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FLUORIDE DATING OF SKELETONS OF THE IRON AGE CEMETERY OF TABRIZ, IRAN

Masoud B. Kasiri

Department of Archaeometry, Faculty of Applied Arts, Tabriz Islamic Art University, Tabriz, P.O. Box: 51385-4567, Iran

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**Corresponding author: (m.kasiri@tabriziau.ac.ir)*

ABSTRACT

The aim of this research was the relatively dating of the human skeleton samples of the Iron Age site of Blue Mosque in Tabriz, Iran, on the basis of fluoride relative dating method. Totally, four bone samples of the skeletones were selected to be relatively dated. In this way, the ribes bones of the samples were prepeared by according to the standard methodes and their fluoride content was measured by UV-Vis spectrophotometry method. On the basis of their net fluoride content, sample no. 81.9 is the first buried one, while sample no. 80.6 has lowest amount of fluoride and consequently, is the last buried one. Also, comparing the relative fluoride content of the two samples, no. 81.7 and no. 81.8, it can be concluded that sample no. 81.8 has spent more time under the soil. The relationship between soil and the bone fluoride content has also been investigated, where a good linear correlation was found (R^2=0.9161). Moreover, it was shown that at lower pHs of the soil, the fluoride content of the bone is higher.

KEYWORDS: Bone dating; Chemical dating; Fluorine dating; Iron Age cemetery of Tabriz; Relative dating

1. INTRODUCTION

One of the most important concerns of archaeologists, after the discovery of objects during the archaeological excavations, is determining the age of these findings or in other words, is their dating. Developments that have been made in collecting and processing data and archaeological studies at the beginning of 20th century so far, have led scientists to find new approaches to date analyzing, especially to absolute and relative dating methods. For this purpose, different techniques have been developed in the archaeological science to determine the age of an object or to date an event or period. (Goksu at al., 1991; Renfrew and Bahn, 2008)

In relative dating, if the available sample is sufficient (in milligram amounts), the sequence of samples to each other could be determined using the chemical methods such as fluorine, uranium, and/or nitrogen measurement (FUN method) (Kasiri and Alizadeh, 2018) or amino acid racemization technique (Johnson and Miller, 1997). Datelining the findings such as bone, provides the possibility to investigate the precedence, posterior or concurrency of different discovered human species in a certain region.

Human or animal bones are one of the most important findings of every archaeological excavations. The reason of compressive strength of the bone is carbonate containing hydroxyapatite (HAP) mineral, $Ca_{10}(PO_4)_6(OH)_2$, which is stoichiometrically incomplete. This mineral part contains a small amount of other anions and cations, which could be absorbed on the bone grains and substituted by Ca^{2+}, PO_4^{3-}, and the hydroxyl ions (OH^-) in the mineral network of the bone. The hydroxyapatite crystals are morphologically plate-shaped and have a dimension of about 35×5 nm and a thickness of about 2-3 nm, where, this average sizes of crystals increases with tissue growth. There is a close relationship between collagen and hydroxyapatite molecules, and this proximity in the chemical structure is strengthened with the non-cluster protein of osteocalcin, which forms 2%w of the dry bone. These relatively small proteins are bound to both apatite and collagen and play a very important role in the initial crystallization of the skeletal tissue. Mineral crystals lay within the collagen matrix. (Turner-Walker, 2007)

Dry fresh bone also contains 8% of water, which would be evaporated during the heating at 105 °C. But for a material like bone, which has a high microporosity, the total water content of the sample depends strongly on the temperature and the relative humidity (Hedges and Millard, 1995)

Diagenesis refers to the post-burial changes - chemical (e.g., degradation) and mechanical (e.g., crushing) – to the tissue of the organisms. One of the diagenetic processes of bone, is the replacement of chemically unstable hydroxyl ions (OH^-) of the hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] of bone with more stable fluoride ions (F^-), where during this replacement process the hydroxyapatite becomes more stable fluorapatite (Eq. 1). (Lyman et al., 2012)

