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The actinide borates: Inside into nuclear waste storage and new materials for anionic exchange.

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The methods of nuclear fuel vitrification in borate or boroaluminate glasses are very common in nuclear industry. The glasses contain actinides and the products of their decay. For a long time this type of storage of very dangerous components has been described as very safe because of the high kinetic and chemical stability of the borate glasses. Recently, we have found a very easy and efficient method of synthesis of actinide borates. Using a H_3BO_3 flux, we have synthesized several actinyl borates (24 uranyl borates, 4 neptunyl borates, 1 plutonyl and 1 thorium borate). These phases were characterized by X-ray diffraction, spectroscopic and other methods. Several synthesized phases possess unique structural properties, both in actinide chemistry and in chemistry in general. For example, in the structure of Np-borates we have found three different oxidation states (+4, +5 and +6) and three different coordination polyhedra of Np (coordination numbers 6, 7 and 8). The thorium borate (NDTB-1) has a unique supertetrahedral cationic framework with large open channels and pores. This structure allows fast anionic exchange of MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$. The most important particularity of NDTB-1 is that it exchanges TcO_4^-. The results are very promising as NDTB-1 removed 72% of Tc from solution in 36 hours. Many of synthesized uranyl borates are non-centrosymmetric and demonstrated non-linear optical properties. Our results have demonstrated that oxo-borates can easily react with actinides under formation of crystalline products. Unfortunately, within the glass-blocks containing radioactive wastes potential crystallization would mechanically weaken the glass matrix and make it susceptible to possible leaching by water and ensuing release of dangerous species in the environment. Thus, it seems that our results may initiate reconsideration of the whole vitrification process of radioactive waste

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Topological aspects of Cu^{2+}—O networks.

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About 750 minerals (and much more synthetic compounds) contain Cu atoms; roughly half of them are divalent Cu^{2+} ions coordinated by any ligand L like oxygen and/or halogenide atoms. Despite these impressing figures only very few structure types are known exhibiting a substitution of the Cu^{2+} atoms by other cations; $Cu^{2+}L_6$ coordination figures are well known being extremely strong distorted due to the Jahn-Teller effect. The distortion of the $Cu^{2+}L_6$ polyhedron is stronger as compared to most other ions where the effect is predicted. As a consequence, the coordination figure is better described as tetragonal bipyramidal [4+2] or even tetragonal pyramidal [4+1] or square planar [4] rather than (distorted) octahedral. This is supported by common bond-valence calculations, experimentally determined parameters are given *e.g.* by [1]. The four short Cu^{2+}—O bond lengths scatter roughly around 1.97 Å going along with bond strengths ν of 0.48 valence units (*v.u.*). Consequently, more than 90 % of the formal charge of the Cu^{2+} atom is balanced by its four nearest ligands. Additional oxygen ligands are usually in a distance above 2.30 Å (0.19 *v.u.*); only a few exceptions are known. The arrangement of the additional ligands is a consequence of the O—O repulsion, space requirement of the Cu^{2+} ion, and the connection to other cations. The upper limit is not always clear. A Cu—O distance of 2.60 Å (0.08 *v.u.*) reduces the contribution to the charge balance of the Cu^{2+} atom to 4 % only and should be responsible for a very weak bond with predominantly electrostatic interactions.

There is no doubt that for compounds containing Cu^{2+} cations the topological comparison of the connection of CuO_6 polyhedra gives some insight in the structure type. However, structural details are controlled by the orientation of short and long Cu—O bonds. This is shown by a comparison of compounds related to the structure type of brucite, $Mg(OH)_2$, where layers are formed by $M^{2+}O_6$ octahedra sharing each six edges. They can be described as two sheets of O atoms forming a close-packed arrangement with the octahedrally co-ordinated positions occupied by cations. The layers are interconnected by hydrogen bonds. In compounds where the M sites are substituted by Cu^{2+} atoms, the orientation of the short and long Cu—O bonds modify this parental structure by moderate shifts of the O atoms. Vacant M sites occur frequently. Instead, the layers are decorated by (protonated) anion groups; their connection is controlled by the orientation of the axes of the tetragonal bipyramids $Cu^{[4+2]}O_6$. In $KCu_3(OH)_2[(AsO_4)H(AsO_4)]$ one of the Cu^{2+} atoms is in a very rare [2+4] coordination which obviously is stabilized by the close-packed oxygen sheets [2].

