

Fig. S1 Thin-section images of the studied teeth in normal and cross-polarized light. A, B: *Lamiopsis temminckii*. C, D: *Hemipristis elongata*. E, F: *Sphenodus nitidus* (SNA). G, H: *S. nitidus* (SNB). EN: enameloid. OR: orthodentine. OD: osteodentine. PC: pulp cavity. SLE: shiny layered enameloid (single crystallite enameloid). RT: root.

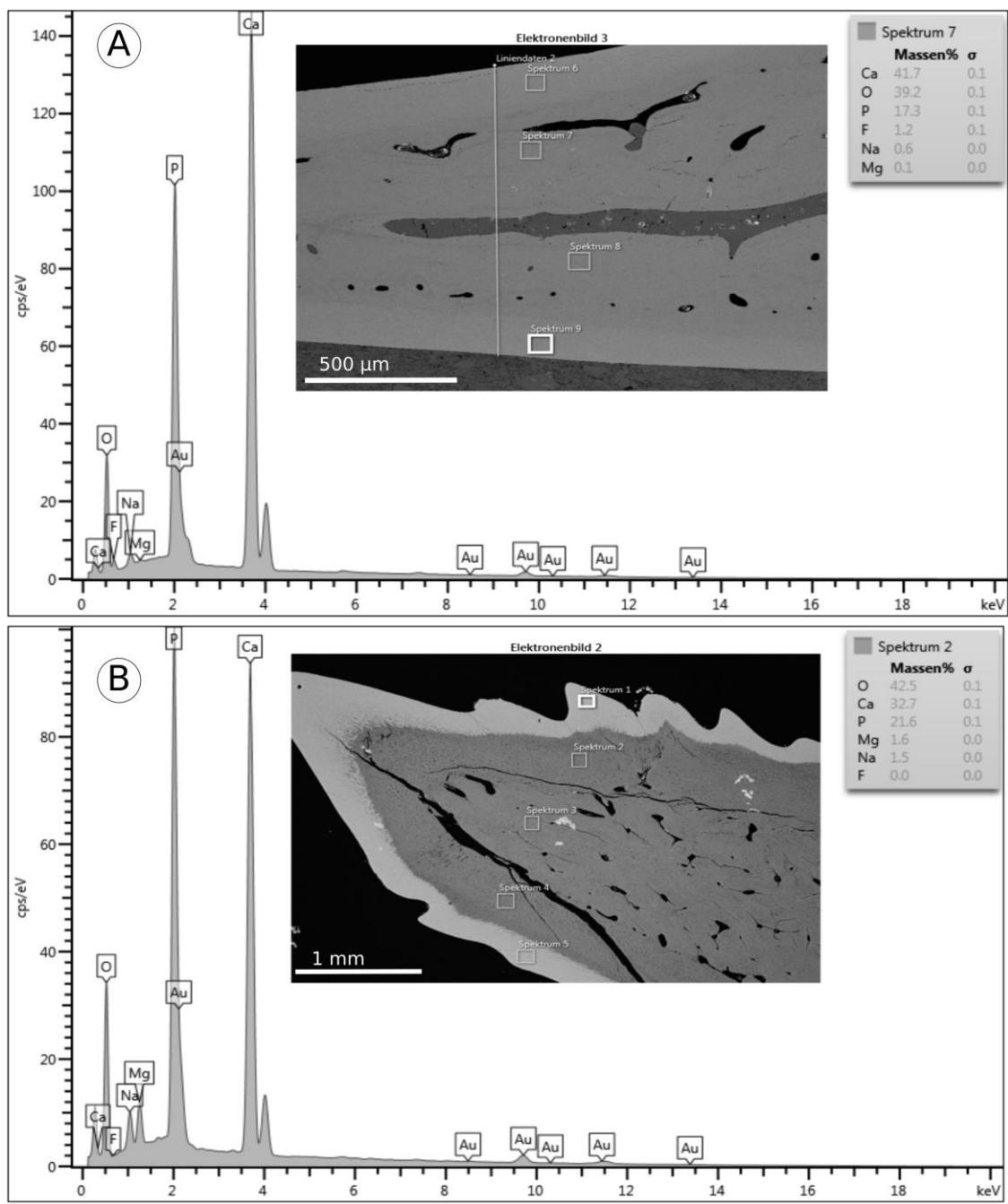


Fig. S2. EDX-spectra **A:** fossil shark tooth of *Sphenodus nitidus*. (SNB). **B:** Recent shark tooth of *Hemipristis elongata*. The dentine of the fossil tooth is fluorapatite, while the recent tooth dentine is hydroxylapatite.

