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THE GEOMETRIES OF STABLE ISOTOPES IN TOOTH ENAMEL AND THEIR RADIATION CYCLES AND ARCHAEOLOGICAL SIGNIFICANCE

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Abstract

Original scientific paper

Archaeologically, the elements in the tooth enamel and their isotopes provide a lot of information about the related period, such as the way of life and nutrition culture. In this study, it was determined how the durability or brittleness of tooth enamel varies with the presence of H, C, N and S elements, which are mostly detected in tooth enamel, and their most stable isotopes, D (deuterium), ^{13}C, ^{15}N, ^{34}S elements. These elements were moved inside and on the surface of the hydroxyapatite (HAp) crystal, which is the most abundant in tooth enamel and the cornerstone of enamel. At the end of the study, it was revealed that Nitrogen (N) and Sulphur (S) elements, especially Ca atoms that ensure the durability of the HAp crystal, and Oxygen atoms make bonds that prevent electronic charge sharing. In addition, this type of bonding (in geometries holding many Ca atoms) increase the fragility as the number of Ca-O bonds decrease. At the same time, such bindings create difficulties in determining the isotopes of the relevant elements. C bonding, on the other hand, provides a strong stretching action as it provides a double bond with the Oxygen atom, so the isotopic state of the carbon atom easily shows itself. The same situation was observed for element H and its isotope D. These findings better explain the brittleness of the teeth of ancient people, especially those who were fed marine life.

Keywords: *Carbon, sulphur, nitrogen, hydrogen, hydroxyapatite.*

DİŞ MİNESİNDEKİ KARARLI İZOTOPLARIN GEOMETRİLERİ VE RADYASYON DÖNGÜLERİ VE ARKEOLOJİK ÖNEMİ

Özet

Orijinal bilimsel makale

Arkeolojik olarak diş minesinde bulunan elementler ve bunların izotopları, ilgili döneme ait yaşam biçimi ve beslenme kültürü gibi birçok bilgi sağlamaktadır. Bu çalışmada diş minesinde en çok tespit edilen H, C, N ve S elementleri ile bunların en kararlı izotopları olan D (döteryum), ^{13}C, ^{15}N, ^{34}S elementlerinin varlığı ile diş minesinin dayanıklılığının veya kırılganlığının nasıl değiştiği tespit edilmiştir. Bu elementler diş minesinde en bol bulunan ve minenin temel taşı olan hidroksiapatit (HAp) kristalinin içine ve yüzeyine taşındı. Çalışma sonunda HAp kristalinin dayanıklılığını sağlayan Ca atomları başta olmak üzere Azot (N) ve Sülfür (S) elementleri ile Oksijen atomlarının elektronik yük paylaşımını engelleyen bağlar yaptığı ortaya çıktı. Ayrıca bu tip bağlar (çok sayıda Ca atomu içeren geometrilerde) Ca-O bağlarının sayısı azaldıkça kırılganlığı artırmaktadır. Aynı zamanda bu tür bağlanmalar ilgili elementlerin izotoplarının belirlenmesinde de zorluklar yaratır. C bağı ise Oksijen atomu ile çift bağ sağladığı için güçlü bir germe etkisi sağlar, bu nedenle karbon atomunun izotopik durumu kendini kolayca gösterir. Aynı durum H elementi ve onun D izotopu için de gözlemlenmiştir. Bu bulgular, özellikle deniz yaşamıyla beslenen eski insanların dişlerinin kırılganlığını daha iyi açıklamaktadır.

