# THE PRESERVATION OF BONY SUBSTANCES IN THE SOIL OF PREHISTORIC SITES (1)

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Although there are many instances in which animal bones, horns, and human bones have not been found in the refuse deposits, this does not warrant the conclusion that they had never been buried at the sites in question. It is necessary to ask in such cases whether the bony remains might not have been lost in the relatively short period of time that had elapsed. At least it may be safer to assume that all the refuse deposits once contained bone remains to some extent unless it can be proven that there had never been any such remains deposited at the sites. In contrast to refuse deposits, the Japanese shellmounds usually contain bony remains.

In order to find the explanation for this difference between the two kinds of sites, I conducted some studies on the nature of the soil samples from each of them.(2) I also considered the nature of the various bones and the possible chemical changes which one might expect of these remains in the two types of soils. In doing this I assumed that there had been no basic changes in the nature of the soil since prehistoric times.

## The Soils of the Sites

As the refuse deposit I chose the one at Kitami-machi, Setagaya-ku, Tokyo where earthen wares of the Middle Jomon period have been found. Pieces of earthenware, stone implements and pieces of tiles, but no bony remains, were found here. The shellmound at Ubayama, Chiba prefecture, where earthenware of the Middle Jomon period was also found, was chosen as the other site. Many bony remains were uncovered in the shell layer. Some human skeletons were found in the soil layer below the shell layer and above the loam layer.

The cross-sections of the accumulated layers at the two sites are similar to the ones at Kitami Sites Nos. 1 and 2 which were previously reported in the Journal of the Anthropological Society of Japan. The lower Kantow loam layer consists of volcanic ashes and the upper black soil layer of sand brought here by the wind and of decay products from vegetation. There was no material difference in the mineral content of these two layers. According to Nakao (1932-1941) the loam layers at the two sites have similar soil and mineral compositions. The soil of volcanic origin belongs to the diluvial soil from the geologic viewpoint and is found widely in Hokkaido, Honshu, Shikoku and Kyushu. It constitutes the hill at the site and has a great capacity for retaining water. It is high in iron content, but scanty in base; the top layer as a whole is slightly acidic.

The nature of the soil is dependent on the mother substances it contains, the elements that arise after the decomposition of these substances, and particularly on the climate and the topography. Our country has a mild climate and abundant rainfall, so that the water which percolates through the soil carries various substances, causing a decrease in soluble contents and an increase in plant decay products. This washing process is naturally more effective on the high spots and hills while the soluble substances accumulate in the lower places. In general the soil from which bases are washed away becomes acidified, and the places where these accumulate become basic. In our country the neutral or basic soils are found only in association with limestone or in places where bases accumulate as mentioned above. According to Arrhenius (1926) the acidic soil below pH7 makes up 83% of the total in Denmark, 74% in Sweden, 52% in Italy, 0% in Egypt, 14% in Java, and 95% in Japan. It is characteristic of Japanese soil that the acidic region occupies the major portion (Watanabe, 1949).

The characteristic feature of shellmounds is that they are locally basic in reaction, representing an exception to our soil. This reaction is caused by the fact that the inorganic constituents of the shell are chiefly argonite crystals from which $CaCO_3$ is hydrolized and gives rise to base. The Ubayama shellmound and the Kitami refuse deposit are both on flat tabletops, have similar geological backgrounds, and are subject to identical conditions of climate and precipitation. The fundamental difference between the two stems from the reactions due to shell, so that this becomes of primary importance in this study.

The acidity of the soil is caused by the H ions arising from the soluble acids and the H ions adhering to the soil particles. The soil colloids are negatively charged particles and are surrounded by $Ca^{++}$, $Mg^{++}$, $Na^{+}$, $K^{+}$, and $H^{+}$. As the water containing various substances flows through the soil, some cations are replaced by the $H^{+}$; the more $H^{+}$ adhere to the particles the more acidic the soil becomes.

The colloid particles to which $H^{+}$ ions are attached may be looked upon as free acids, but unlike ordinary acids these are insoluble since they are the collections of many atoms. These adhering $H^{+}$ ions go into solution when the soil is treated with KCl or NaCl. The adhering $Ca^{++}$ ions are then also replaced. The acidity due to these replaced $H^{+}$ ions is called the exchangeable acidity, and the freed $Ca^{++}$ is called the exchangeable Ca. As the soil becomes more acidic the exchangeable acidity increases.

