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Structural and functional characterization of enamel pigmentation in shrews

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ABSTRACT

Pigmented tooth enamel occurs in several vertebrate clades, ranging from mammals to fish. Although an iron compound is associated with this orange to red colored pigmentation, its chemical and structural organization within the enamel is unknown. To determine the nature of the iron compound, we investigated heavily pigmented teeth of the northern short-tailed shrew *Blarina brevicauda* using combined characterization techniques such as scanning and transmission electron microscopy and synchrotron X-ray diffraction. We found that the pigmentation of the enamel with an iron content of around 8 wt% results from a close to amorphous magnetite phase deposited around the nm-sized enamel crystals. Furthermore, the influence of the pigmentation on the enamel hardness was determined by nanoindentation measurements. Finally, the biomechanical function and biological context are discussed in light of the obtained results.

1. Introduction

Pigmented teeth are common in nature. Pigmentation has been documented in several extant vertebrate taxa, including shrews, salamanders (Clemen, 1988; Anderson and Miller, 2011), and fish (Motta, 1987; Sparks et al., 1990; Suga et al., 1992). The best known examples are the incisors of many species of rodent which are typically pigmented and vary in color from yellow, orange to dark red (Miles, 1963). Pigmented teeth have also been recovered from fossil taxa such as a Late Cretaceous mammal (Smith and Codrea, 2012) and an early Pleistocene shrew (Furio et al., 2010). The color of this pigmentation is caused by an iron-bearing compound that is assumed to be incorporated in vivo into the enamel by ameloblast activity during biomineralization processes (Stein and Boyle, 1959; Reith, 1961). Although several hypotheses have been proposed for the composition and spatial distribution of the iron-bearing pigmentation and its incorporation into the enamel the exact chemical composition and biological function are still uncertain.

It has been postulated that the pigmentation affects the function of the incisors during feeding. Iron, causing this pigmentation, is thought to make the teeth harder (Adamsczewska-Andrzejewska, 1966; Selvig and Halse, 1975; Churchfield, 1990; Akersten et al., 2001, 2002) and more resistant to wear (Vogel, 1984; Strait and Smith, 2006). Additionally, it has been postulated that the iron pigmented layer present in rat incisor enamel increased its hardness and resistance to acids (Stein and Boyle, 1959; Dötsch and Koenigswald, 1978; Selvig and Halse, 1975; Halse, 1974; Heap et al., 1983; Kato et al., 1988). In contrast, Suga et al. (1992) concluded that the iron present in the enameloid of fish teeth is more related to their phylogeny rather than an adaptation to a particular feeding habit. Moreover, unlike invertebrates, in which the iron is present as oxides crystallized in a layer on the surface of the teeth forming a cap (e.g., Lowenstam, 1967; Kim et al., 1989; Gordon and Joester 2011), the chemical composition and the structural arrangement of the iron pigmented layer in vertebrate teeth remain unclear. For example, observations in amphibians proposed that iron is present in oxidized form as a separate hematite mineral phase (Fe_2O_3) (Kerr, 1960; Schmidt, 1971), while in rat incisors it is suggested that iron is bound to the surface of hydroxyapatite crystals (Selvig and Halse, 1975) and does not constitute a separate iron-bearing mineral phase.

The extant northern short-tailed shrew species *Blarina brevicauda*, common in the North-Eastern US and adjacent Canada, was selected for our study because the coloring of their enamel is very

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