Biologists, paleontologists, and pathologists are doing comprehensive studies on the archaeological bone findings. The first step at such studies is determining the age of findings. Datelining the findings such as bone, provides the possibility to investigate the precedence, posterior or concurrency of different discovered human species in a certain region. There are several ways to determine bone age, that can be classified into two main groups including direct dating and indirect dating. In indirect dating of findings, the age of samples is estimated by dating the upper and lower layers that circled the bones. For example, we can refer to dating the other findings such as pottery and charcoal that there is a possibility to direct and precise dating. For direct dating and in possession of a sufficient amount of sample, the absolute dating such as radiocarbon (^{14}C) dating or Electron Spin Resonance (ESR) are used. Choosing the method of dating depends on sample rate, the time limit for dating with the considered method, the required precision, the available navigation equipment, and the costs associated with the for dating tests (Hashemi Zarj Abad, 2004). If there is no possibility of the absolute dating of samples, direct comparative methods of dating can be used. In this case, only the chronological sequence of findings in a certain place is obtained. (Bahrololumi, 2014)

In the relative dating, if the available samples is sufficient (in milligram amounts) using the methods of chemical detection such as fluorine, uranium, and nitrogen measurement (FUN) or amino acid racemization, the sequence of samples to each other can be determined. FUN dating method is based on the measurement of content of three elements of fluorine, uranium, and nitrogen in the samples of the studied bone.

Fluorine (F) usually exists in nature as calcium fluoride (CaF_2) and is abundant in the groundwater (Woittiez and Das, 1980). Hydroxyl groups of the hydroxyapatite in the structure of the bone or teeth mineral matrix could be substituted by fluoride ions existing in mineral water. (Eq. 1) (Kottler et al., 2002)

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^- \quad (1)$$

Fluorine is mainly found in the form of fluorite mineral, CaF_2, as well as fluoride ion in various amounts in groundwater (Woittiez, 1980). Due to the intense reaction of fluoride with any other molecule and a very weak reaction between fluoroapatite and hydroxyl ions, fluoroapatite does not substitute any additional ions. Fresh bone contains 0.05% fluorine and can attain a theoretical maximum fluorine amount of 4.8%, a value much higher than the average F concentration in ground water (~0.1 μg/g) or soil (up to several mg/g) (Kottler et al., 2002). The amount of fluoride accumulated in the bone depends on the climatic conditions, the chemical composition of the site, the amount of moisture, the groundwater condition, the surface water of the site, and the local ecosystem (Kottler et al., 2002).

Recent researches have shown that the chemical dating of ancient bones is possible based on the monitoring of diagenetic changes. Accordingly, under stable conditions, the concentration profile of fluoride increases slowly towards to the marrow (Kottler et al., 2002). In one of the leading researches in this field, Johnson et al. (1997) measured the fluoride and silicon content of 87 human fossils found in southern Sweden and reported that silicon, like fluorine, could replace the hydroxide ions in the structure of bone hydroxyapatite. They have reported that the fluoride and silicon content, along with the molar ratio of calcium to phosphate plus carbonate (Ca: (PO_4 + CO_3)), is dependent on time and can be used as a criterion for dating.

In a pioneer research, Coote et al. (1982) have shown that in bones which had been exposed to ground water, the fluorine concentration at the surface was usually in the range of 0.2-1%, while it was lower at 3 mm depth by a factor between 0.1 and 0.9, depending on the duration of burial time. They have concluded that such profiles could be a promising means of sorting bones of different provenance or age in a time sequence.

In a similar research, Gaschen et al. (2008) have reported that archaeological fragments of bone and teeth that are exposed to a humid environment take up fluorine from the surrounding soil, where it replaces the hydroxyl group in the mineral phase of the bone, forming chemically more stable fluorapatite. It has been shown that geological time spans are needed for this process to reach equilibrium and for the distribution to become uniform. This means that the shape of the profile, which can be described by a diffusion model, contains information on the exposure duration of the bones.

Due to climate changes in the past that could alter the concentration of fluorine in the water, and given that it is not always possible to reconstruct the past climatologic condition, instead of comparing the concentration of fluoride in the samples with the control sample, the determination of the ratio of fluorine to phosphate ions (PO_4^{3-}) is considered for the samples. It should be noted that the fresh bone contains about 42% of phosphate ions.