I examined the pH, exchangeable acidity and exchangeable Ca of a water suspension of the soils of the sites (Table I). The 1% citric acid soluble P content of the Kitami refuse deposit was reported in a previous article (Watanabe, 1949). The method used was that used in soil science.

The $CaCO_3$ of the shell is very insoluble in pure water but is soluble in $CO_2$-containing water, producing $Ca(HCO_3)_2$. The rainwater contains atmospheric $CO_2$ and thus is acidic so that as it passes through the soil it dissolves many substances and increases in its acidity. As a result the shells in the acidic soil are gradually dissolved when washed by the water. However, when the layer of shell reaches a certain thickness only the shells on the top are dissolved. The shells on the bottom are no longer soluble in $H_2O$ saturated

## TABLE I

### The pH Exchangeable Acidity, Exchangeable Calcium at Kitami and Ubayama Sites

### KITAMI REFUSE DEPOSIT

| Depth cm. | pH | 1st Lot Exch. Acid | 1st Lot Exch. Ca | 2nd Lot Exch. Acid | 2nd Lot Exch. Ca | 3rd Lot Exch. Acid | 3rd Lot Exch. Ca |
|---|---|---|---|---|---|---|---|
| 10 | -- | 7.9 | 117.6 | -- | -- | -- | -- |
| 20 | 5.45 | 5.2 | 137.9 | 7.7 | 136.9 | 8.7 | 129.9 |
| 30 | -- | 3.9 | 195.4 | -- | -- | -- | -- |
| 40 | -- | 3.4 | 153.6 | 7.7 | 171.4 | 7.1 | 137.8 |
| 50 | 5.59 | 3.6 | 159.9 | -- | -- | 5.1 | 149.4 |
| 60 | -- | 2.8 | 150.5 | 8.9 | 119.6 | 4.8 | 163.5 |
| 70 | -- | 2.9 | 115.5 | 8.0 | 124.3 | 3.9 | 132.7 |
| 80 | 5.54 | 3.1 | 122.3 | 5.9 | 135.3 | 4.8 | 108.2 |
| 90 | -- | 1.5 | 101.4 | 4.4 | 83.6 | 5.4 | 123.3 |
| 100 | -- | 1.1 | 88.8 | 4.1 | 79.9 | 4.3 | 107.1 |
| 110 | -- | 3.0 | 107.6 | 4.4 | 62.7 | 4.2 | 72.1 |
| 120 | 5.79 | 5.3 | 128.5 | 3.1 | 61.1 | 3.0 | 85.5 |
| 130 | -- | 5.2 | 87.3 | 3.0 | 46.0 | 2.7 | 53.3 |
| 140 | 5.75 | 3.4 | 107.6 | -- | -- | -- | -- |
| Floor layer | 5.71 | 5.5 | 81.0 | | | | |

### UBAYAMA SHELLMOUND

| Depth cm. | | pH | Exch. Acid | Exch. Calcium 1st Filtrate | Exch. Calcium 2nd Filtrate |
|---|---|---|---|---|---|
| 60 | Layer above Shell layer | 8.05 | 1.0 | 358.8 | 164.0 |
| 80 | Shell layer | 8.14 | 1.3 | 594.5 | 164.0 |
| 110 | Layer below Shell layer | 8.07 | 1.5 | 584.3 | 143.5 |

TABLE II

pH OF VARIOUS SITES

<u>Refuse Deposit at Toyooka, Saitama prefecture</u>

| | | |
|---|---|---|
| Bottom of Middle Period Pit | 25 cm. | 6.09 |
| Same | 10 | 6.09 |

<u>Refuse Deposit at Senmaihara, Mishima City</u>

| | | | |
|---|---|---|---|
| 10 cm. | 5.85 | 40 cm. | 6.11 |
| 20 | 5.73 | 50 | 6.11 |
| 30 | 5.63 | 60 | 6.38 |

<u>Shellmound at Hikozaki, Okayama prefecture</u>

| | |
|---|---|
| Layer under Shell layer | 8.45 |
| Near Human Skeleton in Shell Layer | 8.47 |

<u>Shellmound at West Kyuhonmaru in Imperial Palace</u>

| | |
|---|---|
| Layer above Shell layer | 7.66 |
| Shell layer | 8.15 |
| Layer below Shell layer | 7.87 |

with $Ca(HCO_3)_2$. The operation of this principle is the reason why a shell-mound in acidic soil is fairly well preserved over a long period of time.

