The Chemical Analysis of Bone from Glozel

There are many pieces of bone from Glozel which, even with unlimited funds, could not be dated by AMS carbon-14, simply because they are regarded as too precious. Thus a programme of chemical analysis was initiated to determine the amounts of the two elements most likely to indicate the age of each specimen, nitrogen and fluorine. Such analyses require just a few milligrams using modern techniques. Even so, it was recognized from the outset, the exercise was partly to demonstrate the authenticity of the decorated and human bone, and partly to indicate which pieces might be best used for subsequent AMS dating. Chemical analysis, though it will indicate relative trends, is no substitute for carbon dating.

It is known that there are a number of phases at Glozel. The most recent would seem to be the early medieval period and there are a number of ceramic TL dates on vitrified material which indicate a date around 1250. Recent carbon dating of two bone tubes, from Tomb 2, also indicate a similar date. So it may be that the tombs are connected with the glass working of the early medieval period. Then there are the earlier, gallo-roman period, dates. There are a large number of TL measurements which indicate such a dating but the wide spread in these dates is puzzling. There are also two carbon dates which support such a period. And then there is the writing from Glozel, on both ceramics and bone, which in all logic for such a developed alphabet should be of this period as well. Finally, there is a very early Solutrean carbon date from fifteen pieces of bone, carried out before AMS dating was routine.

For all these reasons a preliminary study by chemical analysis of the Glozel bone seemed very desirable. It was recognized that the date of a piece of bone in no way parallels the date of engraving on that bone. But such an analysis is a start and one which it is hoped might lead to useful and continuing work concerning this very complex site.

Nitrogen and Fluorine Analysis

The use of fluorine as an indicator of the relative age of bone goes back to the beginning of the l9th. century. Carnot in France and Middleton in Britain both demonstrated that as bone lies in the ground, so it builds up its fluorine content. The initial fluorine level in bone is about 0.02 % and this increases to around 2 % over many tens or hundreds of thousands of years. The fluorine derives from the very low levels of soluble fluoride in natural ground water. The water flows over the buried bone and the fluorine is chemically trapped by the bone as fluorapatite. Fluorapatite is very stable in other than acid soils. The consistency of the fluorine level at a given site would be expected to say something about the general authenticity of that site and so the technique was considered appropriate for Glozel. Bayle, or more accurately Maheu and Randoin, following the police raid of 1928 at Glozel, analyzed the bone pieces confiscated for their fluorine content and these analyses seem to be valid and quite reliable. The interpretation put on them by Matheu and Randoin is, however, very questionable. Even so, their parallel analyses of bone from many sites and periods is extremely valuable. No other such a comparative list is known.

The use of nitrogen as an indicator of bone degradation follows from a consideration of the protein, collagen (gelatin) present at up to 30 % in modern bone. The collagen contains nitrogen and this amounts, quite consistently, to about 4.1 % in such bone. Burial rapidly decreases the nitrogen level in bone but the rate of decrease has many variables; temperature, pH, soil conditions and water flow to name but a few. It is thus not possible to derive any simple connection between the age of a piece of bone and its nitrogen content. Even so, clearly, with so many claims of modern fraud for the Glozel bone, such an analysis should prove or otherwise the validity of such claims. Equally, with a likely medieval phase at Glozel, nitrogen analysis should help resolve at least some of the likeliest medieval pieces. But, bearing in mind that nitrogen is found in much bone from the entire Quaternary period, it might well not be useful as a pointer for determining the age of bone older than the medieval period. Its main value will lie, really, in detecting whether or not the Glozel bone is modern.

Analytical Techniques

The method used for chemical analysis was ion selective electrodes. The sensitivity of such procedures is such that just a few milligrams would be needed both for fluorine and nitrogen. Modern combination electrodes, such as manufactured by Orion, require no reference electrode for these elements and can readily be used on as little as 2 mls of stirred solution. The detection limit for fluorine is 0.02 ppm (parts per million) and for nitrogen is 0.01 ppm. The other great advantage of using ion selective electrodes is that the millivolts output (the reading) changes by almost exactly the same amount for a ten fold increase or decrease in the concentration of the element being detected. In other words they are invaluable for materials which would be expected to vary considerably in its levels of nitrogen and fluorine.

