Stable Isotope Geochemistry: A Tribute to Samuel Epstein
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Oxygen isotopes in phosphates of fossil fish—Devonian to Recent

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Abstract—The isotopic composition of oxygen in the phosphate of apatite ($\delta^{18}O_p$) was determined in 159 fish bones and teeth from museum collections throughout the world. The fossils were both marine and fresh water, ranging in age from Devonian to the Recent. In 45 of those we also determined the isotopic composition of oxygen and carbon of the lattice carbonate in apatite ($\delta^{18}O_c$ and $\delta^{13}C$). In most cases the isotopic results are compatible with previously available geological information: the difference between marine and fresh water, the indication of previously known warm and cold time periods, and the ranking of fishes from warm to cold according to their inferred life habitat. The relationship between $\delta^{18}O_p$ and $\delta^{18}O_c$ suggests early diagenetic replacement of an originally phosphatic phase by carbonate fluor apatite (CFA). The correlated latitudinal variation in $\delta^{18}O$ of meteoric water and temperature should result in a small variation of $\delta^{18}O_p$ in fresh-water fish. The large range in $\delta^{18}O_p$ of Recent fish is the outcome of the "altitude effect" (DANSGAARD, 1964), *i.e.* of the existence of post orogenic high altitudes.

INTRODUCTION

THE "ESTIMATION OF the paleotemperatures of ancient oceans by measurement of the oxygen isotope distribution between calcium carbonate and water" has been heralded as "one of the most striking and profound achievements of modern nuclear geochemistry" (CRAIG, 1965). The idea was initiated by H. C. Urey and it was the group led by Sam Epstein that provided geologists with the first reliable values for temperatures of the past (EPSTEIN *et al.*, 1951, 1953; UREY *et al.* 1951; EPSTEIN and LOWENSTAM, 1953; LOWENSTAM and EPSTEIN, 1954). In the almost four decades since, the great bulk of paleothermometric studies have centered on measuring $\delta^{18}O$ of carbonate secreting organisms, mainly molluscs and foraminifera (*e.g.* EMILIANI, 1955; SAVIN, 1977). The applicability of the carbonate-water paleotemperature scale is, however, restricted for the most part to the Cenozoic and late Mesozoic record because of poor preservation of older fossils (SAVIN, 1982). Furthermore, practically all paleotemperature determinations were limited to marine fossils, again because well-preserved carbonate land-fossils are scarce and because of the difficulty in estimating the isotopic composition of continental water in which the animal grew.

The possibility of measuring $\delta^{18}O$ in biogenic apatites was first demonstrated by TUDGE (1960) and further developed by LONGINELLI (1965), LONGINELLI and NUTI (1973a,b), and KOLODNY *et al.* (1983). A major advantage of the phosphate oxygen paleothermometer is that isotope exchange between phosphate oxygen and water is very rapid in biochemical enzyme catalyzed reactions but is extremely slow in inorganic systems (KOLODNY *et al.*, 1983). Thus, the problem of preservation in the case of apatitic fossils should become less acute than it is with calcium carbonate. The apatite-water thermometer has been calibrated with living, marine and fresh-water, fish. It has been applied to the analysis of conodonts of the North American Paleozoic (LUZ *et al.*, 1984), of fossil fishes from the Cretaceous and Tertiary of Israel and other Mediterranean countries (KOLODNY and RAAB, 1988), and of phosphorites from the entire geological record (SHEMESH *et al.*, 1988). We present here the results of a survey of $\delta^{18}O$ analyses of fossil fishes from many parts of the world which sample a time period of about 400 million years: from the Devonian, the time of appearance of the first fish, to the Recent.

SAMPLES AND ANALYTICAL METHODS

The sample set was obtained by contribution of Museums, as well as by donations of individuals from several universities. In Table 1 the sources are identified as following:

AGF	A. G. Fisher, USC, Los Angeles
AMNH	American Museum of Natural History, New York
AT	A. Tintori, University of Milan, Italy
BB	B. Buchardt, Kopenhagen University, Denmark
BM	The British Museum, London
FA	F. Albarède, CRPG, Vandoeuvre-les-Nancy, France
MNH	Muséum National d'Histoire Naturelle, Paris
FMNH	Field Museum of Natural History, Chicago
LACM	Natural History Museum of Los Angeles County, Los Angeles (J. D. Stewart)
NHT	N. H. Trewin, University of Aberdeen
UCLA	The UCLA fossil collection, Los Angeles

The samples designated KLN and KR were collected

Table 1. Isotopic composition of oxygen in phosphate of fossil fishes.