The aim of this study was to evaluate the performance of fluoride relative dating method on archaeological bones of the Iron Age cemetery of Tabriz, where the priority and posteriority sequence of the skeletons burial time could be determined. To materialize this purpose, fluoride content of the samples taken from the skeletons was measured and the sequence of their burial time was determined.

2. MATERIALS AND METHODS

2.1. The Iron Age cemetery of Tabriz

In this research, the skeletons of Iron Age museum of Blue Mosque in Tabriz, Iran, were selected for analysis of their fluoride content. The Blue Mosque (Kabud Mosque) is a famous historical mosque in Tabriz, Iran, that was constructed in 1465 AD upon the order of Jahan Shah, the ruler of Kara Koyunlu dynasty. (Figure 1)

Recently and during the restoration of the Blue Mosque in 1997, the remaining of a pre-historian cemetery have been discovered.

The acquisition of a large number of graves in various layers indicated the long use of this site in different periods of the past time (Figure 2). On the basis of the discovered objects with the burials, which in some of the graves comprise the cultural effects of the Iron Age I and II, it can be concluded that, first, there was a cultural continuity between the two layers in the cemetery and second, its usage time dates back to the early Iron Age II. Moreover, this site has been abandoned before the prevalence of the indigenous species of pottery of Iron Age III. The most important findings of Blue Mosque site are graves belong to the Iron Age II, where all of the burials are contracted type with different positions (Kasiri and Karimi, 2017). Considering radio carbon dating of historical sites such as Hasanlu and Dinkha tepe, as well as by comparing the Kabud Mosque data with other sites, it can be dated about 1200-800 BC.

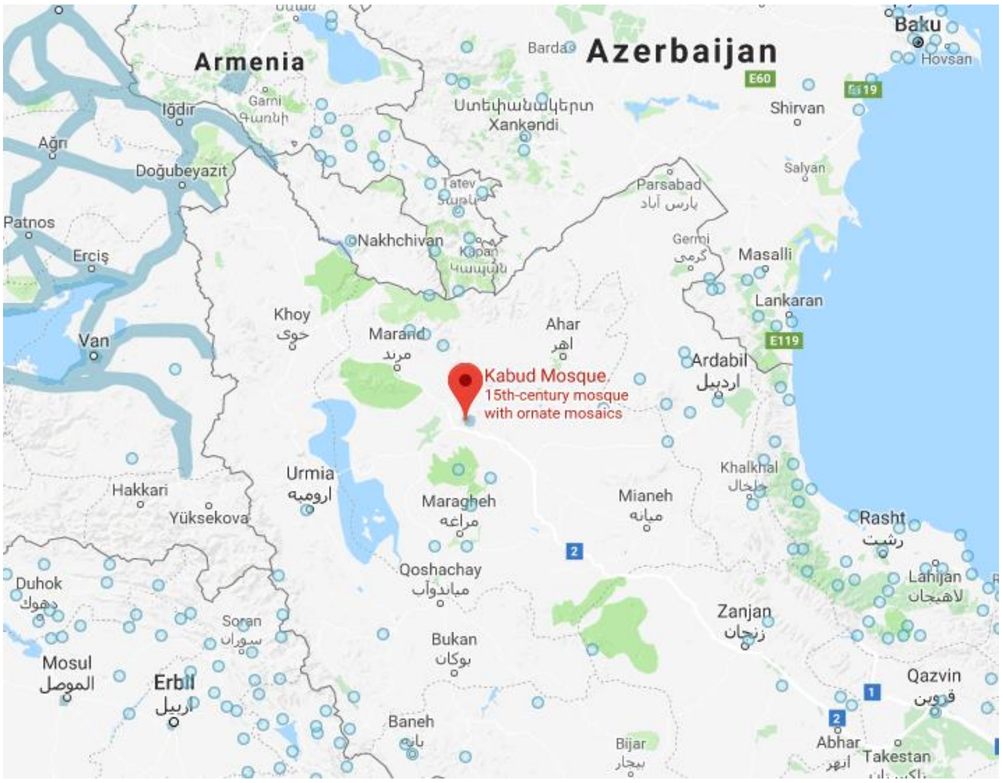

Figure 1. Geological map of Tabriz city and Kabud Mosque

Figure 2. A sample grave of Iron Age museum of Tabriz, along with the accompanying objects

2.2. Sample bones of the skeletons

Review of the published literature shows that many pieces of the human skeleton have been selected for elemental analysis, probably depending on the type of the bones and the extent of damages. The manner and the importance of sampling of ancient bones as well as the scientific basis of the analysis of each part of the skeleton has been explained by Grupe (1988). By according to the scientific rules, the ribs bones of the skeletons were selected for realizing the fluoride relative dating tests.

