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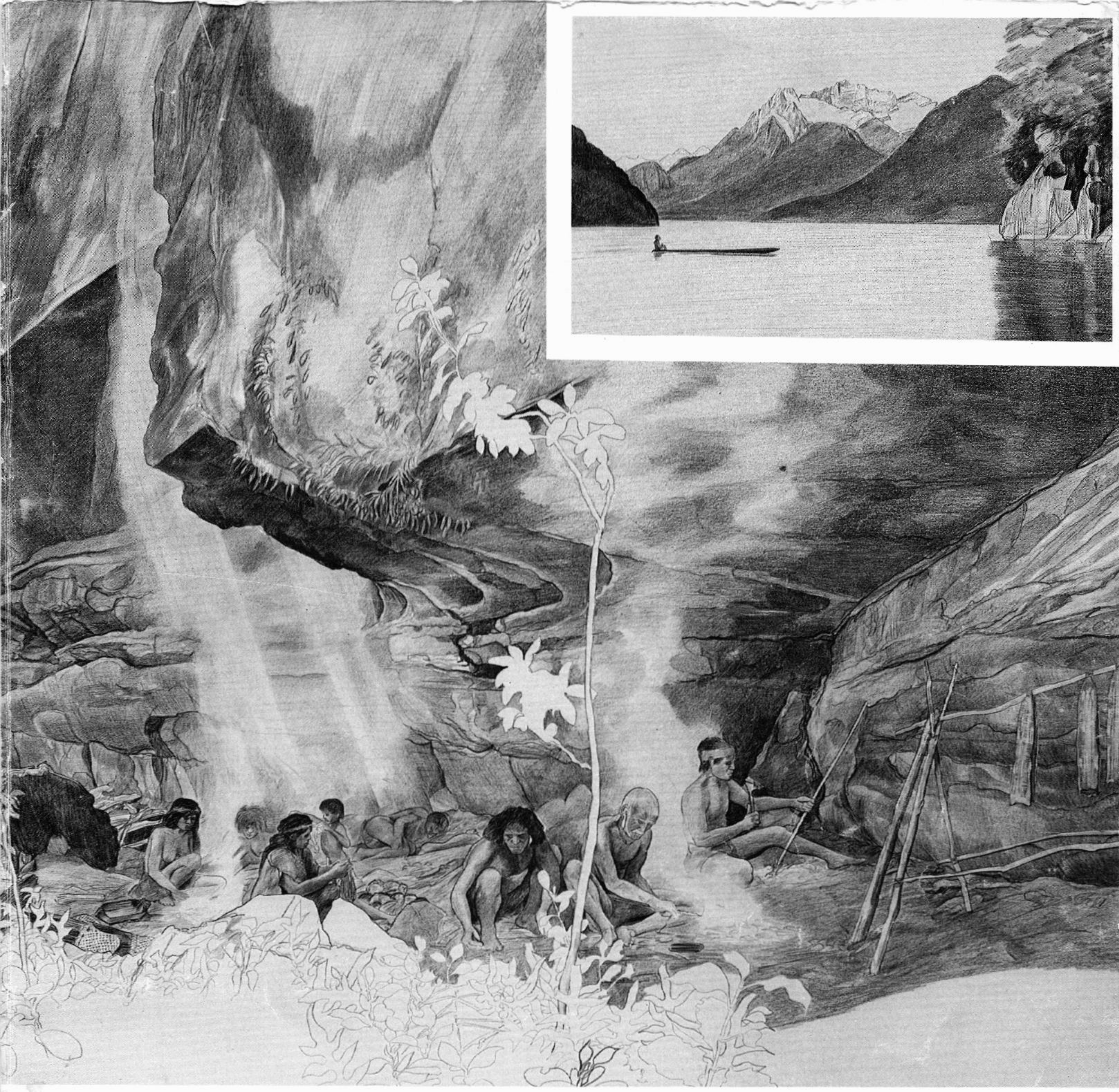
Atholl Anderson and Richard McGovern-Wilson (eds), ***Beech Forest Hunters***



Beech Forest Hunters

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New Zealand Archaeological Association Monograph 18

TRACE ELEMENT ANALYSIS OF HAIR

Richard McGovern-Wilson and Michelle Horwood

On rare occasions samples of human hair have been found in New Zealand caves or rockshelters, as at Monck's Cave (Duff 1977:260-261), the Lake Hauroko burial (Simmons 1968) and in a number of sites in Chalky and Preservation Inlets in Southern Fiordland (Coutts 1972).

