RECONNAISSANCE STUDY OF MACROFOSSILS FROM THE UPPER PURUS RIVER - WESTERN AMAZÔNIA.

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SUMMARY

Fossils of wood, bone and teeth found along the Upper Purus River of Amazonia were studied using conventional microscopy and scanning electron microscopy. Mass spectometry was also used to investigate minor and trace element signatures of bone samples.

The microsopy studies showed that there was little alteration of original textures. In the fossil wood samples, identified in thin section as tropical hardwood trees, the replacement of the original material with siderite suggests that fossilization occured in shallow sediments in which interstitial waters were saturated with respect to iron carbonate. In samples of both fossilized bone and wood, precipitation of secondary iron phases was commonly observed in cracks and volds. Other secondary phases included silica, iron oxides, manganese carbonate. The intimate association of these secondary phases with the original biological structures could be evidence for a microbiological role in the formation of these phases. The similarity in rare earth element (REE) signatures for 2 fossil bone samples from different modern locations indicates their having shared similar diagenetic histories.

The virtually complete preservation of original textures suggests that microsopic studies could be useful in classifying fossil and even in identifying original materials. Rare carth signatures in fossilized bone may reflect ground water compositions at the time of fossilization.

INTRODUCTION

Macrofossils are commonly found along the tributaries and channels of the Acre and upper Purus Rivers (Figure 1). Most fossils are skeletal remains of reptiles and mammals, that are being eroded from the Tertiary and Pleistocene sediments which dominate the drainage basins of the Acre and Upper Purus Rivers. The fossils found in this region are

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of special interest because the environmental and geological settings of Western Amazonia have been strongly influenced by the tectonic events accompanying the formation of the Andes mountains in Cretaccous and Tertlary time and by periods of drier climates as a result of major glacial advances in Pleistocene Time.

A partial record of the changes in geological setting as the Amazon platform was tilted by the Andean uprising is found in the Acre Sedimentary Basin, a major sub-basin of upper Amazonia (Alto Amazonas). The boundaries of the Acre Basin are the Iquitos Arch (to the northeast, east and southeast), the Brazilian shield (to the soth) and the eastern Andean cordillera (Cordillera Oriental) in Peru (Miura, 1972). Preliminary studies show that the Acre Basin sediments (e.g., evaporites, marine and intracontinental sediments) and their relation to each other are consistent with the truncation of a continental margin to the west followed by the development of an intracontinental geological setting. By the late Tertiary an eastward draining fluvial system was well established (Asmus and Porto, 1972).

The samples studied here include petrified wood, a croccodile tooth and a sample of fossilized bone from the Upper Purus River. Another fossilized bone sample found along the Acre River was used for comparison of rare earth element signatures. The intention in this study was to explore the usefulness of optical and scanning electron microscopy as well as minor and trace element studies in obtaining information on paleoenvironments.

Experimental Work

a) Petrified Wood - In these samples the original cellular chemical components were replaced mainly by siderite ($FeCO_3$). From observations both in thin section and with scanning electron microscopy (SEM) there is no evidence for physical alteration of the original cell framework and tissue structure during fossilization (Plate I, Photo A). Minor secondary phases were commonly observed infilling voids (Plate 1, Photo B) and these included iron sulphide (a), potassium aluminosilicate (b), mixed iron/silica phases (c), manganese associated with iron phases (d), and silica (e). The samples of petrified wood were tentatively identified as tropical hardwoods due to the lack of growth rings and the presence of multicelled rays and vessels (Plate 1, Photo A).

b) Croccodile Tooth - Carbonate hydroxyapatite is the major component of this sample and replacement of the original material by secondary carbonate fluorapatite was also evident. In thin section both the enamel and the dentine appear intact and the latter is observed as a system of minute tubules radiating outwards. Plate 1, Photo C shows a fracture infilled with a carbonate phase (presumably rich in iron), surrounded by opaque phases and iron stained material. The dentine on either side of the fracture appears as parellel tubules whose physical arrangement is unaltered from the original material. In SEM observations (Plate 1, Photos D, E) there was little evidence of chemical replacement of the original material. Microfractures (Photo D) within the apatite framework (a) were infilled by iron sulphide (b), iron carbonate (c) and iron oxide. Cu and Pb were detected as minor components of iron sulphide phases (d). Photo E shows a cross-section of dentine tubules, some of which are infilled by iron sulphide phases. The intimate association between these phases and the apatite framework suggests that iron mobilization and the formation of secondary iron phases may have been influenced by microbiological activity.

c) Bone Samples - In the bone samples (one from the Upper Purus and the other from the Acre River), the major phases are carbonate fluorapatite, carbonate hydroxyapatite and calcite. Marcasite is a minor component. In thin section cut perpendicular to the osteon canals, the fossil bone structure appears as parallelly aligned submicroscopic birefringent crystallites. Secondary phases are found as precipitates within the voids of the original structure. For example, Photo F shows a void infilled with a carbonate phase and surrounded by a more opaque (iron rich) phase. These voids appear as openings in fractures (upper left of photo F), which presumably served as pathways for fluids during fossilization. The doubly refracting cystallites surrounding voids indicates that the framework of the original material is intact and suggests that only minor postmortal alteration has occurred. In SEM observations (Plate 1, Photo G) some osteon voids were observed to be filled with a zoned precipitate of iron and manganese carbonate in the core (a), surrounded by iron sulphide (b) and unaltered apatite (c). Photo H shows another osteon void infilled with a barium sulphur phase (presumably barite).

Trace element fingerprinting of the bone samples was carried out using spark source mass spectrometry (SSMS) (Table 1, Appendix 1) and rare earth elements (REE) were analysed quantitatively using inductively coupled plasma mass spectrometry (ICPMS) (Figure 2, Appendix 1). About half of the minor and trace elements surveyed by SSMS (B, Cl, Sc, V, Cr, Ni, Cu, Ga, Br, Rb, Zr, Nb, Sn, Cs, La, Ce, Pr, Nd, Hf, Pb, Th) have levels below those found in average crustal rocks. As and U are the most strongly enriched (100 times relative to crustal abundance), followed by Sr and Ba (> 10 times crustal abundance). Most other elements surveyed have crustal concentrations. Quite similar REE patterns (constructed from the ICPMS data) were found for bone samples from the Upper Purus and Acre Rivers (Figure 2).

DISCUSSION

The most remarkable feature of the fossils studied here is the preservation of original textures. This would imply that these fossils have never been deeply buried. The fossil wood samples are the most extensively chemically altered and the replacement of the original material mainly by siderite would indicate that the pore waters of the enclosing sediments at the time of fossilization were saturated with respect to siderite. In other work on lake sediments has been shown that interstitial waters only 20-30 cm below the sediment surface were nearly ten-fold supersaturated with respect to siderite (Emerson, 1976).

The preservation of primary apatite minerals forming fossil bones and teeth and the apparently small amount of secondary replacement would imply that more detailed chemical information using minor and trace element signatures could provide information on environmental parameters at the time of formation or fossilization. Lambert **et al.** (1981)

have pointed out that tooth enamel is much more compact than bone and thus chemical replacement is slower. Thus minor and trace element levels in fossilized teeth may reflect dietary conditions at the time of formation. Lambert et al. (1984) have also shown from work on human fossils that Sr and Zn may be the elements least mobile during diagenesis. Sr has been shown to be an integral part of the hydroxyapatite lattice (Parker and Toots, 1970). $^{87}Sr/^{86}Sr$ ratios in marine fossils have been used to monitor variations in seawater over geological times (Koepnick et al., 1985), and this parameter may be useful in monitoring the changes in geological setting and climate in upper Amazonia.

Rare earth element (REE) patterns (Henderson et al., 1983) in fossil human bones have also been to suggest that REE are incorporated from ground waters during fossilization. The REE patterns they obtained showed stronger light REE enrichment and heavy REE depletion with respect to chondritic values than did the patterns obtained here. A major difference was the lack of a Ce anomaly in our data, corroborating the oxygen poor diagenetic environment suggested by the presence of siderite.

The microscale variations in chemistry underscores the complex distribution of chemical gradients during diagenesis and the observations documented here would suggest a high degree of microbiological activity during diagenesis.

CONCLUSIONS

Both conventional microscopy and scanning electron microscopy were used in studies of fossils found along the Upper Purus River of Upper Amazonia. The most striking features of these samples is the preservation of original textures. This suggests the usefulness of microscopic studies in fossil classification and possibly in identification of original materials. From the minor and trace element studies, it appears that rare earth element signatures may be useful in identifying fossils with similar diagenetic histories. High strontium levels in fossilized bone samples indicate that strontium isotope signature merit further investigation.

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RESUMO

Fósseis de madeira, ossos e dentes achados no Estado do Amazonas, ao lor Purus e do rio Acre, foram estudados, usando-se microscópia convencional e micr varredura. A espectrometria de massa foi utilizada para investigar os níveis (tos menores e traços em algumas amostras de osso fossilizado. Os estudos microscópicos mostram que há pouca alteração das texturas originais. As amostras de madeira fossilizada foram identificadas em lâmina delgada como madeira de lei. Nestas amostras a subs-tituição da matéria original por siderita sugere que a fossilização ocorreu em sedimentos rasos, nos quais as águas intersticiais foram saturadas pelo carbonato de ferro. A precipitação de fases secundarias de ferro foi observada freqüentemente nas rachaduras e vãos, nas amostras tanto de osso fossilizado como de madeira fossilizada. Outras fases secundárias incluem a sílica, óxidos de ferro e carbonato de manganês. A associação ín-tima dessas fases secundárias com as estruturas biológicas originais pode ser evidência para um papel microbiológico na formação dessas fases. Os padrões de concentração seme-lhante de terras raras em dois ossos em localidades modernas diferentes indicam histori-as diagenéticas semelhantes. A preservação virtualmente completa das texturas originais sugere que estudos microscópicos podem ser úteis na classificação dos fósseis e até na identificação de materiais originais. Padrões de concentração de terras raras em os-sos fossilizados podem refletir as composições de água subterrânea na época de fossilização.

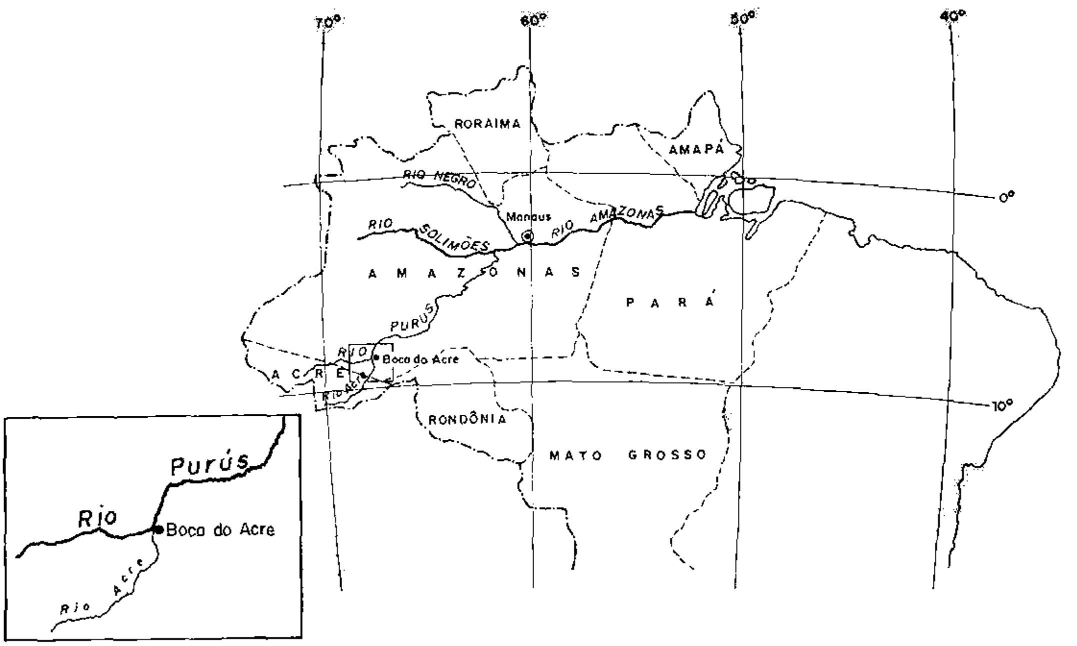

Fig. 1. Sketch Map of Amazonia.

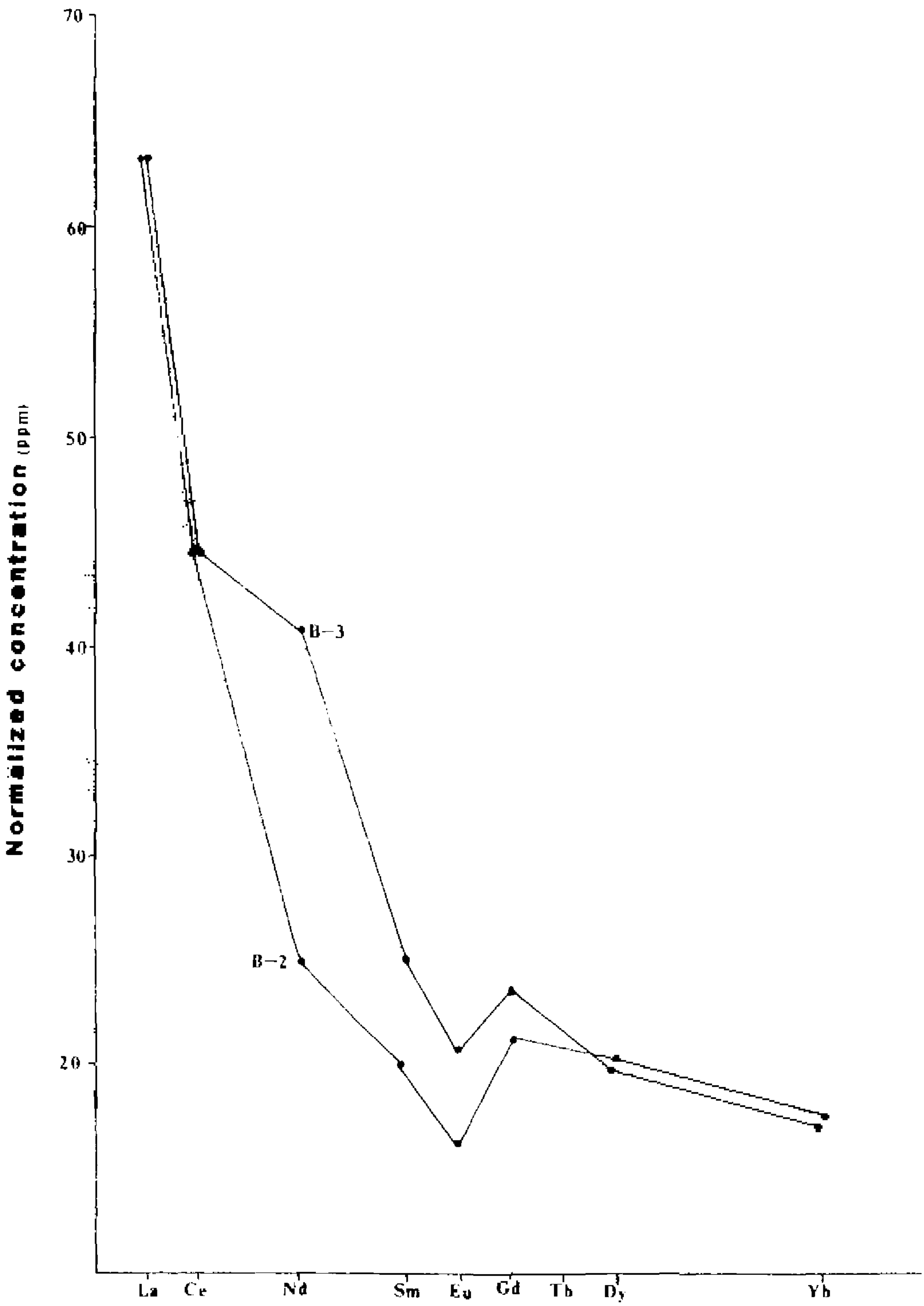

Fig. 2. Rare Earth Element Patterns (Bone Samples).

