

MS11 O1

Nanoscopic calcium phosphates: From bone substitution to gene transfer Matthias Epple, *Inorganic Chemistry, University of Duisburg-Essen, 45117 Essen, Germany*. E-mail: matthias.epple@uni-due.de

Keywords: Calcium phosphate, biomaterials, bone

Calcium phosphates are the inorganic component of human hard tissue, i.e. of bone and teeth. Except for enamel, they occur in a nanocrystalline form in a delicate arrangement with an organic matrix, typically collagen. We have developed a continuous method to prepare bone mineral-like nanocrystalline calcium phosphate by a rapid precipitation. The internal crystallinity can be varied from nanocrystalline to X-ray amorphous and other ions can be included by addition to the crystallization mother liquor. Especially the case of carbonate is important because all biologically occurring calcium phosphates contain a few percent of carbonate in the lattice. Chemically and crystallographically, there is almost no difference between the synthetic bone mineral and natural bone mineral. After processing the nanocrystalline calcium phosphates into stable objects, they can be used as biodegradable bone substitution material in surgery.

If the nanocrystals are functionalized with biomolecules and kept in solution as a stable colloid, they can be used as nanoscopic agents to transfer such biomolecules into living cells. In the cases of DNA and siRNA, the production of specific proteins in cells can be selectively turned on and off ("transfection" and "antisense", respectively). Calcium phosphates are especially well suited for that purpose because of their high biocompatibility.

MS11 O2

Crystal chemistry of new anhydrous uranyl phosphates and uranyl arsenates. Evgeny V. Alekseev^{a,b}, Sergey V. Krivovichev^c, Wulf Depmeier^a,

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Keywords: phosphorus, arsenic, uranium, crystal structure

In the course of our ongoing research in uranium structural chemistry, 19 new uranyl phosphates and arsenates have been prepared by high temperature solid-state reactions. The structures of these compounds have been solved by direct methods. The following compositions were obtained: Li[(UO₂)(PO₄)] (1), Li₂[(UO₂)₃(P₂O₇)₂] (2), Li₆[(UO₂)₁₂(PO₄)₈(P₄O₁₃)] (3), Li[(UO₂)(AsO₄)] (4), Li[(UO₂)₄(AsO₄)₃] (5), Li₅[(UO₂)₁₃(AsO₄)₉(As₂O₇)] (6), Na[(UO₂)₂(P₃O₁₀)] (7), Na₆[(UO₂)₃(AsO₄)₄] (8), Na₆[(UO₂)₂(AsO₄)₂(As₂O₇)] (9), α-K[(UO₂)(P₃O₉)] (10), β-K[(UO₂)(P₃O₉)] (11), K[(UO₂)₂(P₃O₁₀)] (12), K₂[(UO₂)₃(As₂O₇)₂] (13), K₂[(UO₂)(As₂O₇)] (14), Rb₂[(UO₂)₃(P₂O₇)(P₄O₁₂)] (15), Rb₂[(UO₂)(As₂O₇)] (16), Rb[(UO₂)₂(As₃O₁₀)] (17), Cs₂[(UO₂)(As₂O₇)] (18), Cs₂[(UO₂)₃(As₂O₇)₂] (19). All these compounds are based upon uranyl linear groups UO₂²⁺ and TO₄ tetrahedra (T = P, As). The compounds 1, 4, 5, and 8 contain isolated TO₄ tetrahedra; together with uranyl polyhedra, they form 3-D frameworks in 1, 4, and 5 and 2-D sheets in 8. The

compounds 2, 13, 14, 16, 18, and 19 contain [T₂O₇] double tetrahedra: compounds 2, 13 and 19 have framework structures, whereas all other compounds crystallize in the melilite structure type and are based upon 2-D units. The compounds 7, 12, and 17 belong to the same structure type and have framework structures based upon [T₃O₁₀] linear trimers. The structures of α- and β-K[(UO₂)(P₃O₉)] (10, 11) consist of infinite [PO₃]_∞ chains and are based upon complex uranyl phosphate frameworks. Crystal structures of 3, 5, 6, 9, and 15 contain different types of tetrahedral anions. The compounds 3 and 6 have framework structures consisting of isolated [TO₄] tetrahedra and either linear tetramers [T₄O₁₃] (3) or double [T₂O₇] tetrahedra (6). The structure of 9 is based upon heteropolyhedral sheets consisting of [AsO₄] tetrahedra and [As₂O₇] dimers. The phase 15 has a framework structure consisting of [P₂O₇] dimers and 4-membered rings [P₄O₁₂]. In the structures of 5 and 6, uranyl cations interact with each other, a rather rare behaviour for uranium compounds.