The skeletons of graves no. 80.6, 81.7, 81.8, and 81.9 of this archaeological site were selected for the study. Figure 3 shows the graves and the selected bones of these skeletons for running the fluoride dating experiments.

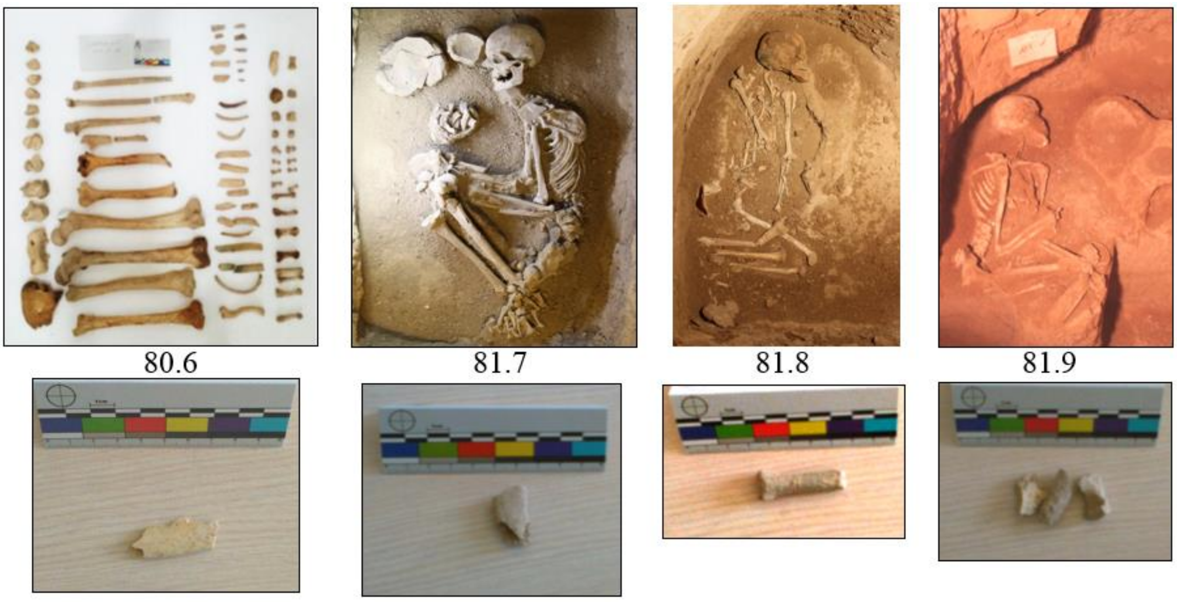

Figure 3. Selected bone samples for the analysis (First row is the graves)

Table 1 shows the physical and archaeological characteristics of the bone samples, too. As it could be seen, all of the samples belong to mature bodies and are a mix of feminine and masculine skeletons, except sample no. 80.6, that was not sexually recognized.

Table 1. Physical and archaeological characteristics of the bone samples

No.	Grave No.	Trench	Sex	Weight (g)	Dimension (cm)
1	80.6	N	---	1.076	1.3×3.6
2	81.7	B	M	2.422	1.5×3.0
3	81.8	B	F	2.468	1.7×4.0
4	81.9	B	F	2.414	1.0×2.5

2.3. Preparation of samples and measurement procedures

After documentation and measuring the weight and dimension of the samples, they were cleaned for sampling. Before sampling, the sediments on the samples were first sampled with a razor blade, so that, if necessary, it would be possible to study the sediments of the bones. Sediment of the samples were kept in the special bags for future studies.