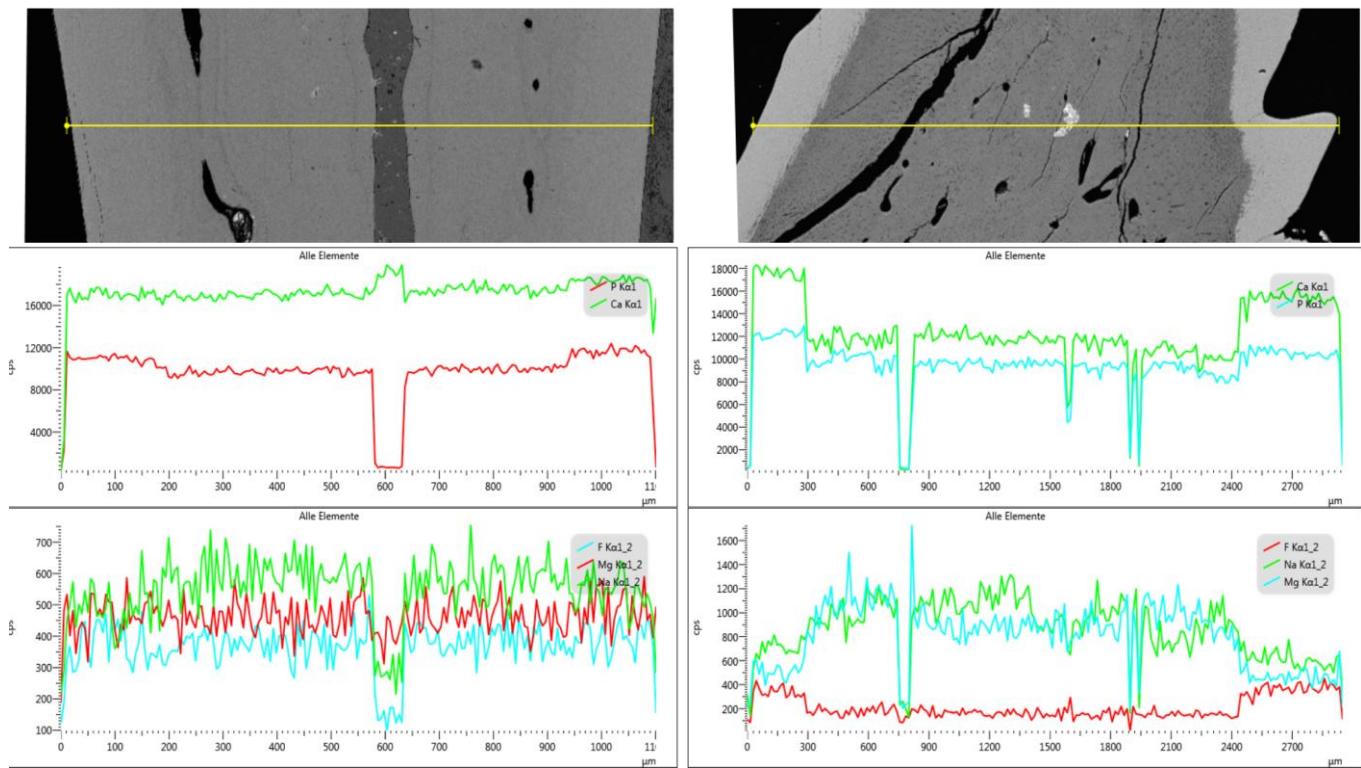
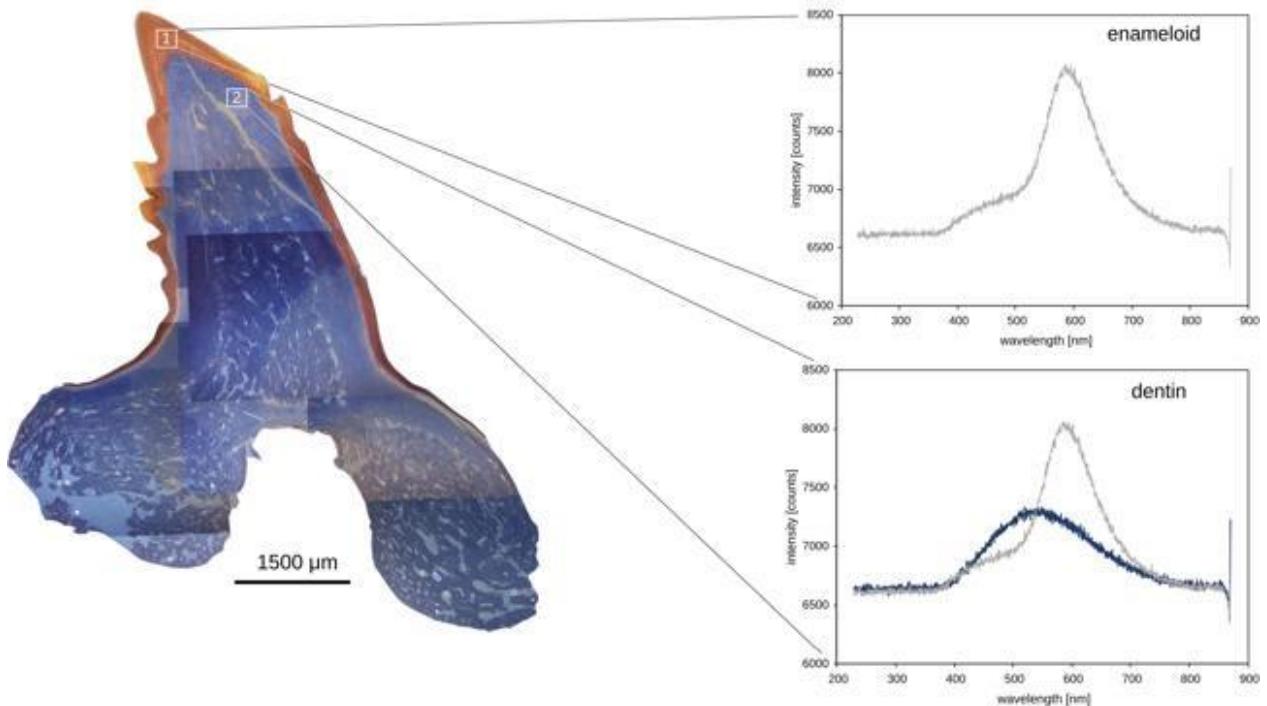