Fluorine

About 5 mg (0.005 grams) of bone was quantitatively transferred to a test tube and dissolved in 0.4 M hydrochloric acid by warming. 1 gram of this cooled solution was then buffered to a pH of about 4.8 using four drops of an acetic acid/sodium acetate buffer with cresol red indicator. The whole was then diluted to exactly 2 mls and fluoride was determined using the combination electrode. Standards of exact amounts of fluoride in the same buffer were prepared to cover the range detected. The response of the electrode was very rapid, typically two minutes.

Nitrogen

About 5 mg of bone was placed quantitatively in a 50 ml semimicro Kjeldahl flask and 0.20 grams of a potassium sulphate/copper sulphate/selenium mixture was added. I gram of concentrated sulphuric acid was also added and the whole was then digested for half an hour using an electrical pyromantle. The acid fumes were extracted to an external vacuum pump. After cooling for five minutes the whole was taken up in about 10 mls of water then quantitatively transferred to a polypropylene beaker and made up to exactly 20 grams. I gram of this solution was then treated with one drop of thymol phthalein indicator and three drops of 20 % sodium hydroxide were added. The whole was then diluted to exactly 2 mls and the free ammonia was determined using the ammonia electrode. Standards were prepared of exact amounts of ammonium ion in the same sulphuric acid/potassium sulphate mixture. The same procedure for releasing the ammonia gas was adopted. The response of the ammonia electrode was less rapid than that of the fluoride electrode, typically four minutes being taken, with stirring, to achieve a constant reading.

Analytical Results

All the analytical results are detailed in the table which follows on pages 6 and 7. Original Glozel museum numbers have a GF prefix and the Morlet collection, which was later added to the main collection on the death of Mine Morlet, have a 984.2. prefix. There are though a few pieces from this latter collection which have no museum number and these have been identified specifically in the table of analyses. Additionally they can be identified from the photographs which follow the analytical results.

The Gannat results are from a wide range of Quaternary materials provided as useful background reference material. Only bone and ivory items were sampled as teeth have a quite different response to burial.

Conclusions

Two artifacts, harpoons, numbers 984.2154 and 984.2.152, may be modern. Both were identified as different whilst sampling. Drilling modern bone produces, not a powder, but lengthy spirals of bone, and this exact process was noted at the time of sampling. Furthermore both pieces have a nitrogen content around 4 % which is exactly that of modern bone, and both have a fluorine content quite consistent with modern bone. Whilst there may be an explanation which could yield such results, such as possible impregnation with plastic, the provisional conclusion is that both are modern. These are the first such pieces from more than 25 years of studying Glozel, that seem of doubtful provenance.

All the rest of the material is genuinely ancient.

The human bone, which included a femur which had been dated at Oxford to about 1600 BP, seems mostly to be medieval. It is believed that nitrogen values of 2 % and higher almost certainly come from this phase at Glozel. There is even one analysis (GF743) which has 4 % of nitrogen but this may not be modern (the obvious conclusion) as such figures have been found, occasionally, at other sites. And it is quite possible that bone which is medieval in date might well have less than 2 % of nitrogen. Thus the two bone tubes dated by carbon-14 to 700 BP have 1.2 and 1.3 % of nitrogen. So it would seem that the medieval period at Glozel might well yield nitrogen values from I % upwards. The mean nitrogen value may be around 2.5 % but the spread of values around this mean, is likely to go as low as 1 % and as high as 4 %. Such a spread is, unfortunately, perfectly normal and has been reported from a number of sites.

A rather striking confirmation of this situation is that of the bone identified as coming from Tomb 1. The nitrogen values for the three pieces so identified (GF719, GF743 and GF427) are 2.0, 4. 0 and 1. 0 %. It would be hard to see these as other than medieval though the latter may be intrusive. And Tomb 2 has two carbon dates which put that tomb at 700 BP, again medieval. It would be stretching the evidence to suggest that, basically, Tomb I was not like Tomb 2 and that it probably dated also to the early medieval. Bone identified as coming from Tomb 2 are the two carbon dated bone tubes, GF1773 and GF403 as well as a machoire fragment, GF755. All three pieces have nitrogen values varying from 1.0 to 1.3 %. The same conclusion as above probably obtains for the two tombs at Glozel. Namely that a mean nitrogen value of between 2 and 3 % probably holds, but this can fall as low as 1 %.