MS11 O3

Crystal chemical puzzles: distribution of cations inside anionic packing Olga V. Yakubovich^a, Werner Massa^b, ^a*Department of Geology, Moscow State Lomonosov University, Russia.* ^b*Department of Chemistry, Philipp-University of Marburg, Germany.*

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Keywords: phosphates, structure topology, atom packing

The ability of different compounds to crystallize in one structure type is well known in crystal chemistry. This phenomenon is widely spread in nature, from the simplest structures (halite NaCl – periclase MgO – galena PbS) to more complicated ones in minerals stilwellite CeBSiO₅ – rhabdophane CePO₄H₂O, to name a few. Solid state phases isotypic to minerals can often be prepared in laboratory: in different chemical compositions, but in systems that can potentially be encountered in the earth crust. Some examples of crystal structure interconnections between synthetic phosphates and natural compounds from different mineral classes will be discussed here.

A product of hydrothermal synthesis, Na_{2-x}Zn_xFe₃(OH)₂._xO_x[PO₄]₂ has a natural analogue – the mineral seamanite Mn₃(OH)₂[B(OH)₄][PO₄]. Both structures contain triplets of face sharing transition metal octahedra; the function of tetrahedral borate oxocomplexes in seamanite is played by PO₄ groups in phosphate. The main difference between the two structures based on identical anionic subcells lies in the degree of cation packing: a microporous character of seamanite structure changes in the phosphate analogues because of interstitial Na/Zn atoms.

Two fluoride phosphates K₂Fe²⁺₂F₂[P₂O₇] and K₂Mn²⁺₂F₂[P₂O₇] grown in hydrothermal conditions are isotypic to minerals melanotekite Pb₂Fe³⁺₂O₂[Si₂O₇] and kentrolite Pb₂Mn³⁺₂O₂[Si₂O₇], and also to synthetic germinate Pb₂Fe³⁺₂O₂[Ge₂O₇]. Anionic Kagomé nets in all these structures are distorted in accordance with the types of cations centering the hexagons. The phosphates and the silicates (germinate) differ by the distribution of large cations: the splitting of lead's position due to a stereoactive lone pair of Pb²⁺ ions corresponds to the unsplit K position.

Two synthetic phases $\text{Li}_4\text{Ni}_2\text{F}_2[\text{PO}_4]_2$ and $\text{Li}_5\text{Fe}^{3+}\text{F}_2[\text{PO}_4]_2$ crystallize in the structure type found in mineral grandierite $\text{MgAl}_3\text{O}_2[\text{SiO}_4][\text{BO}_3]$. Topologically identical three anionic subcells differ in case of grandierite because of an ordered vacancy in the position of one O, bringing forward a triangular configuration of the borate group. The way of cations' distribution in the voids of anionic packing leads to a dense 3D framework ordered in the Ni variety. In the Fe phosphate, four of five "metallic" positions have isomorphous or vacancy defects and all of them contain Li^+ cations. Very high degree of structure deflection with Li atoms in all possible positions allow to predict ionic-conductive properties for the $\text{Li}_5\text{Fe}^{3+}\text{F}_2[\text{PO}_4]_2$. The second ordered vacancy also takes place in the grandierite structure. It corresponds to a Li octahedron fully populated in the Ni phase, stabilized by holes in the Fe variety and empty in the grandierite.

Topologically identical units of Ti octahedral sharing vertices with six tetrahedra $\{\text{TiT}_6\text{O}_{24}\}$ which form synthetic $\text{Cs}_2\{\text{Ti}(\text{VO}_2)_3[\text{PO}_4]_3\}$ phase ($T = \text{P}$) are the essential fragments of the framework in mineral benitoit $\text{BaTiSi}_3\text{O}_9$ with $T = \text{Si}$. Three-membered rings of tetrahedra in the benitoit structure are interrupted by hexagonal rings of V polyhedra in synthetic compound changing its tetrahedral motive from circular (as in benitoit) to "ortho".

Several other cases of microporous synthetic phosphates and their mineral analogues will be shown.

MS11 O4

Pressure-induced phase transitions in phosphate-like α -quartz-type solid solutions J. Haines^a, O. Cambon^a, R. Le Parc^b, C. Levelut^b, A. S. Pereira,^c ^aInstitut Charles Gerhardt Montpellier UMR 5253 CNRS-UM2-ENSCM-UMI, Equipe PMOF, Université Montpellier II, Montpellier, France., ^bLaboratoire des Colloïdes, Verres et Nanomatériaux, UMR CNRS 5587, Université Montpellier II, Montpellier, France., ^cInstituto de Física and Escola de Engenharia, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS, Brazil.