## The Composition of Bone

The chemical composition of human skeletal material, dentine, and enamel is as shown in the table below.

| | Organic | Inorganic | | | |
|---|---|---|---|---|---|
| | | $P_2O_5$ | CaO | MgO | F |
| Bone | 30-40% | 40.3 | 52.2 | 1.2 | 0.1 |
| Dentine | 29.2 | 42.7 | 53.9 | 2.1 | 0.7 |
| Enamel | 6.8 | 43.7 | 54.0 | 0.8 | 1.8 |

The inorganic composition of bone was taken from Berzelius et al mentioned by Funaoka (1930).

The tooth composition was from Bertz as mentioned in Shibata's "The Structural Studies of Tooth."

The organic portion also contains some fat but the principal structural component of the bone is a tough protein called ossein. The enamel of a tooth hardly contains any organic substances but is characterized by a high F content and is the strongest substance in the entire animal body. The chief component of the inorganic substance has been identified as apatite from the X-ray crystographic study and I have personally confirmed this by X-raying some powders of human bones. There are many theories as to the detailed structural composition of the bone, Bale (1940) suggesting hydroxyl-apatite. The general formula for apatite is $3Ca_3(PO_4)_2CaX_2$, in which X can represent acidic ions, F, Cl, OH, etc. Although fluorapatite is believed to be present in the F-rich enamel, its presence has not been verified by the X-ray powder analysis. The crystals of apatite in bones and teeth are extremely fine-- $2.4 \times 10^{-6}$ cm in the dentine and $2.7 \times 10^{-5}$cm in the enamel, according to Bale and others (1934), who also showed that the apatite in the enamel of a tooth is in a special arrangement. Henschen and others (1932) showed the ossein of long bones to have a spiral fibrous structure by rotation X-ray photography. The apatite in the bone is generally believed to be in irregular arrangement although there are some reports which state that like ossein it is in spiral arrangement. Ossein fibers and apatite crystals are believed to be held in place by adherence.

The exchangeable acidity was determined by Daikuhara's KCl method. The total acidity was taken as 3 times the amount of 0.1 N NaOH consumed in the first suspension $H_2O$. (3) The exchangeable Ca was determined on the suspension water used for determining the exchangeable acidity by Shiwoiri's microanalytic method. For the samples from the shellmound, Ca was determined on the 2nd filtrate obtained by adding the same amount of KCl solution to the residue which was obtained upon filtering the initial KCl suspended shell sample. The values given are for 100 g air-dried samples.

The characteristic chemical and anatomical structures of bone discussed above are of importance in considering the changes that the bones undergo in the soil. Although the bones of animals may be chemically and anatomically different from those of humans, the differences may be of minor importance in discussing their preservation. Horn and deer antler may be treated similarly to bones.

## The Preservation of Bones in the Soil

The apatite making up the inorganic constituent of the bone is easily soluble in various acids. In nature apatite is sparingly dissolved in $CO_2$-saturated $H_2O$ at normal temperature and pressure. Under 3.5 times atmospheric pressure $CO_2$-saturated water was found to dissolve 1.82-2.12% of the $P_2O_5$ and 1.95-2.17% of the CaO in 50 days (Doelter). Part of the $CO_2$ dissolved in $H_2O$ becomes $H_2CO_3$ and the $H_2O$ is slightly acidic. Since the water seeping through the acidic soil dissolves $CO_2$ and other substances and becomes acidic, it may be seen that the inorganic substances of the bone are dissolved easily by the $H_2O$. The inorganic P combines chiefly with Ca in basic or neutral soil and with Fe or Al in acidic soil. It combines with Ca to form $Ca_3(PO_4)_2$ and in soil rich in $CaCO_3$ it is said to exist as practically insoluble carbonato-apatite $3Ca_3(PO_4)_2 \cdot CaCO_3$. $Ca_3(PO_4)_2$ is at least soluble at pH 7-8, the solubility increasing suddenly below this pH. These facts indicate that apatite, the inorganic constituent of bone, is easily soluble in acidic soil and hardly soluble in such basic soil as the shellmound rich in $CaCO_3$.