Anahtar Kelimeler: *Azot, hidrojen, hidroksiapatit, karbon, sülfür.*

1 Introduction

The utility of stable carbon, nitrogen, and sulphur isotope analysis derives from the expression that means that you are what you eat. Since its primitive applications in anthropology in the 1970s [1, 2], stable isotope analysis is now widely used to study past human diet through time and across space. The analysis of stable isotopes is also important in the tool kit of bioarchaeologists, who are curious about human past diet or human provenience [3, 4]. An examination of the component parts of stable isotopic paleodietary provided a revolutionary suite of

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tools for bioarchaeologists interested in reconstructing past dietary behaviour also related to population adaptation. Stable isotopes do not change over time, although their concentrations change with physico-chemical processes such as evaporation and condensation [5]. Such stable isotopes in relative abundance can be found experimentally by isotope analysis and a found isotope ratio can be used as a test tool. It can be said who in nature is affected by the abundance of isotope fractionation relative to each other. The differences do not alter to any great extent the chemical properties of the atom, but of course, do change the physical properties. Fry [6] stated that lighter isotopes such as hydrogen (H), carbon (C), nitrogen (N), Oxygen (O), Sulphur (S) constitute between 95%–99.6% of their natural abundance whereas heavier isotopes only constitute between 1%–5%. Stable isotope ratio described as the ratio of the heavy isotope to the light isotope such as $^{13}C/^{12}C$, $^{15}N/^{14}N$ in connection with a known standard. The methods investigate the chemical composition of bones or teeth for the reconstruction of paleodiet provide the most relevant information about the original contents of the diet. The stable isotope analyses have been found an established method for reconstructing infant feeding and weaning practices, paleodiet, geographic origin, migration routes from the human skeletal and dental remains [7]. The various tissues of the human body are principally composed of atoms of elements such as carbon, hydrogen, nitrogen, sulphur, oxygen, and phosphorus which have significant variations in all of the isotope ratios. If a human has been eating a uniform diet for a period of time that is long compared with the rate of turnover of a given tissue, then the isotope ratio of each tissue and organic molecule in the body will achieve a steady state value. That value will generally differ from that of the dietary intake (fractionation between the tissue and the diet). The overall isotopic composition means weighted mean of all components itself represents a steady state between intake and outputs such as urine, feces, expired CO, and H, O in normal conditions [8]. Considering that rain water accumulates in the seas and fresh water resources, it can be mentioned that the accumulation percentages of carbon and nitrogen isotopes in tooth enamel are higher in the diets in these geographies and brittleness increases in these geographies. [9]. Variation in trophic level, photosynthetic pathway, and environmental conditions with other biogeochemical processes can also have a strong influence over patterning of the natural abundances of ^{13}C and ^{15}N in aquatic, and especially freshwater, environments. Because these biogeochemical processes often play an important role in structuring the isotopic composition of aquatic food webs at a range of spatial and temporal scales, it is important that they are adequately considered in isotopic studies of past human and animal populations [10]. In the examination of adult teeth, the data obtained from the enamel of deciduous or permanent teeth showed that the development was completed in childhood and isotopic developments were more important at that time. [11]. Tooth enamel develops together with the dentil part of the tooth. However, since it does not have a self-repetitive feature, it is shaped in the developmental processes of childhood. [12]. It has been seen that it is possible in today's scientific age to take weekly or even daily records of historical processes from some scales rather than months and years. However, meanings can be deduced from tooth enamel in different periods (depending on age, in childhood and adulthood). [13]. It differs from bone collagen and dentin in that the enamel is resistant to deformation and deterioration. [14].

Stable isotopes in nature occur in high temperature plasma environments. these environments are often known as lightning flashes. Nuclear-based radiations such as neutrons and gamma rays, which are produced by lightning strikes, are emitted:

$$\text{Lightning Flash} + (\text{Air-99\% N, O}) \rightarrow \text{Gamma, X-Ray} + \text{Neutron} + \text{UV} + \text{Visible} + \text{Trace particles} \quad (1)$$

According to Eq. (1), neutrons are released from N and O atoms in the air, which are referred to as trace particles. These enter the stable isotope cycle as follows:

$$^{14}N + \text{Heat} \rightarrow {}^{13}N + n \;\; ({}^{13}N \rightarrow \beta\text{-decay} + {}^{13}C) \quad (2)$$

$$^{16}O + \text{Heat} \rightarrow {}^{15}O + n \;\; ({}^{15}O \rightarrow \beta\text{-decay} + {}^{15}N) \quad (3)$$

As can be seen from Eq. (2) and Eq. (3) above, the effect of lightning flashes on isotopes is very effective when both the stable isotopes formed by the unstable trace elements when they become stable and the stable isotopes that the free neutron can form by interacting with the N and O atoms in the air under collision statistical. It is a fact that the isotope population will be effective in places where precipitation or lightning flashes are effective. As these isotope gas molecules interact with water and enter living life with groundwater, they become partners in the life cycle.

