755–17760.

[22] Sitepu H (2008) In situ structural and texture analyses of monoclinic phase for polycrystalline Ni-rich $Ti_{49.86}Ni_{50.14}$ alloy from neutron diffraction data. *Powder Diffraction* 23:35-40.

[23] Slebodnick C, Angel RJ, Hanson BE, Agaskar PA, Soler T, Falvello LR (2008) Disorder and Pseudo-symmetry in Octakis(trivinylsilyl)octasilicate. *Acta Crystallographica Section B: Structural Science* B64:330-337.

[24] Timmons DJ, Pacheco MR, Fricke KA, Slebodnick C (2008) Assembling Extended Structures With Flavonoids *Crystal Growth and Design* 8:2765-2769.

[25] Vanpeteghem C, Angel R, Zhao J, Ross N, Redhammer G, Seifert F (2008) The effect of oxygen vacancies and aluminium substitution on the high pressure properties of brownmillerite-structured $Ca_2Fe_{2-x}Al_xO_5$. *Physics and Chemistry of Minerals* 35:493-504.

[26] Wang GB, Slebodnick C, Yee GT (2008) Synthesis, Structure and Magnetic

Properties of a Geminal ^{2}-Tetracyanoethylene Radical Anion Bridged Coordination Polymer. *Inorganica Chimica Acta* 361:3593-3596

[27] Zhao S, Arachchige SM, Slebodnick C, Brewer KJ (2008) Synthesis and Study of the Spectroscopic and Redox Properties of Ru^{II},Pt^{II} Mixed-Metal Complexes Bridged by 2,3,5,6-Tetrakis(2-pyridyl)pyrazine. *Inorganic Chemistry* 47:6144-6152.

[28] Angel RJ, Jackson JM, Reichmann HJ, Speziale S (2009) Elasticity measurements on minerals: a review. *European Journal of Mineralogy* in press:

[29] Camara F, Nestola F, Angel RJ, Ohashi H (2009) Spontaneous strain variations through the low temperature displacive phase transition of $LiGaSi_2O_6$ clinopyroxene. *European Journal of Mineralogy* in press:

[30] Detrie TA, Ross NL, Angel RJ (2009) Crystal chemistry and location of hydrogen atoms in prehnite. *Mineralogical Magazine* in press:

[31] Detrie TA, Ross NL, Angel RJ, Gatta GD (2009) Equation of state and structure of prehnite to 9.8 GPa. *European Journal of Mineralogy* in press:

[32] Gatta GD, Cappelletti P, Rotiroti N, Slebodnick C, Rinaldi R (2009) New insights into the crystal structure and crystal-chemistry of the zeolite phillipsite. *American Mineralogist* 94:190-199.

[33] Laurent Gautron L, Daniel I, Schmidt BC, Beck P, Guignot N, Angel RJ, Gréaux S, Andrault D, Dupree R (2009) Crystal structure of the CAS phase $CaAl_4Si_2O_{11}$ up to 50 GPa and 2200 K: possible signature of pentacoordinate silicon. *Earth and Planetary Science Letters*

[34] Spencer EC, Angel RJ, Ross NL, Hanson BE, Howard JAK (2009) Pressure-induced Cooperative Bond Rearrangement in a Zinc Imidazolate Framework: A High-Pressure Single-Crystal X-ray Diffraction Study. *Journal of the American Chemical Society* in press:

[35] Spencer EC, Levchenko AA, Ross NL, Kolesnikov AI, Boerio-Goates J, Woodfield BF, Navrotsky A, Li G (2009) An Inelastic Neutron Scattering Study of Confined Surface Water on Rutile Nanoparticles. *Journal of Physical Chemistry A* in press:

[36] Wang GB, Slebodnick C, Yee GT (2009) Two Transition Metal Coordination Polymers of 7,7',8,8'-Tetracyanoquinodimethane Dianion ($TCNQ2^{-}$). *Acta Crystallographica Section C: Crystal Structure Communications* C65:m28-m32.

[37] Yu Y, Angel RJ, Wentzcovitch RM (2009) First principles study of the thermodynamics and phase transition in low-pressure ($P2_1/c$) and high-pressure ($C2/c$) clinoenstatite $MgSiO_3$. *Journal of Geophysical Research* submitted:

[38] Zhao J, Ross NL, Angel RJ, Carpenter MA, Howard CJ, Pawlak DA, Lukasiewicz (2009) High-pressure Crystallography of $PrAlO_3$ perovskite. *Journal of Physics: Condensed Matter* submitted: