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Elemental Analysis of Siwalik Fossil Bones Using X-ray Spectrometry

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X-ray fluorescence technique is employed to determine the concentration of Ca, Ti, V, Mn, Fe, Cu, Zn, Sr, Y and As in Siwalik bone samples collected from five different locations. The concentration of Ca, the major constituent, is found to vary from 40.00 to 65.60%. U content in these samples as determined by fission track technique varies from 37.5 to 418.0 ppm. Inverse correlation between U and Ca is obtained in all the samples. The high value of Fe (6.52%) in molar teeth of Stagdon supports our earlier findings by fission track analysis for U enrichment in Ferruginous matrix. An enrichment of Ti, V, Cu, Y and As (path finder elements of U) is reported in the some bones with anomalous U content.

The presence of sceondarily enriched uranium in Siwalik fossil bones has been reported by various workers[1-4]. Sharma *et al.*[4] were the first to estimate the uranium distribution in a Siwalik vertebrate fossil and they concluded that the uranium present in the phosphatic and ferruginous substance in the bone shows a sympathetic linear relationship with the consituents of the bone. Sahni *et al.*[5] have established that Siwalik mammals exhibiting ferruginous calcic replacements show a higher concentration of U in comparison to mammals exhibiting to a large extent non-ferruginous, calcareous and siliceous matters during fossilization process. Singh *et al.*[1] have observed U enrichment in ferruginous matrix of molar teeth of Stagdon by fission track radiography. The present elemental analysis using XRF technique is undertaken to confirm the above observation and to study the possible correlation and enrichment of some other elements (viz. Ca, Ti, V, Mn, Cu, Zn, Sr, Y and As) with uranium.

Experimental technique—The elemental analysis of the fossil bones was carried out using X-ray fluorescence technique[6]. Brief description of the experimental procedure is as follows.

The samples in the form of thin pellets were bombarded with X-rays using an X-ray tube (Mo anode). Characteristic X-rays induced due to different elements present in the samples were analysed using the X-ray spectrometer arrangement consisting of Si(Li) detector coupled to a mutichannel analyser. A characteristic X-ray spectrum of a fossil bone sample (FN1) is shown in Fig. 1. The concentration of different elements were determined from the intensity of characteristic X-ray peaks.

Results and discussion—The elemental concentration of Ca, Ti, V, Mn, Fe, Cu, Zn, Sr, Y, As and U in the bone samples are reported in Table 1. The data show that elemental concentration varies significantly from sample to sample. The concentration of Ca, the major constituent of the bone material (collophane), has been found to vary from 40.00 to 65.60%. The elements Ti, V, Cu, Y and As have been detected only in some of the bone samples with anomalous U content (threshold value for U content in these samples is already reported[2] to be 56.2 ppm). These are path finder elements of U and their presence suggests that besides uranium, Ti, V, Cu, Y and As also got enriched in bone samples with anomalous U content. The uranium anomalies found in the samples from Saharanpur (UP), Naraingarh (Haryana) and Nalagarh (HP) are typical of those found in Siwalik Himalayas. Moreover, the U concentration in fossil bones is controlled by availability of uranium in contemporary environment in which the vertebrates lived and the nature of the mineralizing solution acting as the carrier of uranium.

Correlation of U with other elements—Correlation coefficients (r) between U and elements, i.e. Ca, Mn, Fe, Zn and Sr in bone samples of five dif-