The sample from Lee Island was recovered from S131/4, from the adjacent excavation squares: -A11, -A12 and A12. These were close to the shelter wall at the rear of the site and the hair was found in a dry to slightly damp sand and silt matrix at a depth of 50-120 mm. Both the samples of hair are discrete hanks which appear to have been cut from the head and subsequently discarded. In addition to these two samples, the surrounding soil contained a large number of loose hairs.

The larger of the two samples was recovered from Square -A11, Layer 1, and weighed 1.26 g. The hair is light brown to sandy in colour, of a straight to wavy character and measuring up to 79 mm in length. The material from Squares A12 and -A12, Layer 1, is more wavy and browner in colour. The individual hairs measure up to 64 mm in length, and the sample weighed 0.80 g. It was hoped that analysis of these samples would provide information about the age and gender of the people, their diet, and their health status.

Advice from D.S.I.R. consultants indicated that none of the techniques suitable for establishing age or sex were suited to the material from Lee Island, because of the breakdown of cellular material adhering to hair of such age (L. Sharman pers.comm.).

Trace element analysis was used to tackle questions of diet and health. It has been used on prehistoric human bone as a method of determining the relative proportions of meat and vegetable components in the diet and to isolate unusual concentrations of elements which might reflect variations in health or social status. There are various problems associated with the technique, including environmental variation of trace element levels (most notably strontium), as well as diagenetic (post-mortem) alteration of trace element levels, but despite these useful results have been obtained (Horwood 1989). Studies to date, have focussed on strontium (Brown 1973; Helsby 1974; Schoeninger 1979; Szpunar 1977), although other elements have been investigated as well. With regard to diet, strontium, magnesium, manganese, cobalt and nickel can be used to determine the vegetable component of the diet, while zinc, copper, molybdenum and selenium may reflect animal protein consumption (Horwood 1989). An important point to note with regard to the Pacific region where shellfish can provide a significant contribution to the diet, is that heavy metals tend to accumulate in the flesh of some filter feeding shellfish. Elevated heavy metal levels, therefore, may be a result of the consumption of significant quantities of marine molluscs and this needs to be considered prior to interpretation of results.

METHODS

The samples were analysed in the Nutrition Department, University of Otago, by means of atomic absorption spectrophotometry. The method used in the present study had been developed over a period of several years as a result of the regular testing of hair from the mothers of babies born at the Queen Mary Maternity Hospital, Dunedin (J. Parnell pers comm). The amount of material required for this technique is minimal - only 0.34 g of the sample from Square -A11 and 0.22 g of the Squares A12 and -A12 sample was needed. In addition, a sample of hair from the person (Brian Kooyman) who excavated these squares was also run to ensure that the samples being analysed were in fact archaeological and not modern. A total sample of 0.13 g from Kooyman was submitted for analysis along with the Lee Island material.

The preparation of the hair initially involved picking out by hand all plant material and other foreign matter, and then cutting the sample into 5 mm or smaller pieces which were washed in 1% Decon (a non-ionic detergent) on an automatic shaker for 30 minutes. The sample was then rinsed in multiple washes of de-ionized water. Following washing, the hair was dried in an oven for 18 hours at a temperature of 60-80 C, during which it was turned repeatedly to prevent clumping.

Once dry, the hair was ashed in a muffle furnace with the temperature progressively increased at 3-4 hour intervals by 50 degree steps to a final temperature of 450 C. The sample was then allowed to cool, dissolved in 5 ml concentrated Analar HCl (Baker) which was heated to boiling for a few minutes until dissolution was complete, rinsed quantitatively with hot 0.1M HCl, filtered, and made up to 25 ml. The acid extract solutions were analysed undiluted except for zinc, for which a four-fold dilution with de-ionized water was necessary for some samples.