However, for the preservation of bones, not only the inorganic constituents but also the decomposition of the closely bound ossein and other organic substances must be considered. The organic component is mostly decomposed by the soil bacteria, but these simply serve to weaken the basic structure of the bone, thereby calling physical decomposition into play. This decomposition produces acid which attacks the inorganic constituents, causing organic and inorganic decomposition to occur simultaneously. The decomposition of protein, fat, and carbohydrate in ossein on the surface of bones, in marrow, and in tubular structures give rise to various organic and inorganic acids, while the $CO_2$ eluted gives rise to $H_2CO_3$, all of which aid in the decomposition. In neutral and basic soil the bacterial decomposition is catalyzed chiefly by bacteria and ray fungi and in acidic soil by ciliated bacteria. Bacterial activity is most important in neutral or slightly basic soil. The bacterial decomposition of fibrous structures in decaying vegetation also gives rise to acids which help in dissolving the inorganic bony material. When $CaCO_3$ exists in the soil the particles become composite, assuming neutral or basic reactions, and although the organic decomposition takes place, the acids formed are immediately neutralized and are unable to dissolve the inorganic bony constituents. Thus, the decomposition of ossein cannot progress into the interior of the bone and the bones can be preserved well.

According to Tables I & II Ubayama and other shellmounds had pH of 7.66-8.47 whereas kitami and other refuse deposits showed pH of 5.45-6.38. The bones were preserved in the former but not at all in the latter. The exchangeable acidity at Ubayama is around 1, at Kitami 1-8; at the 1st Lot (30-110 cm) it is lower than other places and higher in the $B_2$ layer. The exchangeable Ca is over 500 in Ubayama and 40-200 at Kitami. The former quantity is due to the presence of $CaCO_3$, whereas the latter shows variation with lot and depth as well as with exchangeable acidity, and is higher at Lot 1 $B_2$ layers. As far as exchangeable Ca goes, its ratio to the total exchangeable base should have been computed, but this step was omitted. There is no doubt that the nature of the soil at Kitami and Ubayama shows quite a contrast.

If bony remains did once exist at Kitami refuse deposit and if they were later dissolved, it is conceivable that the P formed very insoluble Fe and Al compounds and is still present in the soil. With this in mind, the P content of the soil was analyzed around the vertical hole and shown to be 10 to 50 times higher there than at other places (previously reported). This P was 1% citric acid soluble P and represents only a portion of the total P. The $B_2$ layer at Lot 1 is black and shows rich vegetation decay which points to the artificial accumulation of vegetation by man, consequently the P and other P-rich substances need not necessarily have come from bones. Since the $B_2$ layer at Lot 1 was relatively rich in Ca, it was thought that perhaps some pulverized remains of apatite existed there. A negative result was obtained by the X-ray powder analysis, however. Even if the apatite corresponding to the known amount of P exists, it is doubtful that the X-ray method can detect it.

As far as Kitami site goes, although it is clear that the preservation of bone here is impossible, it was not possible to prove conclusively that the bones once existed here. However, it cannot be overlooked that, when an ancient tomb was dug at a hilly point about 300 m to the east of Kitami, thin pieces of chemically resistant enamel were found although not a piece of bone was discovered in a stone compartment. Similarly, when Kamiwo dug a shellmound at Nojima, Kanagawa, he found an alignment of animal teeth but no bones. I was told that the nature of the soil there is such that cotton clothes were attacked. It is believed that at Nojima shellmound strongly acidic substances were introduced there relatively recently by some unknown cause and, as at the ancient tomb of Kitami, resulted in the disappearance of the bones. There are examples from Europe showing that even when the original material is completely decomposed some substance is left behind which serves to differentiate the remains from the soil, or else the outline of the material leaves a negative imprint. These remains can be recognized by a careful search at the time of excavation; sometimes the existence of a substance can be guessed at even though everything is completely destroyed. But these deductions require more than just careful observation at the time of digging.

Referring to some reports on the chemical changes of bones in the soil and their rates of changes, Inoue and others (1936) buried rabbit bones for six months to four years and then determined the C & N contents. After four years the ossein showed no material changes in the content of these elements but there was a definite decrease in the bulk. The chemical analysis of fossilized bone was conducted widely in the last century by the French for the purpose of estimating the age of the bone. Rather recently Bayle and others (1939) studied the human bone dating from the Acheulean to the present day with respect to content of organic substances, $CaCO_3$ and F but no regular changes with age were observed. Gangl (1936) extracted fat with acetone-ether from bones between 3700 and 5500 years old, and found a difference in the iodine no. Sidersky (1934) found that the ratio of $F:P_2O_5$ increased with age. There are some reports on N content and on changes in ossein with time, but none of these refer to the nature of the soil whence the bones in question came. The time element is not the only factor in the change, since the soil environment is also of importance. Unless the soil factor is constant for all these examples, the changes cannot be a function of time alone.