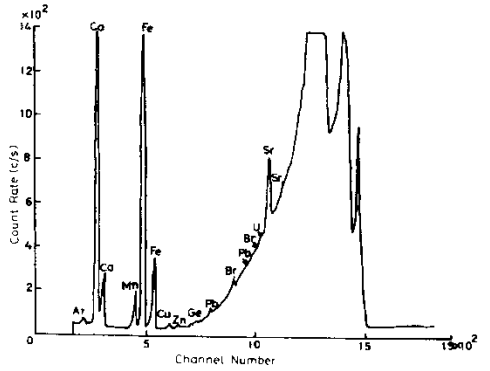

Fig. 1—Characteristic X-ray spectrum of fossil bone sample FN1

Table 1—Concentration of Elements in Siwalik Fossil Bones

Sample location	Lab symbol	Ca (%)	Ti (%)	V (%)	Mn (%)	Fe (%)	Cu (ppm)	Zn (ppm)	Sr (ppm)	Y (ppm)	As (ppm)	U (ppm)
Naraingarh	FN1	38.26	3.44	1.55	2.77	8.54	26.18	654.90	1665.70	183.10	244.30	120.9
(Haryana)	FN2	57.20	ND	ND	0.53	0.61	32.40	215.60	1244.80	ND	ND	98.5
	FN3	44.30	2.13	0.62	2.76	5.28	ND	333.30	1235.20	ND	ND	108.9
	FN4	48.34	ND	ND	1.35	9.74	ND	195.00	1160.00	804.00	209.60	119.7
Saharanpur	FS1	45.04	ND	ND	1.24	1.86	105.20	263.00	993.10	562.40	4072.00	118.6
(Uttar Pradesh)	FS2	56.83	3.89	ND	1.18	6.52	485.00	727.00	1876.90	825.40	19286.00	93.8
	FD4	41.77	ND	ND	0.47	5.71	ND	350.00	659.02	ND	1486.00	159.7
Kangra	F3	52.30	ND	ND	0.26	1.60	ND	442.20	412.50	ND	ND	49.7
(Himachal	F4	62.30	ND	ND	.05	3.70	ND	308.10	2061.60	ND	ND	39.4
Pradesh)	FA	62.90	ND	ND	2.25	1.74	ND	391.40	2892.60	ND	ND	38.2
Tirlokpur	F5	47.40	ND	ND	1.35	0.21	ND	169.02	921.40	ND	ND	41.3
(Himachal	F6	55.21	ND	ND	1.59	0.43	ND	280.60	2000.30	ND	ND	37.5
Pradesh)	F9	63.15	ND	ND	1.68	0.43	ND	248.00	1889.70	ND	ND	51.6
	F8	65.60	ND	ND	0.77	1.30	ND	535.90	1937.20	ND	ND	50.2
Nalagarh	FV1	40.00	0.97	0.17	7.39	4.58	157.20	253.56	246.79	ND	ND	418.0
(Himachal	FV2	51.38	ND	ND	0.81	1.25	63.70	364.70	1658.20	ND	517.80	292.8
Pradesh)	FV3	50.62	ND	ND	0.82	0.10	51.30	170.80	788.80	ND	ND	131.7

ND: Not detected

Table 2—Correlation Coefficient (r) Values of U Content with Other Elements in Bone Samples of Different Locations

Element	Naraingarh (r)	Saharanpur (r)	Kangra (r)	Tirlokpur (r)	Nalagarh (r)
Ca	−0.66	−0.90	−0.99	−0.79	−0.79
Mn	0.36	−0.90	−0.86	−0.32	0.83
Fe	0.93	−0.02	−0.47	0.53	0.94
Zn	0.48	−0.67	0.72	0.47	0.49
Sr	0.43	−0.92	−0.97	0.30	−0.31

ferent locations are reported in Table 2. Values of correlation coefficient of U with Ca are found to vary from −0.66 to −0.99 indicating a strong inverse correlation. Neumann *et al.*[7] have reported that in fossil bones, Ca is replaced during U absorption which is supported by the high value of inverse correlation of U with Ca observed in elemental analysis. Fe shows a positive correlation with U in bone samples of Naraingarh and Nalagarh locations because of the anomalous U content. Also, a high value of Fe (i.e. 6.52%) is recorded in molar teeth of Stagdon in which U enrichment was observed in ferruginous matrix by fission track radiography. The above results confirm that U enrichment is directly associated with Fe content of the bone samples with anomalous U content as reported earlier[4,5]. This may be due to the fact that the ferrous ions chemicaly help the uranyl complexes to reduce which accounts for the observed higher concentration of U in ferruginous rich bones and may be due to the similarity in the electron affinity of uranyl and iron ions[8]. The correlation of U with elements, i.e. Mn, Sr and Zn is inconsistent and varies with sample location.

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