The solutions were analysed by flame atomic absorption spectrophotometry (Instrumentation Laboratories, model IL251) and compared against standard solutions of appropriate concentrations

Table 8.1. Technical details of parameters used for atomic absorption spectrophotometry.

Element	Wavelength (nm)	Slit width (micro m)	Sensitivity (ppm)	Linear range (ppm)
Zinc	213.9	320	.02	1
Cadmium	228.8	320	.01	2
Iron	248.3	320	.04	5
Manganese	279.5	320	.03	3
Copper	324.7	320	.04	4

in 0.1M HCl. Table 8.1 gives the values for the machine parameters used in this study.

There was sufficient sample prepared in all cases to allow for a second run and this ensured that the results were consistent and any high or low values were not due to experimental errors.

RESULTS AND DISCUSSION

The results of the atomic absorption analysis are shown in Tables 8.2-3. Also included are values obtained from the hair of modern vegetarian and semi-vegetarian subjects.

Awareness of the interactions of various trace elements must be considered when interpreting results from this method of analysis. For example, with regard to the elements investigated here, zinc and copper have been described as antagonistic (Blakely and Beck 1981:421), and it might be expected that if the intake of zinc declined, copper concentrations might increase. Small sample size and lack of information on the surrounding soil trace element levels, however, makes it difficult to ascertain whether this is the reason for the resulting Lee Island hair trace element concentrations. Other factors which require consideration relate to the physical well-being of the individual under study. For example it

Table 8.2. Concentrations of trace elements for the Lee Island and modern hair samples in parts per million (ppm).

Sample	Number	Zinc	Copper	Manganese
S131/4 -A11	1	16.0	73.2	18.6
	2	14.8	72.6	19.2
S131/4 A/-A12	1	11.6	64.8	0
	2	12.5	65.9	0
B.K. (modern)	1	116.6	0	0
	2	117.4	0	0
	3	116.0	2.0	-
	4	121.0	1.0	-
Subject L.M.	1	109.0	11.0	-
	2	111.0	13.0	-
Subject S.J.	1	108.0	16.0	-
	2	105.0	17.0	-
Subject C.B.	1	112.0	14.0	-
	2	115.0	15.0	-

Table 8.3. Means and standard deviations for the repeat runs of zinc, copper and manganese in ppm for the Lee Island and modern hair samples.

Notes: 1. n = number of reruns; 2. +- figures are the standard errors.

	Mean	Standard deviation
S131/4 -A11		
n = 2		
Zinc	15.4 +- 0.35	0.693 +- 0.25
Copper	72.9 +- 0.17	0.346 +- 0.12
Manganese	18.8 +- 0.17	0.346 +- 0.12
S131/4 A/-A12		
n = 2		
Zinc	12.1 +- 0.26	0.520 +- 0.18
Copper	65.4 +- 0.32	0.634 +- 0.22
Manganese	not detected	
B.K. (modern)		
n = 4		
Zinc	117.8 +- 1.12	2.241 +- 0.79
Copper	1.5 +- 0.29	0.577 +- 0.20
Manganese	not detected	
L.M. (modern)		
n = 2		
Zinc	110.0 +- 0.58	1.155 +- 0.41
Copper	12.0 +- 0.58	1.155 +- 0.41
S.J. (modern)		
n = 2		
Zinc	106.5 +- 0.87	1.732 +- 0.61
Copper	16.5 +- 0.29	0.577 +- 0.20
C.B. (modern)		
n = 2		
Zinc	113.5 +- 0.87	1.732 +- 0.61
Copper	14.5 +- 0.29	0.577 +- 0.20

been demonstrated that zinc deficiency may result in marked growth retardation, lowered disease resistance, and reduced wound healing abilities (Halstead et al. 1972; Hambidge et al. 1972; Chen et al. 1985).