It might be thought that all the bone from Glozel, human and decorated, could be medieval in date. But such a thought would certainly be in error. Because, firstly, we have a large number of TL dates which are considerably older than medieval, and secondly we have two carbon dates which are again much older. But thirdly, and probably most importantly from the analytical viewpoint, a plot of the nitrogen content versus the fluorine content is particularly revealing. The first chart enclosed plots fluorine on the y axis using a logarithmic scale, so as to include all results, against nitrogen on the x axis. The tipper, right hand part of such a plot contains bone items that are probably medieval in date. The bottom, left hand corner, as drawn, contains within it all but one (984.2.119) of the carved, decorated or alphabeticised pieces of bone. And only one artifact (GF427) is found within this lower, left hand area which may be medieval. There thus seems no reason to doubt that the bone pieces within the lower left hand area are of a different origin from the medieval pieces. The simplest differentiation may be that they are earlier than the medieval period. How much earlier though is more problematic.

If we examine the Gannat analyses we can see some of these problems. Nitrogen should decrease with age and fluorine increase. So material of the age of all the Gannat specimens might be thought to be likely to have little nitrogen and a markedly increased fluorine. And some do indeed have such features. But some do not. The neolithic specimens from Hautaget, GI 0 and GI 1, certainly fit the usual pattern. As ‘indeed do all the other white coloured samples, G06, G13/1, G16 and G17. But material that is coloured does not fit the normal expectations. And unfortunately GI 6 and GI 7 have no attached date. Even so, a simple plot of the nitrogen contents of bone material from modern to the 200,000 BP of La Nauteuil, shows a sensible decrease in nitrogen with time. The second graph thus shows the result of plotting the age of the bone against the nitrogen content. This for modern bone, the three carbon dated bone artifacts from Glozel, GI 0, GI I and GI 3/1. But such can be very deceptive and the curve on the graph has not been used to estimate any ages.

The reason why it has not been used follows from a consideration of the Maheu and Randoin data on 28 neolithic bone samples from 24 different sites. These authors measured the % loss of weight on ignition. Combining their data with the results of Cook and Heizer, who measured the % nitrogen as well as the % loss of weight on ignition, shows that probably nitrogen values ranging from 0.2 to 1.7 % apply to neolithic material. Such, unfortunately, is the way with chemical analyses. What, however, this demonstrates is that the average nitrogen value of the lower left hand area from the first plot, may date to any period back to the neolithic or mesolithic. Accurate dating simply is not possible.

The fluorine values of the Glozel bone require some explanation. The highest values found were 0.21 and 0.36 % from the medieval (carbon dated) bone tubes, the lowest was 0.002 % from the well known chasseur and 0.003 % from a beautifully carved reindeer. Had the bone tubes not been carbon dated their fluorine values would undoubtedly have suggested a much older date. And had the nitrogen values not been so low the latter two pieces might well have been thought to be modern. In fact the fluorine values seem to be reversed, the medieval pieces having the highest values and the older pieces the lowest values. Clearly more work is required but the provisional assessment might be that the longer a piece lies in the ground at Glozel, the lower its fluorine content becomes. The reason might be the unusual burial conditions with the very low permeability of the soil playing a large part in reducing the water flow to and around a buried object.

Even so, the relative uniformity of the fluorine contents of both main groups of bone from Glozel seems a clear proof of authenticity, if such was needed.

Final Thoughts

With two possible exceptions, all the bone analysed from Glozel is genuinely ancient. The carved, decorated and alphabeticised material seems clearly to have a single provenance. There is a medieval period which can clearly be distinguished from an earlier period. The date of this earlier period may, however, be anything from 2000 to 10,000 years.