Fig. S3 Left side shows EDX-line scans through the fossil shark tooth of *Sphenodus nitidus* (SNA), which display a uniform distribution of fluoride in the dentine and enameloid. Right side shows that in the recent tooth of *Hemipristis elongata* the enameloid is enriched in fluoride relative to the dentine.

(A)



(B)

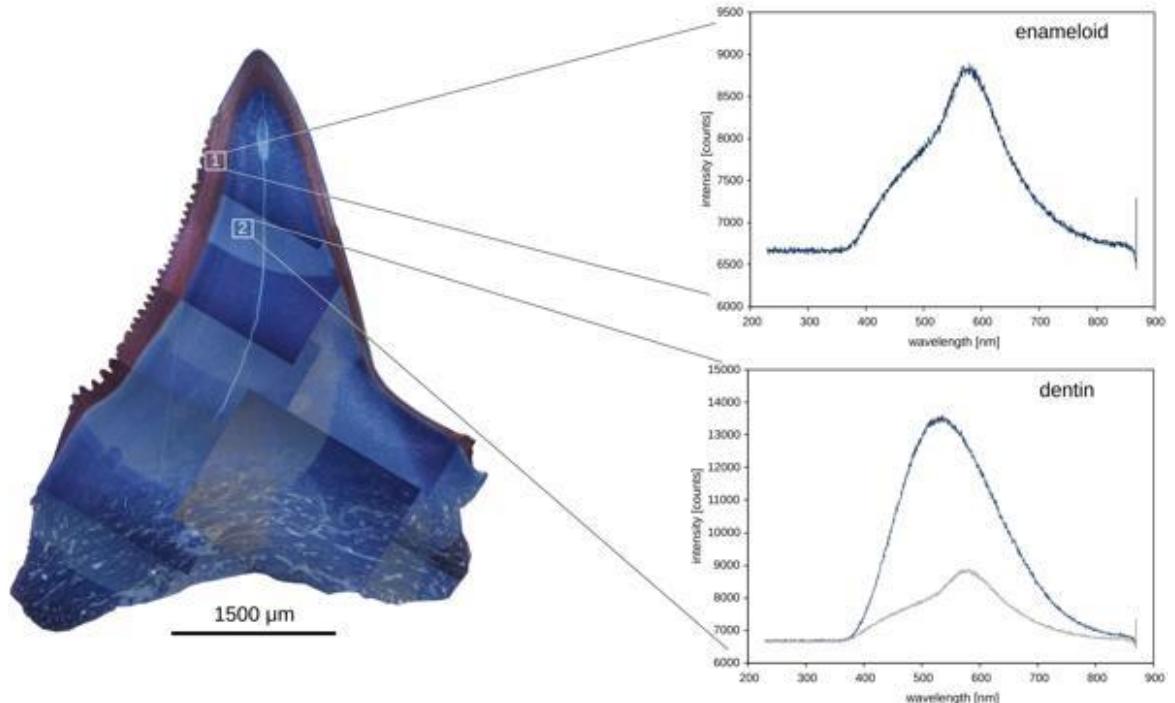


Fig. S4 A: CL-images of the recent *Hemipristis elongata* and **B:** *Lamiopsis temminckii* teeth with CL-spectra of the enameloid (1) and the dentine (2). The spectra indicate the presence of Mn in only the enameloid, while the dentine displays blue intrinsic CL.

