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RECRYSTALLIZATION OF FOSSIL HORSE TEETH

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INTRODUCTION

The mineralogist of today has extended his inquiry into disciplines only remotely associated with earth science. The methods of mineral study have reaped a great harvest in the electronics, ceramics and cement industries, to name a few. Little has been done, however, in applying mineralogical methods of investigation in the field of medicine. Perhaps this is not so unusual, considering the differences in training associated with the two disciplines. It does seem strange, however, that, within the earth sciences, the mineralogist has largely neglected the abundance of fossil material available for study, and that the paleontologist has not fully availed himself of mineralogical techniques.

The writers became interested in the mineralogical changes that occur in vertebrate material during the process of fossilization when one of us (T. M. H.) selected the problem for a senior Honors Thesis. In reviewing the literature of medicine and dentistry related to the composition of bone and teeth, it has become obvious that disagreement exists among investigators concerning the chemical and crystallographic nature of bone and teeth.

THE INORGANIC COMPONENT OF BONE AND TEETH

There is general agreement that bone and teeth have as their inorganic phase a calcium phosphate hydrate which is a member of the apatite series. Rogers (1924) studied numerous specimens of fossil bone and concluded the material consists of a hydrous calcium carbonate phosphate which he considered to be collophane and stated (p. 540), "It often approaches in chemical composition the crystalline mineral dahllite . . . of which it may be regarded as the amorphous equivalent."

Gruner *et al.* (1937) determined that dental enamel is a crystalline rather than amorphous carbonate hydroxyapatite. Since that time the mineralogical composition of dental material has been studied by McConnell (1952 a,b; 1955; 1960) giving evidence that such material is in fact very similar both chemically and structurally to the mineral dahllite.

The medical researcher, however, being unfamiliar with mineralogical methods of investigation, appears reluctant to accept the findings of the mineralogist, and considers bone and enamel to be hydroxyapatite with adsorbed CO_3^{2-} (Carlström, 1955; Neuman and Neuman, 1958).

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TABLE I. SPECIMENS OF DENTAL MATERIAL

Genus	Locality	Type of Enclosing Sediment	Age
Equus	?	—	Recent
Parahippus	Snake Creek Beds, Sioux County, Nebraska	Specimen from stream channel sandstone	L. Pliocene
Merychippus isonesus	Sheep Creek Beds, Sheep Creek, Nebraska	Sandstone with some silt filler	M. Miocene
Mesoreodon megalodon	Upper Harrison Beds, Van Tassel, Wyoming	Sandstone with abundant filler	L. Miocene
Merycoidodon culbertsoni	White River Beds, Big Bad Lands, South Dakota	Impervious silts	Oligocene

The study of fossil material, virtually devoid of organic materials by natural dispersal, may provide information of value to an understanding of the structure, composition and behavior of the inorganic phase of bone. Investigation is being continued under a grant (D-1636) from the National Institute of Health.

RECRYSTALLIZATION OF FOSSIL TEETH

Materials studied

Several specimens of teeth selected from the orders Artiodactyla and Perrisodactyla have been investigated to determine (i) the type of recrystallization that has occurred, (ii) whether a relationship exists between age and degree of recrystallization, and (iii) the dependence of recrystallization on the permeability of the enclosing sediment. The specimens (Table I) are from the collections of Amherst College, and were selected with the aid of Professors George W. Bain and Albert E. Wood, to whom the writers express their appreciation.

Thin sections of all specimens were prepared to insure that no material other than the apatite-like component of the enamel was present. Chips of enamel and dentin were selected for *x*-ray and chemical analysis.

Microscopic examination

Thin sections of various dental specimens all reveal a marked difference between the dentin and enamel portions. In general it can be stated that the enamel portion consists of well-defined radiating fibers of low birefringent (0.001) material with the fibers essentially perpendicular