Hugh McKerrell, Isle of Arran, Scotland 30/03/97

Human Bone

	% Fluorine	% Nitrogen	
GF760	0.010	2.6	human bone
GF737	0.016	2.4	femur gauche
Morlet no number 1	0.017	1.1	femur carbon date 1600 BP
994.2.227	0.062	2A	machoire Morlet collection
GF734	0.008	1.2	femur
GF721	0.028	0.8	femur,
GF754	0.043	2.5	machoire fragment
GF752/748	0.028	3.0	crane
GF755	0.040	1.0	machoire fragment Tomb 2
Morlet no number 2	0.055	1.0	human bone
GF719	0,018	2.0	femur droit Tomb I
GF743	0.022	4.0	crane Tomb I
GF1670	0,006	0.5	reindeer
984.2132	0.011	1.4	reindeer + letters
984.2.167	0.010	I.5	panther
GF306	0.021	1.4	deer running + letters
984.2.118	0.012	Lo	long pendant Tomb 1
GF427	0.005	1.6	
GF1190	0.011	1.3	striations decorated
GF303	0.006	1.9	plaque en os, just letters
GF1853	0.012	0.8	two heads
GF305	0.013	1.0	bovide sur os
GF1680	0.005	1.3	hache en pierre monté
GF1679	0.029	0.8	animal indeterminate
GF1713	0.015	0.7	poignard, bande de chevaux
GF1192	0.11	3.2	small engraved piece
GF1672	0.038	2.1	fish hook ?
GF1819	0.11	Lo	small carved piece
Morlet no number 3	0.035	L4	two animals
984.2.119	0.011	2.6	reindeer and horse facing-
984.2.127	0.006	1.1	reindeer and young one
202.2.154	0.15	4.1	harpoon - drilled unusually
984.2.152	0.011	4.2	harpoon -drilled unusually
984.2.087	0.016	0.9	harpoon
Morlet no number 4	0,025	1.3	harpoon, large
GF1852	0.009	1.3	pendant with letters

Carved, Decorated and Other Bone

	% Fluorine	% Nitrogen	
GFI	0.002	1.3	chasseur loup
GF1848	0.016	1.1	boeuf bondissant
GF1856	0.020	0.9	reindeer
GF311	0.018	1.1	renne grave' sur omoplate
GF1866	0.003	0.8	reindeer
GF1773	0.36	1.2	bone tube, dated 700 BP, Tomb 2
GF403	0.21	1.3	bone tube, dated 700 13P, Tomb 2
GF1816	0.012	1.0	mare suckling
GF3	0.009	1.4	carved head of a man
GF 1818	0.009	1.5	renne blessé
GF1684	0.005	1.0	silex emanché
GF1891	0.020	2.4	decorated bone tube
GF310	0.021	0.5	capride + letters
GF1860	0.011	0.9	pendelogue
GF1771	0.011	1.0	navette
GF1693	0.012	0.8	non determiné
GF1841	0.007	1.0	harpoon
GF1690	0.008	0.7	pendelogue ?
GF1764	0.034	1.4	spatule à ochre
984.2.108	0.012	1.1	pendelogue
GF1766	0.069	1.0	renne phalange Deperet
GF1695	0,008	0.8	renne marchant
GF1716	0,037	1.2	rennes affrontés
GF309	0.021	1.0	troupeaux de chevaux + letters
GF1691	0.008	1.5	comb + horse + letters
984.2.097	0.009	1.1	sanglier (Esperandieu)

Quaternary Material from M Escullier, Rhinopolis, Gannat

	% Fluorine	% Nitrogen	
GOI	1.51	2.4	mammouth, Châtel-de-Neuve, 30,000 BP
G02	0.81	3.8	corne de bos, alluvions de la. Seine, néolithique
G03/2	0.023	2.0	bovidé, Gargas, gouffre de Peyreigne, 18,000 BP
G04	0.015	1.2	cheval, Gargas gouffre de Peyreigne, 18,000 BP
G06	1.00	0.10	ivoire de mammouth, Lyon, fin du Worm
G08	0.041	2.5	ursus spelaeus, grotte Aubert, 40,000 BP
G10	0.29	1.07	bouquetin, Hautaget, Bize, néolithique
Gli	0.37	0.70	cerf, Hautaget, Bize, néolithique
G12	0.006	1.0	Peyreigne (Gargas ?), no date
G13/1	1.27	0.054	ursus deningeri, La Nauteuil ?, Gers, 200,000 BP
G15	0.52	2.3	rangifer tarandus, Unjat, 8,000 - 10,000 BP
G16	0.82	0.19	lynx, Savona, no date
G17	0.11	0.54	lapin, Savona, no date