PS18.03.16 HIGH PRESSURE X-RAY DIFFRACTION STUDIES OF SOME OXIDES WITH LAYERED STRUCTURES. Xu, Y., Carlson, S. & Norrestam, R., Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden

The crystal structures of the vanadium(V) and the molybdenum(VI) oxides has been investigated by single crystal X-ray diffraction techniques at pressures from 0 to < 55 kbar. The studies have been performed using MoKa radiation from a rotating anode equipment and a conventional diamond anvil cell (Diacell Products). Pressures were estimated with the ruby fluorescence method. Single crystal diffraction data have been collected at several different pressures. Preliminary refinements (giving Rvalues well below 0.10) indicate only smooth structural changes in the selected pressure range. Due to the layered structural packings, the compressibilities are anisotropic, which i.a. leads to a pressure-sensitive short V···O contact (< 2.8 Å) in V_2O_5. The experimental studies are supplemented by band orbital calculations with the extended Hückel method.

PS18.03.17 AMBIENT PRESSURE STRUCTURE OF ZrO_2-TYPE $Ca(OD)_2$ BY POWDER NEUTRON DIFFRACTION. Kurt Leinenweber[1], Dan Partin[1], Udo Schuelke[1], Mike O'Keeffe[1], and Robert B Von Dreele[2], Materials Research Group, Department of Chemistry, Arizona State University, Tempe, AZ, 85287-1604[1], The Manuel Lujan Jr. Neutron Scattering Center (MLANSCE), Los Alamos National Laboratories, Los Alamos, NM, 87545[2]

The high pressure form of $Ca(OH)_2$, isomorphous with monoclinic ZrO_2, is known from high pressure in situ powder x-ray diffraction at 8 GPa (Kunz et al., High Pressures, High Temperatures, in press). This phase is unquenchable at room temperature, reverting to the CdI_2-type polymorph at about 1 GPa during decompression.

In the present study, a 170 milligram sample of the high pressure form of $Ca(OD)_2$, synthesized at 10 GPa and 400 C, was recovered to ambient pressure for powder neutron diffraction. The back-transformation to the CdI_2 structure was suppressed by chilling the sample with liquid nitrogen during decompression. The sample was transferred to a cryostat and a neutron powder diffraction pattern taken at 11 K Platinum foil which was originally used to wrap the sample was left on as a dspacing standard.

Rietveld refinement indicates the structure $P2_1/c$, a = 5.409 Å, b = 6.104 Å, c = 5.995 Å, ß = 103.7 . Calcium is in 7-coordination with oxygen, with Ca-O distances ranging from 2.39 Å to 2.59 Å. There are, two O-D bond distances, both close to 1.00 Å. One of the D atoms is hydrogen bonded to an oxygen, with an associated O-O distance of 2.81 Å; the other appears to be nonbonded.

PS18.03.18 CRYSTAL STRUCTURE OF HIGH PRESSURE PNNH. Rosemary E. Gerald Pacalo, Kurt D. Leinenweber and Paul F. McMillan, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604

The crystal structure of a high pressure form of PNNH (phospham) has been determined from Rietveld refinement of xray diffraction data. The new phase was synthesized at 55 kbar and 750°C from an amorphous starting material and is recoverable at ambient conditions. Despite numerous attempts to grow single crystals of the high pressure phase, only polycrystalline samples were produced. High pressure PNNH is monoclinic with a=9.3984(2)Å, b=4.8188(l)Å, c=12.9713(3)Å and ß=91.855(2)°. In this setting the axes are approximately coincident with the axes of the low pressure tetragonal form, although the monoclinic a- and c-axes are nearly double the length af their tetragonal counterparts, resulting in a four-fold increase in unit xll volume. To preserve the similarity to the low pressure cell, the new phase was refined in space group B2.

Both forms of PNNH consist of $(PN_4)^{-7}$ tetrahedra that share all corners with neighboring tetrahedra in a cristobalite arrangement. Tetrahedra in the low pressure phase are reported to be regular, although half of the nitrogen atoms are also hydrogen bonded. The high pressure phase has more distorted tetrahedra, with the four P-N bond lengths differing by 4 - 10%. The hydrogen atoms have not yet been located. The relationship between the high pressure phase, the low pressure phase and the cubic aristotype, Fd3m, will be described in terms of tilting and distortion of the tetrahedra from their ideal (cubic) arrangement. Based on the similarity of xray powder diffraction patterns, the high pressure phase of PNNH appears to be an analogue of he unquenchable SiO_2 cristobalite phase observed at 12 kbar and room temperature [1, 2].

1] Yeganeh-Haeri, A., Weidner, D.J., Parise, J., Ko, J., Vaughn, M.T., Liu, X., Zhao, Y., Wang, Y. and Pacalo, R. (1990) Eos Trans. Am. Geophys. Union, 71,1671.
2] Palmer, D.C. and Finger L.W. (19g4) Amer. Mineral., 79, 1-8.

PS18.03.19 A NEW HIGH PRESSURE PHASE OF SILICA. R. Ahuja, O. Eriksson, J.M. Wills[1], and B. Johansson, Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, S-751 21, Uppsala, Sweden, [1]Center for Materials Science and Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

The search for structural phase transitions in silica (SiO_2) at elevated pressures is of special interest in earth science. This is so since SiO_2 accounts for 50% in the chondritic model of the earths composition. The abundance of silica in the Earth's composition makes the high pressure structural properties of this material especially interesting from an earth science point of view. Based on the first principles full potential linear muffin tin orbital calculations, we show that a new silica polymorph, named SBAD, becomes stable at pressures of the Earth's lowermost mantle. This structure is intermediate between the α-PbO_2 and baddeleyite structures. We find the following sequence of phase transitions; stishovite → $CaCl_2$ → SBAD → Pa3. The first transition takes place at 45 GPa, the second at 80 GPa and the third at 220 GPa. The transition at 45 GPa is in agreement with the recent experiment and calculation. So we conclude on the basis of the first principles calculations, that a structure which so far has not been considered, named SBAD, must be viewed as a strong candidate for silica in the pressure range ~ 80-220 GPa.