Then, the samples were cleaned physically using a silver bristle blade, Silver GT10103, made in China. Subsequently, each of the samples was placed in an ultrasonic bath (Ultrasonic Fuses, UK) for 10 minutes. The frequency of the waves in this bath was about 50-60 Hz, which makes it possible the separation of particles and surface contamination. After drying, re-moistening and brushing of the samples, they were again dried, then immersed and dried in ethanol and in acetone, respectively (to eliminate the possible paraloids traces).

To run the fluoride measurements, the sample was heated up to 70 °C for 48 hours, cleaned using mechanical cleaners, and was powdered by a mortar and pestle. One gram of this powder was weighted and poured in a clean flask. Then, 12 ml of perchloric acid ($HClO_4$) along with 12 ml of distilled water was added into the flask, and finally, 24 ml of Tizab water buffer (10.0 g Aluminon, 29.41 g sodium citrate di-hydrate, 58.0 g sodium chloride and 57.0 ml of glacial acetic acid were dissolved in 800 ml of distilled water. The pH was adjusted to 5.0 with 6 M NaOH, then diluted to 1.00 liter) was added to the mixture (Worbel, 2007). Also, a 1000 ppm fluoride standard was made by dissolving 2.21 g NaF in distilled water and diluted to 1.0 liter.

Calibration curves were typically prepared by adding the following total amounts of 1000 ppm fluoride standard to 10.00 ml of liquid (TISAB and acid): 0.10, 0.20, 0.30, 0.50, 0.80 and 1.30 ml. This preparation produced calibration points ranging 9.90-115.0 ppm fluoride ion.

Recently, different laboratory methods have been used to measure the fluorine levels of samples, each of which requires specific preparation steps or special instrumentation.

In one of the interesting examples of measuring the fluoride concentration in ancient bones, Piga et al. (2009) have used XRD and X-ray fluorescence (XRF) methods to investigate the human and animal bone fossils belong to the Hellenic period. Based on the results obtained, the change in the average size of the hydroxyapatite crystalline units as a result of the substitution of hydroxyl ions by fluoride ions can be expedited as a burial time. By establishing a linear relationship between these two variables, the authors have shown that the age of the samples can be obtained using the X-ray diffraction studies.

In another example, Coote et al. (1982) studied the concentration of fluorine gradient at the human and animal bone using a nuclear microprobe. The results of this study showed that where the bones have been in contact with groundwater, fluorine concentration at bone layers was usually between 1-2%, which decreased from 0.1 to 0.9% at a depth of 3 mm. The amount of this decrease depends on the time elapsed under the soil, so the relative age of the different samples obtained from a specific location can be determined in the range of 0-5000 years.

Heckel et al. (2016) have also investigated the fluorine concentration profile using electron μPIXE/PIGE techniques in the ivory and reported that the different patterns could be seen in the variation of fluoride content in the ivory. In this case, the absorption process of fluorine is more complicated than that of bone.

It should be noted that the presence of phosphate ions causes the experiment results to be false. These ions remove the fluoride ions from the bone environment and consequently, fluoride concentration will be appeared lower than its actual amount. Subtraction of phosphate ions content from the measurement results, can provide more verifiable data (Chlubek et al., 1996). Equation (2) was used to calculate the amount of net fluoride value of the samples. (Woittiez and Das, 1980)

$$\text{(Net fluoride value) } A = \frac{F\%}{PO_4^{3-}\%} \times 100 \quad (2)$$

3. RESULTS AND DISCUSSION

In this research, the samples were prepared and their fluoride concentration was measured by spectrophotometer method. The concentration of fluoride in the solution was measured by an UV-Vis spectrophotometer, model Spectronic Helios-Alpha (England) and a calibration curve.

The measurements were repeated for each sample twice, with the mean of the measured values shown in Table 2. According to archaeological reports of the Iron Age cemetery of Tabriz, the samples dated back to 1200-800 BC, while according to the results shown in Table 2, they contain 1.55 to 1.63% of fluoride.