## Conclusion

It is a well-known fact that the bony remains of prehistoric time occupy a very important place in the study of the culture, the way of life, and the physical features of the ancient man. The physical and chemical resistance of bony remains is the most tenacious of any material except earthenware and stone implements, and their preservative qualities are of importance even for remains of the Paleolithic period. However, the preservation of bones in any condition is generally far inferior to that of earthenware or stone implements. (4)

The problem as to what cultural differences existed between the two groups of people at the shellmound and the refuse deposit arises on the basis of the different numerical relationships found between the earthenware and stone implements at these two sites. The outstanding contrast between the two sites is the presence of bone in one site and its absence in the other. Although the cultural characteristics of a group are subject to some extent to the kinds of natural resources available and to geographic conditions, even uncivilized people were not wholly at the mercy of the environment. The cultural characteristics were maintained by various traditional customs and technical knowledge and these are reflected in the remains. If there were no bony remains at the refuse site from the very beginning, it can be said that there existed a cultural difference in the way the corpse was buried or otherwise disposed of, in the choice of material for food and clothing, in the ways of making bone and horn implements, and in the ways of disposing of refuse between the two sites. However, since the earthenware is of the same nature at the two sites, and on the basis of information gathered from other sites nearby, it seems possible to assume that the bones once existed in the refuse deposit.

The above-mentioned experiment, which was carried out in order to clarify this point, tends to show that the accumulation of implements and refuse substances rich in P had the same purpose at the Kitami site as the process that went to form the shellmound, and that it is not possible to state that there was no deposition of bones or burials at the Kitami site. The absence of bones is, with few exceptions, characteristic of all refuse deposits in our country, since the soil is acidic and prevents the preservation of bone. Consequently it is impossible to say that the presence or absence of bones at the two sites studied bears any reflection on the cultural difference between the two groups.

It is possible that, if no shellmounds had been accumulated during the Japanese stone age, there would be practically no bony remains left. Had corpses never been buried in the shellmounds nor the shellmounds accumulated at the site of burial we would be completely unable to study the physical features of the men of the stone age.

A survey of world soils shows Egypt, Java, part of China and Manchukuo to have extensive basic soils. These areas are suitable for preserving archaeological remains. However, the preservation of bone does not depend solely on the nature of the soil but also on the amount of water and the temperature. That is, the presence of solvent is required for the decomposition of the inorganic constituent, but the progress of decomposition awaits the removal of decomposition products. For organic decomposition, water content and temperature range must be suitable for the microorganisms. If the soil is too dry organic substances and bony remains are often discovered. The rare preservation of some remains at Inume-cave at Izumo may be explained in this way. The preservation of a mummy seems to depend on this condition. On the other hand, in places like peat-bogs where moisture is excessive, the interior is deficient in $O_2$ and is highly reduced. The organic decomposition here is very incomplete, carbohydrate is partially carbonized, and the original remains are preserved. The decomposition here is purely chemical. It is a well-known fact that the preservation of frozen remains is exceptionally good. Limestone areas and the caves therein preserve bones on the same principle as do shellmounds. In our ancient tomb, some remains were well preserved because of the special treatment given them.

I have dealt here with only one special phase of the preservation of the remains at various prehistoric sites. It is very important to determine whether the remains in question never existed there at all, or whether they were lost by decomposition after deposition. The proof that a type of a remains never existed at a particular site or during a particular period is just as significant as the proof that it existed.

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## NOTES

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(2) This research was aided by a Scientific Research Grant from the Ministry of Education.

(3) The pH of the water suspension was determined by quinhydrone electrode on fresh distill-water samples.

(4) Even the very resistant stone implement is not always preserved, its resistance depending on the nature of the original material, the nature of soil environment and time. For example, the stone axe found at Kitami is made of shale which contains siderite. The interior is grey and strong but the surface is covered with a thin layer of yellowish limonite, some of which is pulverized so that the sharp edge is almost lost. This type of shale is found at the upper reaches of the Tama River. It is possible that the rock carried by the river was picked up and used by people living in the vicinity. Siderite is $FeCO_3$ in composition and $CO_2$ is eluted upon treatment with acid. It is conceivable that in the acidic soil the rock is attacked but upon examination under a microscope the rock is found to be made up of fine crystals of siderite and quartz which are closely bound together. Only the surface is attacked, and the limonite layer may be the result of the change of the rock to a stabler form of Fe. If by some means, the surface is removed, deterioration can progress quite rapidly. Thus even the stone implement is not always preserved.

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