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Comment on “Fluorine in Shark Teeth: Its Direct Atomic-Resolution Imaging and Strengthening Function

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Fluorine in Shark Teeth: Its Direct Atomic-Resolution Imaging and Strengthening Function

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In the article “Fluorine in Shark Teeth: Its Direct Atomic-Resolution Imaging and Strengthening Function” the authors claim by ab initio DFT calculations that "fluorine atoms can be covalently bound to the surrounding calcium atoms, ..." and that this Ca–F bond is weakest in teeth and therefore is responsible for tooth decay. The authors state that this is interesting in the view of the high electronegativity of F and the fact that the Ca–F bonding in CaF₂ is ionic: "The presence of covalency in the Ca–F bonds suggest that F is critical to stabilizing the hexagonal frames, namely the loss of F to form the c-empty Ca₅(PO₄)₃ weakens teeth".

Fluorine is the most electronegative element which reacts with nearly all other elements and forms the most ionic bonds. The fluoride ion is the smallest (ionic radius for coordination number (CN) 2 1.285 Å, 1.320 Å (CN 6).) and most rigid ion. Its polarizability is, for example, four times lower than that of oxygen.

The authors state that "The fluorine should be of paramount importance in stabilizing fluoroapatite, because its loss would directly lead to c-empty defective metastable apatite Ca₅(PO₄)₃". However, the cited reference 33 does not offer any solid evidence for the metastability of such defective structure, providing only a converged structural optimization and a density-of-states plot showing the hypothetical neutral Ca₅(PO₄)₃ to be a metal. It seems that the authors have missed that Ca₅(PO₄)₃ will be either a compound containing Ca in oxidation state +1 or a positively charged compound [Ca₅(PO₄)₃]⁺. Both are highly unlikely to exist and of course [Ca₅(PO₄)₃] may not be called “apatite” as an anion is missing in the structure. Apatites have the general formula Ca₅(PO₄)₃X, with X being F⁻, Cl⁻, OH⁻, (OH⁻, F⁻). Furthermore phosphate anions may also be substituted by carbonate and hydroxide ions, and Ca cations can be replaced by alkali and other alkaline earth metals.

The authors state that they modeled the fluorapatite by a periodic supercell with size of 16.41 x 18.95 x 6.96 Å. It is not clear why they used a supercell instead of the primitive cell and why their structural model so clearly breaks the hexagonal symmetry of fluorapatite (a = b).

Based on the charge density isosurface plots, the authors report a "charge connection between F and Ca atoms from the strong hybridization of Ca pd orbitals with F p orbitals". However, such "charge connections" can be obtained for practically every compound by tuning the charge density isovalue and such features are not a proof of covalent bonding. The authors do not state the isovalue they used for their pictures, but using a density isovalue of 0.03 a.u., identical "charge connections" can be seen in the total charge density plots of Ca₅(PO₄)₃F and CaF₂. Since CaF₂ is definitely ionic, the charge density and charge density difference data in the paper do not support the claim that there are covalent Ca–F bonds in fluorapatite.

A population analysis carried out in a previous computational study has shown that the Ca–F
bonding in Ca$_5$(PO$_4$)$_3$F is clearly ionic (Phys. Rev. B 2004, 70, 155104). Carrying out similar population analysis for CaF$_2$ reveals that the Ca/F partial charges and Ca–F overlap populations in Ca$_5$(PO$_4$)$_3$F and CaF$_2$ are practically identical, implying a very similar bonding scenario in both compounds. The overlap populations of the actually covalent P–O bonds are clearly larger.

As F$^-$ is similar in size to OH$^-$ and is isoelectronic, it may substitute OH$^-$ ions of the hydroxylapatite Ca$_5$(PO$_4$)$_3$(OH). So, is it possible, that the teeth strengthening function of fluoride is due to its low basicity and the covalency is irrelevant? The pK$_B$ of F$^-$ is only 10.83 in aqueous media – however the pK$_B$ of OH$^-$ is 0, so protonation by acids is definitely less for F$^-$. In summary, the computational results of Wang and coworkers do not support the claim that Ca–F bonding in Ca$_5$(PO$_4$)$_3$F is covalent and thus it may not be held responsible for tooth strengthening or decay.

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