Table 2. Amount of fluorine, phosphate and calculated net fluorine value of the samples

Measured element	Sample			
	80.6	81.7	81.8	81.9
Fluorine (%)	1.62	1.55	1.60	1.63
Phosphate (%)	36.20	31.24	31.16	31.52
Net fluoride amount	4.47	4.96	5.13	5.17

Other researchers have reported the similar amounts of fluoride in ancient bones. For example, in a similar study, Tankersley et al. (1998) have measured the amount of fluoride in a bone sample of a Pleistocene archaeological excavation site. In this study, the fluoride content of the studied samples was measured in the range of 1.00 to 2.70%, where this difference has been attributed to the type of bone studied and to a small sample of different sections of the large bone.

In a related study, Worbel (2007) measured the amount of fluoride of bones from the Maya archaeological site in Belize. Based on the results of analysis of bone samples, that have been relate to the various periods of the Maya civilization, the fluorine content varies from 0.337 to 1.759%, which could be used to the relative dating of the samples and their burial time sequences.

Lyman et al. (2012) have also measured the amount of fluoride in the Black Bear's bones in the Lawson Missouri Cave (US), dating back to about 630 to 136 BP. Due to the low age of the samples, their fluoride content is also lower and has been reported between 390 and 1797 ppm. However, their relative dates have been successfully established with respect to the amount of fluoride present, where the results obtained have been verified by radiocarbon dating method.

As it was mentioned, the phosphate ion causes the results of fluorine measurement to be incorrect. In other words, phosphate removes fluoride ions from the bone environment and causes its concentration to be less than the actual amount. Therefore, the amount of phosphate ions in the samples was also measured, and the results were presented in Table 2. Then, equation 2 was used to calculate net fluoride content of the samples. (Table 2)

Doing this correction, it is possible to measure the effect of phosphate ion on the experiment results, eliminate its interference, and provide more reliable results. According to the above description, the net fluoride content of the samples was measured (Table 2), and consequently, the priority and posteriority of their burial time was determined.

Figure 4 shows the correlation between fluoride and phosphate amount of the samples. As it could be seen, there is no significant relationship between the amount of fluoride and phosphate in the samples and consequently, the values of the measured fluoride cannot be corrected using a mathematical equation. Therefore, it is always necessary to measure the amount of phosphate concentration in the samples and calculate the amount of net fluoride value by Equation (2).