2 Materials and Methods

2.1 Computational Method

With the chewing of the foods containing the isotope, the related elements take their place in the tooth enamel in a child in the developmental age. Tooth enamel is composed of HAp crystal structure. The unit cell (a=b=9.424 and c=6.879) of this structure was designed as described in the literature [15]. In the system, the bulk structure and the fermi electronic temperature were set at room temperature. The simulation was carried out under the AMS (Amsterdam Modelling Suit) infrastructure by using DFTB3 (third degree density function tight-binding) approach and D4 electronic dispersion as a model [16]. In determination of stable structures by both optimization and PES-Exploration, the 3ob-3-1 function suitable for HAp and isotopic additives was determined as a parameter.

Known as the base substance for tooth enamel and dentin, HAp crystal is the cornerstone of tooth strength. In tooth decay or fracture, the durability of the tooth varies with the breaking of Ca-O bonds or entering into chemical reactions. This reaction starts to react with CaOH, which supports to pH change [17, 18]. Therefore, the decrease in Ca-O bonds reduces the durability of the tooth.

3 Results and Discussions

HAp crystal was used for simulation as the basic lattice form, $Ca_{10}(PO_4)_6(OH)_2$. ^{1}H, ^{12}C, ^{14}N and ^{34}S atoms and their most stable isotopes (^{2}D, ^{13}C, ^{15}N, ^{34}S) were moved in the system to determine the most stable structure on and inside the Crystal surface. Differences in IR vibrations and isotope effects on the most stable structures were tried to be determined. It was also discussed whether these isotopes affect the strength of the HAp crystal. The fundamental vectors of the crystal structure in three dimensions are as follows:

VEC1	9.39685455	0.00000000	0.00000000
VEC2	-4.69842728	8.13791476	0.00000000
VEC3	0.00000000	0.00000000	6.86402560

First, the most stable states were determined by moving the H atom on and inside the HAP crystal surface. As in Fig. 1, "process search" was used to detect transition and minimum points with PES-Exploration. Fig. 1 shows the diagram of these transitions. The most stable configuration is shown in Fig. 2.

In Fig. 1, the most stable energy level is achieved when the H atom is bonded to the phosphorus (P) atom, referenced to "0" Hartree. A total of 8 transition and minimum energy points were detected, depending on the movement of the H atom on and inside the crystal surface via Pes-Exploration. In other high-energy states, the "H" atom is bonded to the "O" atom. Fig. 2 gives a detailed view of the binding of the most stable level. These energy levels in Fig. 1 were detected in best electronic dispersion. It shows the "H" atom that wants to bind to the (OH) endpoint of the $Ca_{10}(PO_4)_6(OH)_2$ (HAp) crystal in higher energy states. In this case, the system becomes unstable. These points will make the unstable system react. It is estimated as the first step in the formation of hydrolysed environments in cases such as the mechanism of decay. However, this end region is the region where there is no effect on the brittleness of the crystal under any external pressure. Another binding site of the H atom is the bonding to the "O" atoms to which the "Ca" atom bonds. Binding to this region occurs at unstable high energy levels. This unstable state increases the fragility of tooth enamel. Because the bonding of Ca atoms with "O" atoms is the indicator of this hardness. The resistance of atoms to a certain stress under any external pressure is at the forefront with their Ca-O bonding. The higher the number of Ca-O bonds, the stronger the crystal. The change in the degree of bonding in the CaO bond group occurs under high pressure. Or it happens with the help of a different external influence.