The bond-valence parameters available form literature and commonly used (e.g. [1]) are sometimes misleading for Cu^{2+} atoms. In some $Cu^{2+[4+1]}L_5$ and $Cu^{2+[4+2]}L_6$ polyhedra with exceptional short additional Cu—O distances as well as in the rare trigonal bipyramidal [5] coordination the Cu^{2+} atom often is formally over-bonded. As for many other cations, the simplified formula $ν_{ij} = \exp[(R_{ij}-d_{ij})/0.37]$ does not describe the bonding character for Cu^{2+} cations always sufficiently.

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The response of frameworks to *P* and *T*: Of tilts and tetrahedra in feldspars.

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The complex and often non-linear structural response of framework structures to changes in pressure, temperature, and especially composition (e.g. the plateau effect), is due to the delicate balance of forces between the framework components of strongly-bonded polyhedra and the interactions between the framework and extra-framework species. For example, we have previously shown [1] that whether the tilts of the octahedra in perovskites increase or decrease with increasing pressure depends on the relative strength of the bonding between the framework and the extra-framework cation compared to the strength of the cation-oxygen bonds within the octahedra.

Feldspars are far more structurally complex than perovskites and have previously resisted the challenge of quantifying their behaviour in this way. However, Megaw (1974) showed [2] that the rigid-unit deformations of the tetrahedral framework of feldspars can be decomposed in to four tilts of the four tetrahedra that comprise the 4-rings that lie parallel to (010). Of these four tilts Megaw showed that only two, an outward tilt of the T2 tetrahedra and a wrinkle of the 4-ring, change significantly between different alkali feldspars. Analysis of the high-pressure and high-temperature data now available, from both experiment and DFT calculations, confirms that these are the dominant tilt mechanisms. In particular, we have found that changes in the wrinkle tilt are responsible for changes in the length of the feldspar crankshaft, and are thus responsible for 70% of the volume change of alkali feldspars with P, T, or composition.

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A Whole New Family of Perovskite Based Structures.

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A family of new complex oxides has been discovered, with structures that are perovskite based, but unlike any known perovskite based structure. [1 - 6] The family is created by introducing periodic crystallographic shear planes, which was previously considered as impossible in perovskites because of the presence of the A cations (in contrast to ReO_3 type structures with vacant A positions). However, when using A cations with a lone electron pair, crystallographic shear planes can effectively be established, slicing the perovskite structure into blocks separated by a periodic interfaces. Along these interfaces the corner-sharing of the metal-oxygen polyhedra is replaced by edge-sharing and tunnels are created, where the A cations and their lone pairs reside. The structures demonstrate enormous flexibility with respect to variations of the cation and oxygen content due to the controllable variable orientation of the shear planes. The common structural characteristics, variety of the chemical compositions and underlying driving forces will be explained.

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Mineralogical Adventures of a Powder Diffractionist.

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Since the saga surrounding jadarite/kryptonite a few years ago [1], a number of weird, wonderful and often very rare minerals have found their way onto our newest powder diffractometer at NRC. Advances in both instrumentation and software for laboratory diffractometers make some older fine-grained minerals worth another look as well as new ones. Our CuKα capillary setup with a focussing primary mirror and PSD detector isn't suited to all mineral compositions but there are many that are amenable to this particular configuration.

Three of the samples were from the Francon Quarry in Montreal, Quebec; strontiodresserite [2], montroyalite and a fluorine-modified gibbsite. Data have also been collected from some Australian minerals, including angastonite [3], stichtite [4], woodallite, and widgiemoolthalite. Although stichtite and woodallite were available in significant quantities, many of these minerals were only available in very small samples and are still very challenging even for capillary geometry. Data were successfully collected from all of the samples, and analyses attempted to extract any new structural information. In one case this was a full *ab-initio* crystal