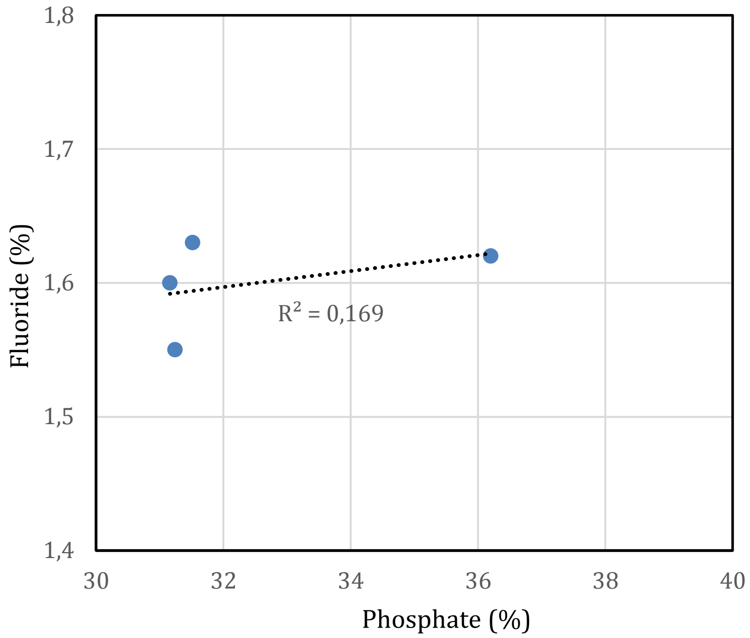

Figure 4. Correlation curve between fluoride and phosphate of the samples

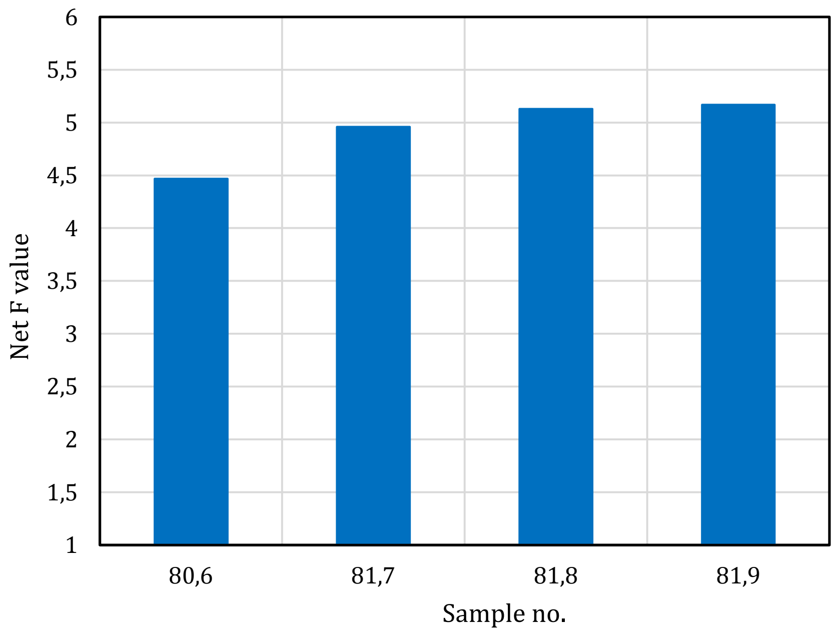

Figure 5. Net fluoride content of the samples

Given that when the level of fluoride in the bone is high, it shows that the bone has passed longer time under the soil and has an older age, it could be concluded that the sample no. 81.9 has absorbed more fluoride than other samples (5.17), and consequently, its burial time is more ancient. The sample no. 80.6 has less fluoride than other samples (4.47), so its burial time is more recent. Also, by comparing the net fluoride content of other two samples, no. 81.8 and no. 81.7 (with 5.13 and 4.96 net fluoride content, respectively), it can be concluded that the sample no. 81.8 is older one and has passed more time under the soil. (Figure 5).

The relationship between soil fluoride, as an independent variable, and bone fluorine, as dependent variable, has been studied. Regarding the regression diagram, when the amount of soil fluoride (as the independent variable) rises, the amount of bone fluoride decreases. This dependence is shown in Figure 6.

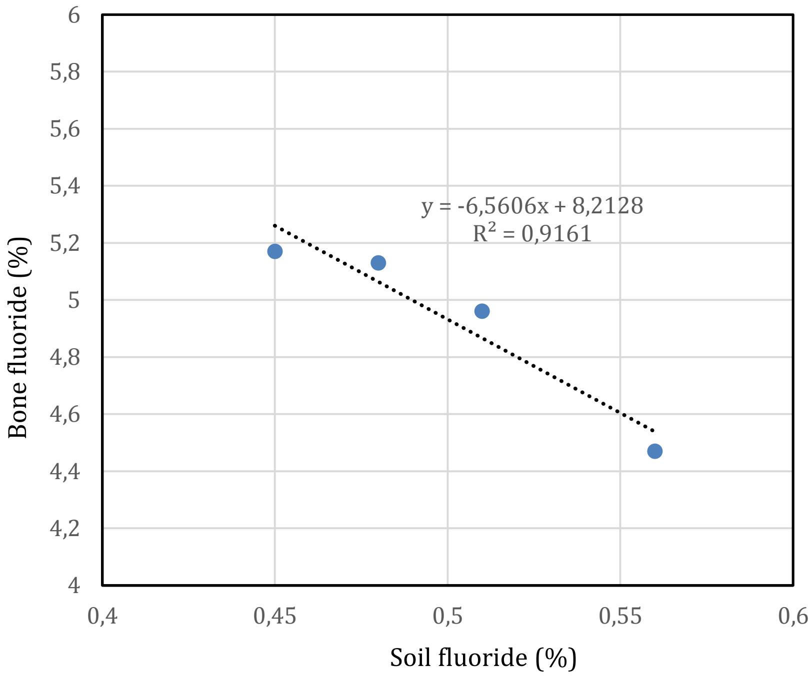

Figure 6. Relationship between soil fluoride and bone fluoride

It could be seen that there is an inverse linear correlation between soil fluoride and that of bone (R^2=0.9518). This correlation could be expressed by Equation (3).