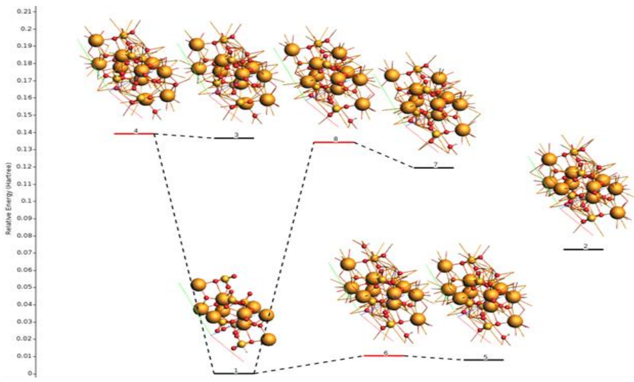

Figure 1. The energy levels obtained by using Pes-Exploration with "Process Search" task.

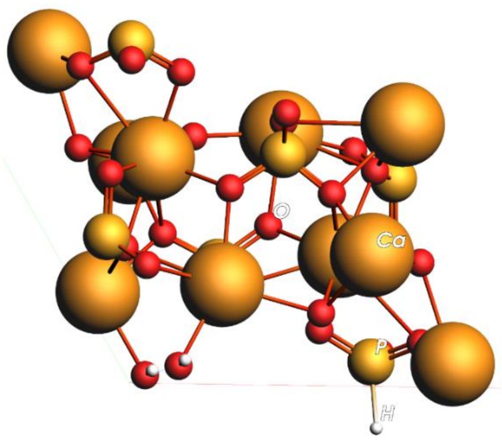

Figure 2. Representation of the most stable binding of the H atom in the HAp crystal. (Symbols of the elements are indicated on the Figure. Atoms of the same kind are shown in the same colour and size.)

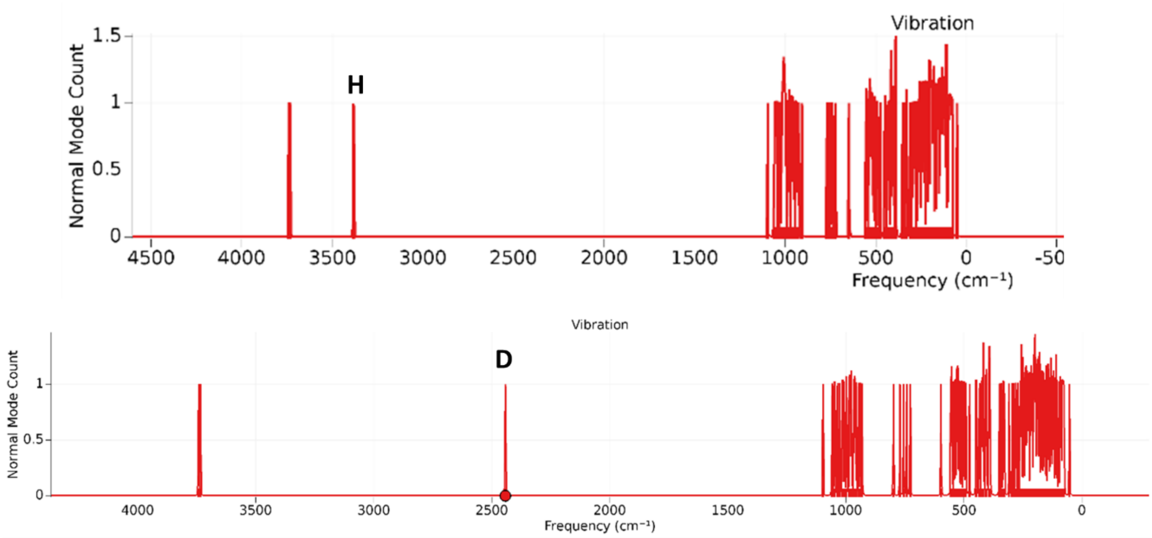

Figure 3. Vibration frequency energy values in the HAp crystal of H (upper part) and D (bottom part) atoms.