The results of several previously published studies of trace element levels in modern hair samples are presented in Table 8.4 for comparison. As can be seen the Lee Island concentrations of both zinc and copper are well outside the range of values obtained in these other studies. The reason for this is not readily apparent. One possibility is that the Lee Island samples reflect a predominantly vegetarian diet. To examine this proposition hair samples were obtained and analysed, as above, from three subjects who had different diets (see Table 8.2). Subject L.M. had eaten very little meat for the past 10 years (red meat once a fortnight, chicken once a fortnight, and fish twice per week). Subject S.J. had eaten no red meat for a year but ate some fish and chicken less than once per week. Subject C.B. had eaten no red meat, fish or chicken for two and a half months and consumed, instead, bread, butter, some cheese

Table 8.4. Published data on zinc, copper and manganese trace element levels in hair in ppm from modern and prehistoric groups.

Notes: 1. R = range; 2. +- figures refer to standard errors of the mean; 3. sex is given where possible, and as far as could be determined only adult individuals have been considered.

Source	No.	Sex	Zinc	Copper	Manganese
1	41	male	x=180 SD=25 R=138-231		
1	54	female	x=195 SD=23 R=154-277		
2	97	male	x=184 SD=66	x=16 SD=9	
2	95	female	x=205 SD=93	x=22 SD=18	
3	122		x=179 R=81-314	x=14.5 R=6.9-35.5(1)	
4	82	male	x=167+-5.1	x=16+-1.2(2)	
4	47	female	x=172+-9.3	x=56+-10.3	
5	33		x=177 R=51-602	x=34 R=7.8-234	x=2.1 R=0.08-22
6#	1	female	54.6	9.1	31.5
6#	1	female	91.9	10.6	82.1
6#			128	8.7	10.8
6			212	10.1	-0.35
6			158	10.3	4.2
7	7	male	x=159 SD=25 R=121-195		
7	8	female	x=190 SD=44 R=103-236		
8	88		x=180+-4		
9	32	male	x=250 SD=96	x=11 SD=2	
9	34	female	x=155 SD=61	x=10 SD=3	
10#	8		x=343+-208 R=122-645	x=16+-10 R=9-39	

(1) n = 114, (2) n = 79

Sources:

1. McKenzie 1979: 572, modern
2. Briggs et al. 1972: 407, modern
3. Harrison et al. 1969: 89, modern
4. Schroeder and Nason 1969: 72, modern
5. Bate and Dyer 1965: 80, modern
6. Toribara and Muhs 1984: 106, modern and prehistoric (#)
7. Gentile et al. 1981: 124, modern
8. Hambidge et al. 1972: 868, modern
9. McKenzie et al. 1978: 424, modern
10. Benfer et al. 1978: 280, prehistoric (#)

and large amounts of fruit. The results (Table 8.2) show that measured variation between these modern subjects is minimal (max.= 7 ppm), and it could possibly be due to the consumption of fish. These results are still much higher for zinc than in the Lee Island samples. It is possible that the Lee Island individuals were virtually wholly vegetarian and that this accounts for the very low zinc levels or, in addition, that the high-fibre diet binds the available divalent zinc cations in the large intestine, thus further reducing the levels (R. Beyer pers.comm.).

Alternatively, environmental contamination may have played a significant part in the trace element levels. An acidic environment will tend to cause leaching and, or, addition of trace elements which will produce levels above or below those occurring naturally. Soil acidity must be minimal (pH > 5) if ionic replacement of trace elements is to be deterred. Although the soil acidity of the Lee Island site was not determined at the time of the excavations it is assumed that this is not an acidic environment as this area consists of limestone. In this case, however, it may be that zinc was seriously affected by leaching, and that copper was affected also by diagenetic processes. In addition these two elements are antagonistic in nature, so that an increase in copper absorption will act to reduce zinc.

CONCLUSIONS

The Lee Island hair samples provided no clear indications of the diets of the individuals concerned. Zinc levels were well below, and copper levels somewhat above, those obtained in other studies. Several explanations have been offered for this situation. Firstly, that the levels reflect extreme vegetarianism, and secondly that diagenetic processes are involved. The latter seems particularly likely, given the situation of the samples beside the rear wall of the shelter where the soil was damp because of periodic run-off from the the drip-line down the shelter wall.

There have only been two reported studies of trace element levels in prehistoric hair samples (Benfer et al. 1978; Toribara and Muhs 1984) and until more cases come to light it will not be possible to say more about the Lee Island evidence.

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