Bone fluoride (%) = -6.5606 × Soil fluoride (%) + 8.2128 (3)

Worbel (2007) has also reported this kind of negative relationship between soil and bone fluoride. On the other hand, the low concentration of fluoride in the surrounding soil compared to that of in the bone, shows that there is not a dynamic equilibrium between soil and bone fluoride (Eq. 1), which proves that fluorapatite is chemically stable, enough.

Different factors relating to the microenvironment of individual graves could also affect the fluoride transportation rate between bone and the surrounding environment and consequently, the amount of bone fluoride. One of the most important influential factors is the soil pH, where it has been shown that more acidic soil will tend to make ions more mobile, increasing the rate of fluoride absorption in bone (Molleson 1990). To find the relationship between soil pH and the bone fluoride content, pH levels of the soil samples of graves was measured using a pH electrode (Figure 7), where the soil pH was ranging from 7.26-7.56. As it could be seen, there is an almost linear correlation between the pH levels and the fluoride content of the bones (R^2=0.9518). This dependency could be expressed in the form of a linear regression (Eq. 4).

Bone fluoride (%) = -2.4038 × pH + 22.691 (4)

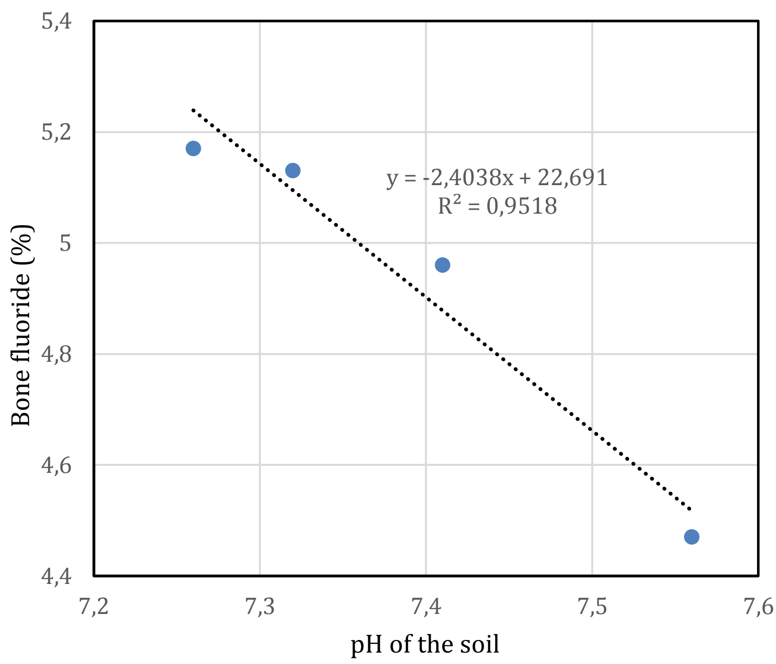

Figure 7. Relationship between bone fluoride and soil pH

It has been shown that during the initial decay of soft tissue, pH levels in the soil become temporarily more acidic, and consequently, the fluoride mobility will be accelerated (Worbel, 2007). After a while soil pH will neutralized, where this could be the reason of low pH variations in different graves of the site.

4. CONCLUSION

Dating of archaeological bones of the Iron Age site of Blue Mosque (Kabud mosque) in Tabriz, IRAN, was successfully materialized by the measurement of their fluoride content. In this way, the ribs bones of the samples were prepared by according to the standard methods and their fluorine content was measured by UV-Vis spectrophotometry method. Totally, four bone samples of the skeletons of the cemetery were selected to be relatively dated. On the basis of their net fluoride content, sample no. 81.9 is the first buried one (net F = 5.17), while sample no. 80.6 has lowest amount of fluoride (net F = 4.47). Also, comparing the relative age of the two samples, no. 81.7 and no. 81.8, it can be concluded that sample no. 81.8 (net F = 5.13) has spent more time under the soil. The relationship between soil and the bone fluoride content has also been investigated, where a good linear correlation was found (R^2=0.9161). Moreover, it was shown that the soil pH has a negative effect on the fluoride content of the bone. In this case, there has been a good negative correlation between the soil pH and the bone fluoride content (R^2=0.9518).

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