The upper part of Fig. 3 shows the frequency at which the Hydrogen atom is in the HAp crystal, while the lower part of the figure shows the vibrational frequency at which the deuterium atom is located. The only different point in both frequency ranges is the oscillation frequency, which indicates the difference between H and its isotope D. In this figure, the vibrational frequency of the phosphorus -bound H-atom in the spectrum is shown at a frequency of 3384 cm^{-1}. It is well known that the H atom is a light mass atom capable of strong stretching action. Thanks to this feature, it is very easy to detect this element and its isotopes in a tooth enamel. With twice the mass difference, the oscillation frequency difference is seen in detail. Although the attachment of the H atom to the oxygen structures in the crystal structure is not shown here, the isotope difference will be evident there as well. The bonds of the H atom with the oxygen atoms in the crystal cause IR oscillations at 3624, 3736, 3762, 3749, 3730, 3742 cm^{-1} frequencies in more unstable structures. In this study, the most stable region where the H-atom can bond was determined and isotope determination was made only on this structure. The deuterium emission frequency is around 2400 cm^{-1}. The highest oscillation frequency in Fig. 3 belongs to the tip region of the HAp crystal (OH).
It does not belong to the externally doped H atom. 1000 cm^{-1} and lower oscillations are buckling and bending oscillations in the crystal. The isotopic study of the H atom adsorbed to the HAp crystal can be easily detected.

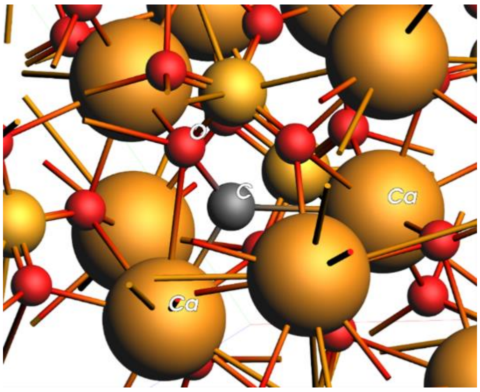

Figure 4. Stable geometric structure of C element in HAp crystal.

Another doped element is "C" carbon. As seen in Fig. 4, the element carbon is bonded to 2 Ca atoms and 1 oxygen atom. In such a bonding, the vibrational frequency difference of the isotopes will show the C-O junction. It is very difficult to determine the isotope difference in the crystal in C-Ca binding. Fig. 5 shows the difference in vibrational oscillations of carbon isotopes. The isotope values of C-O stretching movement are ^{13}C at 1121 cm^{-1} and ^{12}C at 1130 cm^{-1}.

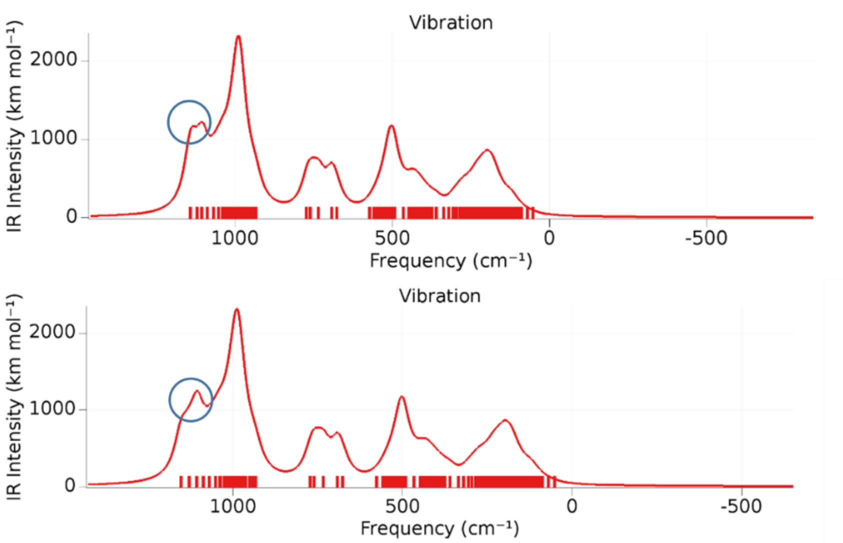

Figure 5. The top side of the figure is ^{12}C and the bottom side is the oscillation frequencies of the ^{13}C element. The difference between the two distributions is the frequency range indicated by the blue ring on the graph of the C-O stretching motion.