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Keywords: phosphates, disorder, high pressure

The high-pressure stability of α -quartz-type materials is of considerable interest for materials (piezoelectrics etc.) and Earth science. Representative compositions of two phosphorus-containing, α -quartz type, solid solutions SiO_2 -PON and AlPO_4 - GaPO_4 were studied at high pressure by x-ray diffraction. These materials exhibit distinct high pressure behavior as α -quartz-type $\text{Si}_{0.56}\text{P}_{0.44}\text{O}_{1.56}\text{N}_{0.44}$ was found to undergo gradual amorphization above 23 GPa, whereas $\text{Al}_{0.30}\text{Ga}_{0.70}\text{PO}_4$ transforms to a poorly-crystallized phase above 12 GPa. This difference in behavior can be linked to the initial degree of positional disorder, particularly on the site occupied by phosphorus, in the two solid solutions. Amorphization is favored in the highly disordered SiO_2 -PON system, in which positional disorder is present on all cation and anion sites. In contrast, disorder affects only 1/2 of the cation sites in the AlPO_4 - GaPO_4 system, those

occupied by Al and Ga, whereas the phosphorus site is ordered. A high degree of disorder on the site occupied by phosphorus favors amorphous forms as it inhibits the formation of ordered phases with increased cation coordination due to the relative stability of PO_4 and PO_4 . $x\text{N}_x$ tetrahedra in the pressure range investigated at ambient temperature. In such cases, an increase in coordination number at random sites (Si positions, for example) in the disordered cation sublattice will further enhance the process of amorphization.

MS11 O5

The structural complexity of phosphates in the Na-Fe(II)-Fe(III) (+ PO_4) system Frédéric Haterf^a

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Keywords: Na-Fe-phosphates, new crystal structures

The alluaudite group of minerals consists of Na-Mn-Fe-bearing phosphates which are known to occur in Li-rich granitic pegmatites. Due to their flexible crystal structure, which is able to accommodate Fe(II) and Fe(III) in variable amounts, alluaudites are very stable and crystallize from the first stages of pegmatite evolution to the latest oxidation processes. In order to assess the geothermometric potential of alluaudite-type phosphates, we performed systematic hydrothermal experiments in the Na-Fe(II)-Fe(III) (+ PO_4) ternary system, between 400 and 700°C, at 1 kbar. Oxygen fugacity was not buffered, and gold capsules (2 mm diameter, 25 mm length) were used in order to keep the initial Fe(II)/Fe(III) ratio constant.

Alluaudite-type phosphates were observed between 400 and 700°C, and occupy the central part of the Na-Fe(II)-Fe(III) diagram. In the Na-poor part of the diagram occur other well known Fe-phosphates, as for example $\text{Fe}_3(\text{PO}_4)_2$ (sarcopsidite), $\text{Fe}^{3+}_4\text{Fe}^{2+}_3(\text{PO}_4)_6$, or $\text{Fe}^{3+}_4(\text{PO}_4)_3(\text{OH})_3$.

The hydrothermal experiments also produced three phosphates which show new exciting crystal structures. They are localized in the Na-rich part of the diagram and were investigated by single-crystal X-ray techniques. The crystal structure of $\text{Na}_3\text{Fe}(\text{PO}_4)_2$ ($P-1$, $a = 5.3141(6)$, $b = 8.5853(9)$, $c = 8.7859(8)$ Å, $\alpha = 114.429(9)$, $\beta = 92.327(9)$, $\gamma = 106.08(1)^\circ$, $R_1 = 0.028$) is based on heteropolyhedral chains running along [100], and formed by Fe1 octahedra linked via corner-sharing to P1 tetrahedra. Sodium atoms (Na-O = 2.222-2.94 Å) occur between the chains, and show topologies of weakly distorted octahedra (Na2, Na4), of distorted pentagonal bipyramid (Na1), and of hexagonal bipyramid (Na3/Na3*).

$\text{Na}_4\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ ($R3$, $a = 8.9543(9)$, $c = 21.280(4)$ Å, $R_1 = 0.035$) shows a structure based on trimers formed by one Na2 octahedron, sharing one face with the Fe4 octahedron and one edge with the Fe1 octahedron. The trimers are connected together via edge-sharing P1 tetrahedra, to form chains which are running along the c axis.

The crystal structure of $\text{Na}_2\text{Fe}^{3+}(\text{HPO}_4)_2(\text{OH})$ has been solved in the $I2/m$ space group ($a = 14.605(4)$, $b = 7.144(2)$, $c = 15.490(4)$ Å, $\beta = 90.06(2)^\circ$), up to $R_1 = 0.053$.