TABLE II. *X*-RAY DIFFRACTION DATA FOR DENTIN AND ENAMEL FROM *PARAHIPPUS, MESOREODON MEGALODON*, AND *EQUUS*

hk.l	*Pa-ahippus* Enamel		*Parahippus* Dentin		*Mesoreodon megalodon* Enamel		*Mesoreodon megalodon* Dentin		*Equus* Enamel		*Equus* Dentin	
	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
10.0	8.28	3	8.26	2	8.24	4	8.135	2				
10.1	5.294	2			5.312	2						
11.0	4.734	2			4.760	2						
20.0	4.082	2	4.156	1	4.092	3	4.051	1				
11.1	3.909	2	3.872	1	3.880	3	3.855	1	3.923	2		
00.2	3.451	7	3.468	8	3.451	8	3.444	7	3.461	8	3.451	7
10.2	3.162	2	3.151	1	3.173	4	3.162	2				
12.0	3.092	5	3.082	1	3.090	4	3.059	2	3.108	3	3.124	3
12.1 / 11.2	2.822	10	2.809	10	2.809	10	2.797	10	2.803	10	2.809	10
30.0	2.722	9	2.712	6	2.710	9	2.694	6				
20.2	2.636	4	2.629	5	2.631	5	2.616	4	2.655	3		
30.1	2.531	1	2.526	5	2.535	1	2.517	0.5				
22.0	2.448	0.5										
13.0	2.271	7	2.265	5	2.261	6	2.256	4	2.272	4	2.271	1
13.1	2.149	2	2.149	1	2.144	1	2.163	1	2.161	1		
11.3	2.066	1	2.066	1	2.061	1	2.061	1	2.080	1	2.060	0.1
20.2	2.033	1	2.002	0.5	1.996	1	1.999	1	1.993	4		
22.2	1.949	1	1.947	6	1.943	7	1.936	5	1.948	4	1.946	2
13.2	1.895	5	1.895	2	1.888	3	1.886	2				
23.0	1.877	7	1.844	6	1.824	7	1.837	5	1.839	4	1.842	2
23.1	1.808	5	1.807	1	1.804	2	1.795	2				
14.0	1.782	5			1.773	2						
30.3	1.757	5	1.758	1	1.751	2	1.759	2				
00.4	1.722	6	1.723	3	1.721	3	1.725	4	1.728	4	1.733	1
50.0	1.643	3	1.652	0.1	1.645	1	1.631	1	1.637	1		
11.4	1.615	2	1.608	0.5	1.616	0.5	1.600	0.1				
20.4	1.584	1			1.580	0.5						
42.0	1.554	3	1.537	0.5			1.523	1				
42.1	1.518	3	1.504	0.5	1.505	1	1.495	1	1.503	1		
51.0	1.476	3			1.475	1						
32.3	1.454	4	1.461	2	1.456	2	1.452	3	1.469	2	1.445	0.5
33.2	1.434	4	1.430	1	1.436	1	1.419	1				
41.3	1.410	1			1.407	0.1	1.396	0.1				
43.1	1.349	0.5					1.341	0.1				
40.4	1.321	2							1.326	1		
20.5	1.308	2	1.302	1	1.308	0.5	1.309	0.5				
42.3	1.281	2	1.277	0.5	1.283	1	1.276	0.5				
20.5	1.253	1	1.258	0.5	1.257	1	1.256	0.5				
51.3	1.239	3	1.233	1	1.240	2	1.234	1	1.244	1		
52.2	1.223	3	1.216	0.5	1.228	0.5	1.217	0.5				
31.5	1.179	1	1.173	0.5	1.179	0.5						
43.4	1.167	2	1.155	0.5	1.158	1						
00.6	1.146	2	1.144	0.5	1.146	1	1.151	1	1.151	1		
11.6	1.118	3	1.115	1	1.117	1	1.115	1	1.119	2		
20.6	1.106	3	1.103	1	1.104	1	1.099	1				

Camera diameter, 114.59 mm.; radiation, Cu/Ni, CuKα=1.5418 Å.

to the enamel surface. The boundary between enamel and dentin is well defined. The dentin portion appears almost structureless under ordinary light. Under crossed nicols it has a lower birefringence, often appearing as isotropic material, and a poorly developed radial structure can be seen.

X-ray analysis

Diffraction patterns of all specimens listed in Table I were obtained using Cu radiation and a powder camera of 114.59 mm diameter. The diffraction data for *Parahippus*, *Mesoreodon megalodon*, and *Equus* enamels and dentins (Table II) and for enamels from *Merychippus*

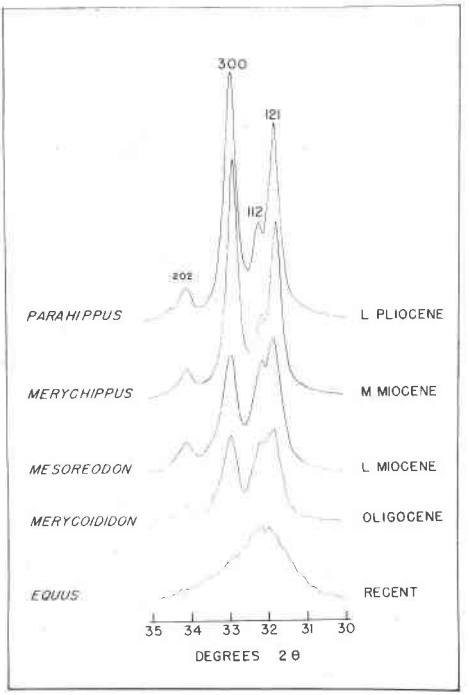

FIG. 1. Partial diffraction patterns of various dental enamels for the region 30 to 35 degrees 2θ. All patterns obtained with filtered Cu radiation with a traverse speed of $\frac{1}{4}°$ 2θ per minute, using a geiger counter equipped Norelco diffraction goniometer.

isonesus and *Merychoidodon culbertsoni* can be assigned in all cases to the apatite structure. Dentin from the last two specimens was not studied. From the diffraction patterns of enamels it is observed that the *Parahippus* enamel produces the best-defined and most intense diffraction maxima. The pattern for *Equus* enamel has produced only a few reflections, and these are broad and diffuse. The resolution of the diffraction maxima is best illustrated by comparing portions of each pattern for the range 30° to 35° 2θ (Fig. 1).