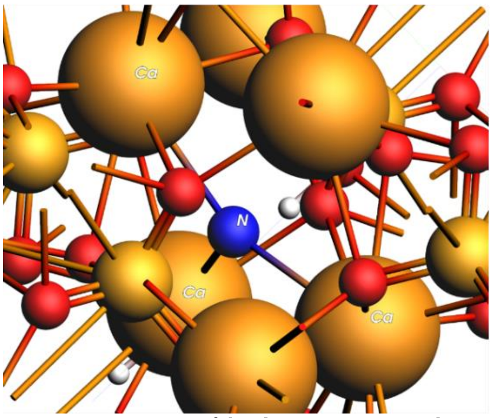

Figure 6. Geometric position of the element Nitrogen in the HAP Crystal.

Another doped element is the nitrogen atom. The most stable structure of the nitrogen atom in the HAP crystal occurs when three Ca atoms form a single bond (see Fig. 6). In such a case, it is very difficult to determine the ^{15}N isotope. The vibration spectra are similar to each other due to the heavy structure of the Ca atom and the triple bond. However, if the N atom is positioned somewhere between Ca and Oxygen, oscillations can be seen at ^{14}N (1682 cm^{-1}) and ^{15}N (1653 cm^{-1}) frequencies. These oscillations are in the N=O double bond state.

Another doped element is sulphur element. This element also bonds to 3 Ca atoms in the HAp crystal (see Fig. 7). Like nitrogen, isotopic oscillation differences in binding to Ca crystal are difficult to determine with IR frequencies.

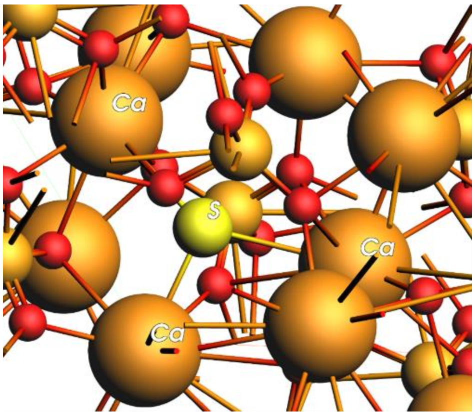

Figure 7. Geometric position of the element Sulphur in the HAP Crystal.

4 Conclusion

The H, C, N and S elements and the HAp crystal in which their isotopes are doped were examined in this study. H and C elements, due to their binding to the oxygen atom, show the situations where IR analysis is sufficient in isotopic differences with their stretching action. However, N and S elements, on the other hand, are very difficult to determine their isotopic differences with the IR spectrum due to their binding to the Ca element. The strength of tooth enamel is also directly dependent on the positions of these doped elements. Under any external pressure, the degree of Ca-O binding is directly affected. When these elements, which are doped from the outside and placed in the crystal, affect the Ca-O bonding, they will affect the strength of the $Ca_{10} (PO_4)_6(OH)_2$ crystal, which is known as the calcium salt. Archaeologically, it enters the life cycle when isotopic elements, which occur with nuclear reactions in the atmosphere under high temperature, in regions with abundant precipitation and lightning flashes, pass into the earth's waters with rain water. Isotopic densities can explain the strength or fragility of teeth, while providing some information from the past. In particular, the contribution of carbon and nitrogen atoms to tooth enamel fracture is explained by the bonds they make with oxygen atoms.

Declaration

The authors declare that the ethics committee approval is not required for this study.

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