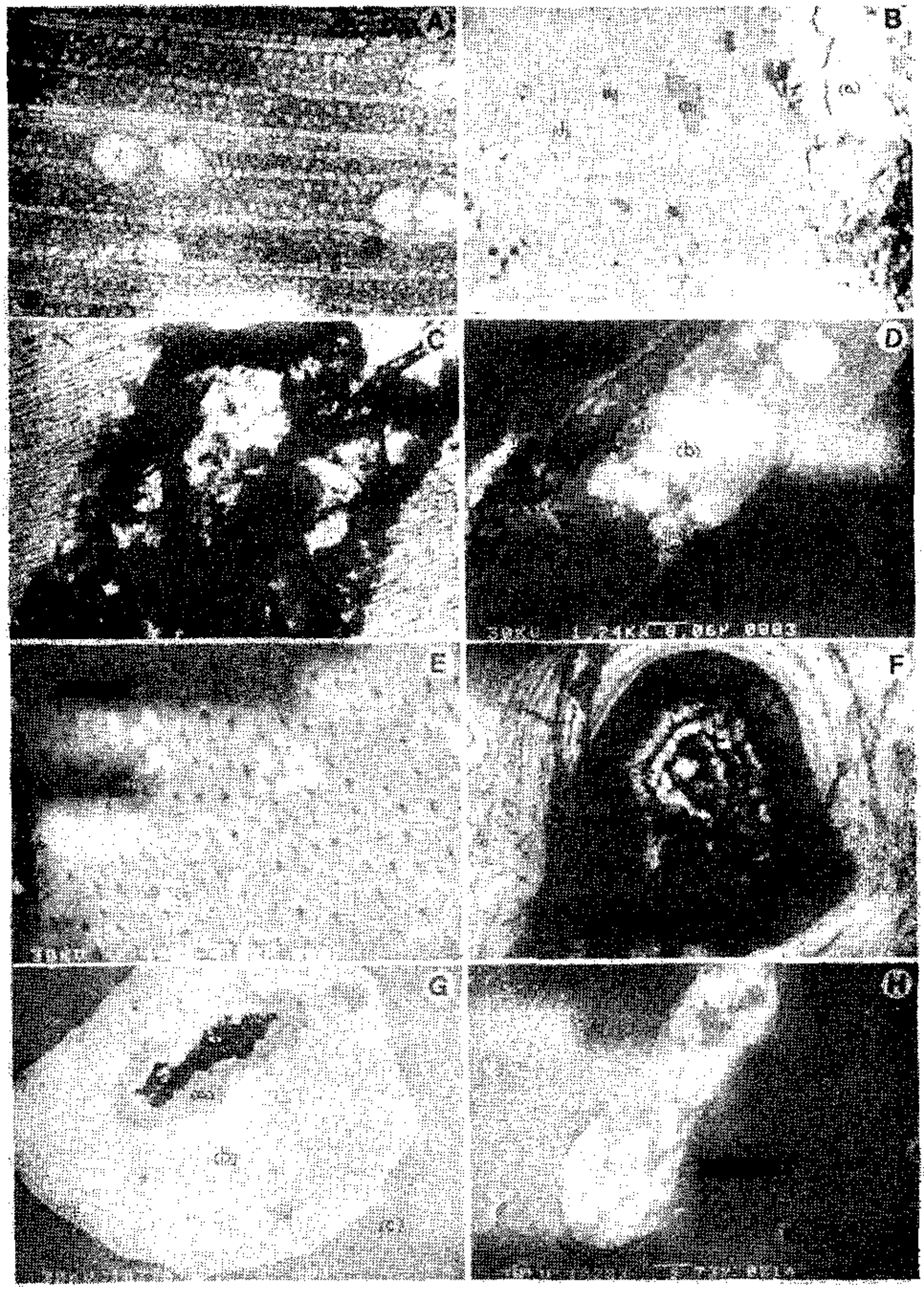

Fig. 3. Photomicrographs of fossilized wood, teeth and bone.
Photo A - fossilized wood (80 x); B - scanning electron micrograph of fossilized wood (1160 x); C - fossilized tooth (200 x); D - scanning electron micrograph of fossilized tooth (1240 x); E - scanning electron micrograph of fossilized tooth (2940 x); F - fossilized bone (200 x); G - scanning electron micrograph of fossilized bone (1029 x); H - scanning electron micrograph of fossilized bone (1028 x).

Tabela I. Spark Source Mass Spectrometry (SSMS) Data - Bone Samples.

Element		Concentration (ug g^{-1})	
B		0.5	
F		>470	
S		>390	
Cl		50	
Sc		3	
V		10	
Cr		0.5	
Ni		15	
Cu		20	
Zn		120	
Ga		0.5	
Ge		2	
As		>200	
Se		0.1	
Br		0.05	
Rb		0.5	
Sr		3300	
Y	(47)[a]		[43][b]
Zr		60	
Nb		1	
Mo		1	
Ag		0.4	
Sb		0.2	
I		0.3	
Ba		6750	
La	(9)		[19]
Ce	(24)		[38]
Pr	(3)		[5]
Nd	(15)		[24]
Sm	(4)		[5]
Eu	(1)		[2]
Gd	(7)		[8]
Tb	(1)		[1]
Dy	(7)		[6]
Ho	(1)		[2]
Er	(4)		[4]
Tm	(0.5)		[0.6]
Yb	(3)		[3]
Lu	(0.4)		[0.6]
Pb		2	
U		170	

(a) REE data () obtained by ICPMS for bone sample from Purus River.
(b) REE data [] obtained by ICPMS for bone sample from Acre River.

Sn, Cs, Hf and Th concentrations did not exceed 1 ug g^{-1}.

Appendix - Analytical Methods Used

X-ray Diffration (XRD) - *The diffraction* of x-rays produced by a Cu-Kα source through sample material was used to determine the major minerals present.

Spark Source Mass Spectroscopy (SSMS) - This technique is used for multi-element (50-60 elements) fingerprinting down to part per billion levels. One advantage is the simplicity of preparation of solid samples by mixing with graphite (Kronberg **et al.**, in preparation).

Scanning Electron Microscopy (SEM) - Using SEM it is possible to obtain micron scale images of surfaces of solid materials. Simultaneous qualitative analysis is possible of the sample if probed with x-rays (EDS).

Inductively Coupled Plasma Mass Spectrometry (ICPMS): In this study ICPMS was used to determine the concentrations of rare earth elements in bone samples. Rare earth elements were concentrated by chromatographic extraction from solution. The analytical solutions are then aspirated into a plasma and analysed by quadrapole mass spectrometry (Bolton **et al.**, 1983).

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