Composition of fossil enamel

A chemical analysis of *Parahippus* enamel (Table III) has been made by G. H. Wheeler and compared with published analyses of various apatites and the dental enamel from a mastodon tooth. Closest agreement is found between analyses of dahllite and *Parahippus* enamel.

Calculations (Table IV) of the *Parahippus* enamel analysis patterned on the scheme of McConnell (1960) demonstrate that the entire CO_3^{2-}

TABLE III. CHEMICAL ANALYSES OF *PARAHIPPUS* AND MASTODON ENAMELS COMPARED WITH VARIOUS APATITES

	1	2	3	4	5
CaO	55.84	53.94	53.16	51.44	53.71
MgO	0.10	0.10	—	0.34	0.10
Na_2O	—	—	0.77	0.80	0.20
K_2O	—	—	0.28	0.05	N.D.
P_2O_5	42.05	38.13	38.57	39.92	38.71
CO_2	—	3.40	4.46	2.72	3.01
H_2O	1.86	0.47	1.20	3.63	3.42
F	0.16	3.71	0.19	0.03	0.10
Cl	tr.	—	0.02	0.42	0.61
Rem.	0.22	2.17	1.23	0.14	0.27
Total	100.23	101.92	99.88	99.49	100.13
O=F, Cl	0.07	1.56	0.08	.10	
	100.16	100.36	99.80	99.39	

1. Hydroxylapatite. Georgia, U.S.S.R. Mitchell *et al.* (1943). Rem. is MnO 0.07, insol. 0.15.
2. Francolite. Wheal Franco, Devonshire. Sandell *et al.* (1939). Rem. is Fe_2O_3 0.34, insol. 1.83.
3. Dahllite. Mouillac, France, McConnell (1938). Rem. is SO_3 0.05, SiO_2 0.40, Al_2O_3 0.44, Fe_2O_3 0.34.
4. Mastodon Enamel. Bluffton, Ohio. McConnell (1960). Rem. is SO_3 tr., Al_2O_3 0.07, Fe_2O_3 0.03, insol. 0.04.
5. *Parahippus* Enamel. Sioux Co., Nebraska. G. H. Wheeler, analyst. Rem. not determined.

content may be assigned to the PO_4^{3-} positions in the structure. Approximately 2 per cent of the hydrogen cations cannot be assigned to a definite structural position. This suggests that in recrystallized dental enamel the carbonate is actually an integral part of the crystal structure as in dahllite.

These data illustrate the importance of the permissiveness of the enclosing sediment to the process of recrystallization of fossil material (see also Paine, 1937). The Lower Pliocene *Parahippus* material has been recrystallized to a coarser carbonate hydroxyapatite (dahllite) than older fossil teeth. The coarser and more permeable the enclosing sediment the better defined are the diffraction maxima of the fossil enamel. Assuming that *Equus* and all other animals of the same genus would produce an enamel of like composition (and there is no basis to assume the contrary) inspection of the positions and intensities of the diffraction maxima (Fig. 1) suggests that minor chemical changes accompanied the

TABLE IV. CALCULATIONS ON ANALYSIS OF DENTAL ENAMEL FROM *Parahippus* TOOTH

Oxides	Weight per cent	Oxide ratios	Relative charges of cations	Cation charges $\Sigma=53$	Cations per unit	Structural locations	
CaO	53.71	.9577	1.915	19.13	9.56	Ca, Mg, Na	9.64
MgO	0.10	.0025	.005	.05	.02	H_3	.36
Na_2O	0.20	.0032	.006	.06	.06	Ca positions	10.00
P_2O_5	38.71	.2728	2.728	27.22	5.44	P	5.44
CO_2	3.01	.0636	.275	2.75	.66	C	0.66
H_2O	3.42	.1898	.380	3.79	3.79	P position	6.00
				53.00		Cl, F	0.22
F	0.10	.0052				OH	1.78
Cl	0.61	.0172				F positions	2.00
Rem.[1]	.27						
	100.13					H_2O excess	0.06

[1] Composition of insoluble residue not determined.

recrystallization which produced the larger crystallite size and reduced the line broadening effect.

CONCLUSIONS

Fossil dental enamels studied show varying degrees of recrystallization which can be related to the permeabilities of the enclosing sediments from whence they were recovered. The recrystallization produces an increase in crystallite size and a change in relative intensities of diffraction maxima. The pattern providing the best defined diffraction maxima (*Parahippus*) is most similar to dahllite, but some minor chemical difference probably exists between the specific material used for comparison and the *Equus* enamel.

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