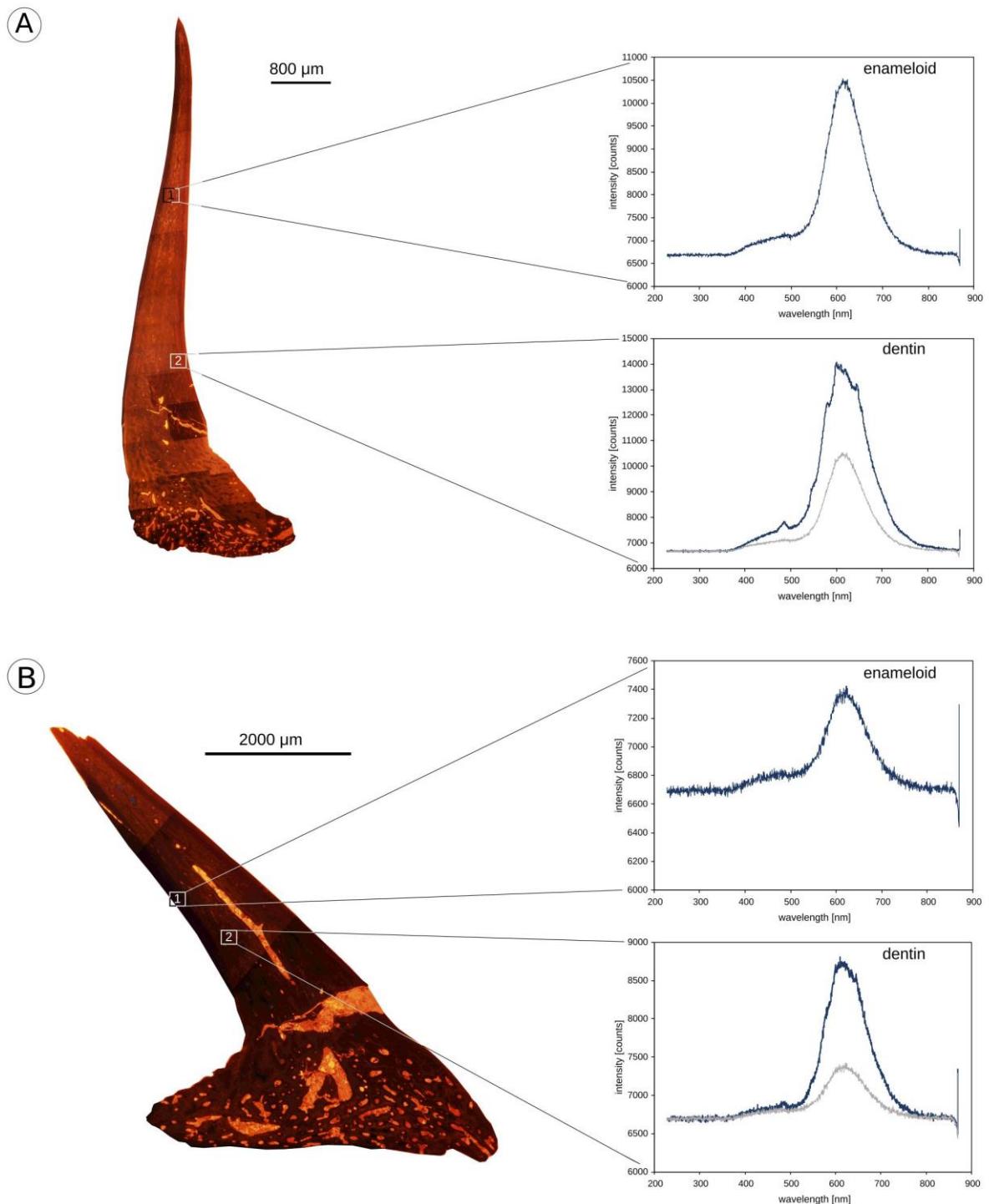


Fig. S5 A: CL-images of the fossil *Sphenodus nitidus* teeth specimen SNA and B: specimen SNB, with CL-spectra of the enameloid (1) and the dentine (2). The spectra indicate the presence of Mn in the enameloid and dentine and secondary REE peaks in the dentine.