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

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charge density · chemical bonding ·
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In the article „Fluorine in Shark Teeth: Its Direct Atomic-Resolution Imaging and Strengthening Function“[1] 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 CaF_2 is ionic by saying: „*The presence of covalency in the Ca–F bonds suggests that F is critical to stabilizing the hexagonal frames, namely, the loss of F to form the* c*-empty* $Ca_5(PO_4)_3$ *weakens teeth*“.

We show that the computational results of Wang and co-workers do not support the claim that Ca–F bonding in $Ca_5(PO_4)_3F$ is covalent and thus it may not be held responsible for tooth strengthening or decay. Consequently, one of the main results of the paper, which is the covalency of the Ca–F bond and its strengthening function (see title) cannot be maintained.

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 1.285 Å for coordination number (CN) 2, and 1.320 Å for 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* $Ca_5(PO_4)_3$“. 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 $Ca_5(PO_4)_3$ to be a metal. It seems that the authors have overlooked that $Ca_5(PO_4)_3$ will be either a compound containing Ca in oxidation state +1 or a positively charged compound $[Ca_5(PO_4)_3]^+$. Both are highly unlikely to exist and of course $[Ca_5(PO_4)_3]$ may not be called „apatite“ as an anion is missing in the structure. Apatites have the general formula $Ca_5(PO_4)_3X$, 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 × 18.95 × 6.96 Å. It is not clear why they used a non-hexagonal supercell instead of the primitive hexagonal cell of fluorapatite.

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 isovalue of the charge density isosurface plot and such features are not a proof of covalent bonding. The authors do not state the isovalue they used in their Figure 4 b, but using an isovalue of 0.03 a.u., identical „charge connections“ can be seen in the total charge density plots of $Ca_5(PO_4)_3F$ and CaF_2 (Figure 1, calculations carried out using the CRYSTAL14 program package and DFT-PBE0/LCAO-SVP level of theory).[2] Since CaF_2 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. Figure 1 also illustrates how the Ca–F „charge connections“ in both $Ca_5(PO_4)_3F$ and CaF_2 disappear when the isovalue is slightly increased from 0.03 a.u. to 0.04 a.u., while the charge density isosurface along the covalent P–O bonds is practically unaffected by changes at such low isodensity values. The spherical charge distribution around the F atoms points to the ionic nature of the Ca–F bonding and the minor polarization towards the surrounding Ca atoms, observed in both CaF_2 and $Ca_5(PO_4)_3F$, does not imply covalent bonding.

A population analysis carried out in a previous computational study has shown that the Ca–F bonding in $Ca_5(PO_4)_3F$ is clearly ionic.[3] Carrying out a similar population analysis for both CaF_2 and $Ca_5(PO_4)_3F$ reveals that the Ca/F partial charges and Ca–F bond overlap populations in CaF_2 and $Ca_5(PO_4)_3F$ are practically identical, implying a very similar,

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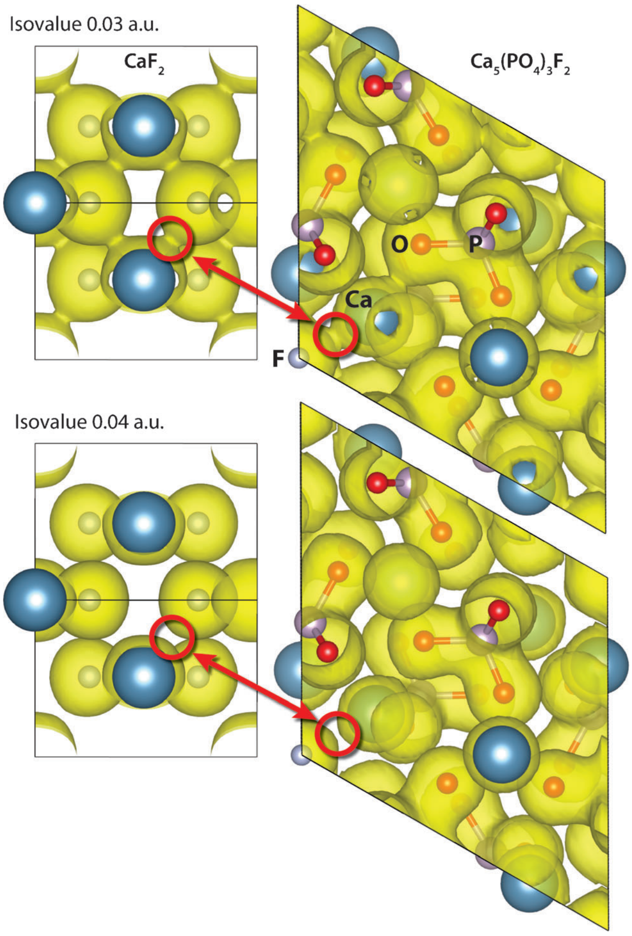

Figure 1. Charge density isosurface plots for CaF_2 and $Ca_5(PO_4)_3F$ for two different isovalues. The charge density between the F and Ca atoms is highlighted by red circles.

ionic Ca–F bonding scenario in both compounds. The partial charges and bond overlap populations obtained from the Mulliken population analysis should be considered qualitative, but the results highlight the similarity of Ca–F bonding in the both compounds: The Ca partial charges in CaF_2 and $Ca_5(PO_4)_3F$ are $+1.28$ and $+1.33$ e^-, respectively, while the partial charge of the F atoms is -0.64 e^- for both structures. The Ca–F bond overlap populations of CaF_2 and $Ca_5(PO_4)_3F$ are only 0.054 and 0.068 e^-, respectively. For comparison, the overlap populations of the covalent P–O bonds present in $Ca_5(PO_4)_3F$ are clearly larger (0.37–0.40 e^-).

As F^- is similar in size and isoelectronic to OH^-, it may substitute OH^- ions of the hydroxylapatite $Ca_5(PO_4)_3(OH)$ to form $Ca_5(PO_4)_3(OH,F)$ and finally $Ca_5(PO_4)_3F$ (e.g. in shark or rat teeth). Could it be possible that the teeth strengthening function of fluoride is due to its low basicity and the „covalent“ Ca–F bond is irrelevant? The pK_B of F^- is only 10.83 in aqueous media—however, pK_B of OH^- is 0, therefore protonation by acids (such as lactic acid from bacterial fermentation of sugars) is definitely less for F^-.

In summary, the computational results of Wang and coworkers do not support the claim that Ca–F bonding in $Ca_5(PO_4)_3F$ is covalent and thus it may not be held responsible for tooth strengthening or decay.

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