

**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<sup>a,b</sup>, Sergey V. Krivovichev<sup>c</sup>, Wulf Depmeier<sup>a</sup>,

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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[(UO<sub>2</sub>)(PO<sub>4</sub>)] (1), Li<sub>2</sub>[(UO<sub>2</sub>)<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>] (2), Li<sub>6</sub>[(UO<sub>2</sub>)<sub>12</sub>(PO<sub>4</sub>)<sub>8</sub>(P<sub>4</sub>O<sub>13</sub>)] (3), Li[(UO<sub>2</sub>)(AsO<sub>4</sub>)] (4), Li[(UO<sub>2</sub>)<sub>4</sub>(AsO<sub>4</sub>)<sub>3</sub>] (5), Li<sub>5</sub>[(UO<sub>2</sub>)<sub>13</sub>(AsO<sub>4</sub>)<sub>9</sub>(As<sub>2</sub>O<sub>7</sub>)] (6), Na[(UO<sub>2</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>)] (7), Na<sub>6</sub>[(UO<sub>2</sub>)<sub>3</sub>(AsO<sub>4</sub>)<sub>4</sub>] (8), Na<sub>6</sub>[(UO<sub>2</sub>)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>(As<sub>2</sub>O<sub>7</sub>)] (9), α-K[(UO<sub>2</sub>)(P<sub>3</sub>O<sub>9</sub>)] (10), β-K[(UO<sub>2</sub>)(P<sub>3</sub>O<sub>9</sub>)] (11), K[(UO<sub>2</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>)] (12), K<sub>2</sub>[(UO<sub>2</sub>)<sub>3</sub>(As<sub>2</sub>O<sub>7</sub>)<sub>2</sub>] (13), K<sub>2</sub>[(UO<sub>2</sub>)(As<sub>2</sub>O<sub>7</sub>)] (14), Rb<sub>2</sub>[(UO<sub>2</sub>)<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)(P<sub>4</sub>O<sub>12</sub>)] (15), Rb<sub>2</sub>[(UO<sub>2</sub>)(As<sub>2</sub>O<sub>7</sub>)] (16), Rb[(UO<sub>2</sub>)<sub>2</sub>(As<sub>3</sub>O<sub>10</sub>)] (17), Cs<sub>2</sub>[(UO<sub>2</sub>)(As<sub>2</sub>O<sub>7</sub>)] (18), Cs<sub>2</sub>[(UO<sub>2</sub>)<sub>3</sub>(As<sub>2</sub>O<sub>7</sub>)<sub>2</sub>] (19). All these compounds are based upon uranyl linear groups UO<sub>2</sub><sup>2+</sup> and TO<sub>4</sub> tetrahedra (T = P, As). The compounds 1, 4, 5, and 8 contain isolated TO<sub>4</sub> 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 [T<sub>2</sub>O<sub>7</sub>] 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 [T<sub>3</sub>O<sub>10</sub>] linear trimers. The structures of α- and β-K[(UO<sub>2</sub>)(P<sub>3</sub>O<sub>9</sub>)] (10, 11) consist of infinite [PO<sub>3</sub>]<sub>∞</sub> 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 [TO<sub>4</sub>] tetrahedra and either linear tetramers [T<sub>4</sub>O<sub>13</sub>] (3) or double [T<sub>2</sub>O<sub>7</sub>] tetrahedra (6). The structure of 9 is based upon heteropolyhedral sheets consisting of [AsO<sub>4</sub>] tetrahedra and [As<sub>2</sub>O<sub>7</sub>] dimers. The phase 15 has a framework structure consisting of [P<sub>2</sub>O<sub>7</sub>] dimers and 4-membered rings [P<sub>4</sub>O<sub>12</sub>]. 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<sup>a</sup>, Werner Massa<sup>b</sup>, <sup>a</sup>*Department of Geology, Moscow State Lomonosov University, Russia.* <sup>b</sup>*Department of Chemistry, Philipp-University of Marburg, Germany.*

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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 CeBSiO<sub>5</sub> – rhabdophane CePO<sub>4</sub>·H<sub>2</sub>O, 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<sub>2-x</sub>Zn<sub>x</sub>Fe<sub>3</sub>(OH)<sub>2</sub>·xO<sub>x</sub>[PO<sub>4</sub>]<sub>2</sub> has a natural analogue – the mineral seamanite Mn<sub>3</sub>(OH)<sub>2</sub>[B(OH)<sub>4</sub>][PO<sub>4</sub>]. Both structures contain triplets of face sharing transition metal octahedra; the function of tetrahedral borate oxocomplexes in seamanite is played by PO<sub>4</sub> 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 K<sub>2</sub>Fe<sup>2+</sup><sub>2</sub>F<sub>2</sub>[P<sub>2</sub>O<sub>7</sub>] and K<sub>2</sub>Mn<sup>2+</sup><sub>2</sub>F<sub>2</sub>[P<sub>2</sub>O<sub>7</sub>] grown in hydrothermal conditions are isotypic to minerals melanotekite Pb<sub>2</sub>Fe<sup>3+</sup><sub>2</sub>O<sub>2</sub>[Si<sub>2</sub>O<sub>7</sub>] and kentrolite Pb<sub>2</sub>Mn<sup>3+</sup><sub>2</sub>O<sub>2</sub>[Si<sub>2</sub>O<sub>7</sub>], and also to synthetic germinate Pb<sub>2</sub>Fe<sup>3+</sup><sub>2</sub>O<sub>2</sub>[Ge<sub>2</sub>O<sub>7</sub>]. 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 Pb<sup>2+</sup> ions corresponds to the unsplit K position.