Regular nano-domains in apatite crystals from developing enamel: Implications for crystal assembly from subunits and protein binding sites for growth modulation

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Enamel apatite crystals are highly crystalline, ~50nm wide, 30-50nm thick and up to 1mm long. Atomic and chemical force microscopy (AFM, CFM) revealed contiguous bead like structures on crystal surfaces in contact with modulating matrix proteins. CFM in lateral force /friction mode was used to probe surfaces of crystals from the maturation stage (after matrix withdrawal, to permit final growth). This revealed regular positively charged bands, ~30nM wide, across the surfaces in place of the bead-like structures. To further characterize crystal surfaces and to determine surface pK, they were exposed to a range of pH values, 4 - 10. Low pH resulted in morphological changes which accentuated the band structure. In addition, each band resolved into spherical domains (~30nM dia.) which exhibited relatively high positive polarity. Using Carboxyl or hydroxyl functionalised CFM tips, surface pK values were determined by adhesion force measurements at the above range of pH values. This revealed pK values an order of magnitude below solution phosphate. The data suggests that crystals may comprise chemically defined spherical subunits, stacked as hexagons or in a shallow spiral. These may reflect initiation or protein binding sites. Supported by MRC (UK) grant G9901098

Stable isotope chemistry of fossil bone apatite as a new paleoclimate indicator

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During fossilization, bone is believed to recrystallize and alter chemically on time-scales of kyr to a few tens of kyr, i.e., similar to the time-scale for formation of soils. Therefore, C- and O-isotope compositions of bone apatite should correlate with trends in soil water composition and aridity, and thus serve as paleoclimate indicators. This hypothesis was tested by analyzing isotope compositions of the CO_3 component of fossil bone apatite from mid-Oligocene through late Pleistocene units in Oregon and western Idaho, including the John Day (19.2-30.0 Ma), Mascall (15.2-15.8 Ma), and Rattlesnake (7.2-7.8 Ma) Formations, whose paleosol sequences have been studied in detail, and the Hagerman (3.2 Ma) and Fossil Lake (25-600 ka) fossil localities. Tooth enamel $\delta^{18}O$ values provide a baseline of meteoric water compositions.

Stable isotope compositions of bone CO_3 do broadly correlate with paleosol CO_3 and benthic foraminifera compositions prior to 7 Ma, but show poor correlation with compositions of paleosol CO_3 at specific horizons in the John Day Formation. Instead, compositional deviations between bone and paleosol CO_3 correlate with compositional deviations with the next higher paleosol; this suggests that the timescale for fossilization spans at least 2 paleosol cycles (i.e. a few tens of kyr), and that bone CO_3 will be prove most useful for sequences spanning at least hundreds of kyr. C-isotopes show negative and strong positive deviations during wet and dry climates respectively, and short-term secular trends correspond well with changes in aridity within the Mascall and Rattlesnake Formations, as inferred from paleosols. A proposed correction to $\delta^{18}O$ values based on $\delta^{13}C$ anomalies [1.25‰($\Delta^{18}O$)/1‰($\Delta^{13}C$)] implies a small, ~1.5‰ increase in meteoric water $\delta^{18}O$ during the late Oligocene global warming event, consistent with a temperature increase of ~4 °C. A strong decrease in $\delta^{18}O$ of 4-6‰ is inferred after 7 Ma, closely paralleling compositional changes in tooth enamel and meteoric water. This latter isotopic depletion is associated with renewed volcanic activity and doubling of the height of the Cascade Range, causing ^{18}O depletions and ^{13}C enrichments due to orographic rainout and increased aridity.