Source	Locality	Description	Strat. age	Abs. age	$\delta^{18}O$ marine	$\delta^{18}O$ fresh
1. AGF	Pacific Oc.	*Stenella longirostric*	Recent	0	19.7	
2. AGF	Iowa	Fish unident.	Recent	0		14.4
3. KLN	L. Kinnereth	*Nirogrex terraesanctae*	Recent	0		19.4
4. KLN	Mediterranean	*Epinephelus sp.*	Recent	0	22.3	
5. KLN	Gulf of Elat	*Scarus sp.*	Recent	0	23.3	
6. KLN	Gulf of Elat	*Scarus sp.*	Recent	0	22.7	
7. KLN	Gulf of Elat	*Variola louti*	Recent	0	22.2	
8. KLN	Bardawil	*Sparus aurata*	Recent	0	25.2	
9. KLN	L. Inari	*Salvelinus namaycush*	Recent	0		11.1
10. KLN	L. Baikal	*Perca*	Recent	0		6.0
11. KLN	L. Baikal	*Coregorius*	Recent	0		7.3
12. KLN	L. Baikal	*Cottus*	Recent	0		9.0
13. KLN	L. Karaun	*Salmo*	Recent	0		14.9
14. KLN	Dan pond	*Salmo gairdneri*	Recent	0		15.4
15. LACM	Off Calif.	**Dermochelys*	Recent	0	21.4	
16. LACM	Off Calif.	**Dermochelys*	Recent	0	21.3	
17. AMNH	Idaho	*Osteichthian* unident.	Pleistocene	1		11.3
18. AMNH	Florida	*Lepisosteus spatula*	Pleistocene	1		21.5
19. LACM	Nebraska	*Stizostedion canadense*	Pleistocene	1		15.0
20. FA	S. France	*Synodontaspis acutissima*	M. Pliocene	2	21.9	
21. LACM	California	clupeid skeleton	Miocene	5	21.1	
22. AMNH	Florida	*Myliobatis sp.*	Pliocene	5	20.9	
23. UCLA	California	Fish, unident.	Miocene	8	21.5	
24. LACM	California	clupeid skeleton	Miocene	8	19.9	
25. LACM	California	clupeid skeleton	Miocene	8	20.9	
26. LACM	California	myliobatid tooth	Miocene	8	21.1	
27. AMNH	Nebraska	*Achtioptorygian* unident.	Miocene	9		13.7
28. FA	S. France	*Mitsukurina lineata*	M. Miocene	14	20.9	
29. AGF	Maryland	tooth	Miocene	15	19.3	
30. AGF	Maryland	tooth	Miocene	15	20.5	
31. AGF	Maryland	shark tooth	Miocene	15	21.3	
32. AGF	Maryland	fish bone	Miocene	15	21.7	
33. AGF	Maryland	shark tooth	Miocene	15	21.7	
34. AGF	Maryland	fish vertebra	Miocene	15	21.4	
35. AGF	Maryland	shark tooth	Miocene	15	21.3	
36. AMNH	Florida	*Carcharodon megalodon*	Miocene	15	20.2	
37. LACM	Calif.	*Chelonid	Miocene	15	22.2	
38. LACM	Calif.	*Psephophorus*	Miocene	15	21.7	
39. LACM	Calif.	*Isurus planus*	Miocene	15	22.1	
40. LACM	Calif.	**Otariidae	Miocene	15	21.2	
41. LACM	Calif.	myliobatid tooth	Miocene	15	21.6	
42. LACM	Calif.	*Cetorhinus tooth*	Miocene	15	21.3	
43. LACM	Calif.	*Psephophorus*	Miocene	15	22.2	
44. FA	Saudi Arabia	*Myliobatis sp.*	Miocene	16	14.3	
45. AGF	Maryland	*Myliobatis sp.*	Miocene	16	21.0	
46. AGF	Baja Calif.	shark tooth	Oligocene	25	19.0	
47. BB	Belgium	*Myliobatis sp.*	Oligocene	30	20.1	
48. BB	England	*Myliobatis sp.*	L. Eocene	35	18.4	
49. BB	England	*Myliobatis sp.*	Eocene	40	19.3	
50. FA	Paris Basin	*Striatolamia macrota*	L. Eocene	43	17.5	
51. BB	England	*Myliobatis sp.*	Eocene	44	18.2	
52. BB	England	*Myliobatis sp.*	Eocene	44	18.1	
53. FA	North Peru	*Isurus praecursor*	M. Eocene	46	19.4	
54. FA	Togo	*Synodontaspis sp.*	M. Eocene	46	19.6	
55. FA	Togo	*Synodontaspis koerti*	M. Eocene	46	18.5	
56. FA	Togo	Sawfish (rostrum)	M. Eocene	46	18.8	
57. FA	Togo	Teleostid (vertebra)	M. Eocene	46	19.4	
58. FA	Togo	Teleostid (bone)	M. Eocene	46	18.8	
59. FA	Togo	*Synodontaspis koerti*	M. Eocene	46	19.4	
60. BB	Belgium	*Squatina prima; St. striata*	Eocene	50	15.2	
61. FA	Morocco	*Striatolamia striata*	M. Eocene	52	18.9	
62. AMNH	Wyoming	*Amia uintaensis*	M. Eocene	50		11.0

Table 1. (Continued)

Source	Locality	Description	Strat. age	Abs. age	$\delta^{18}O$ marine	$\delta^{18}O$ fresh
63. AMNH	S. Carolina	*Myliobatis mordax*	Eocene	50	21.3	
64. KR	Morocco	Shark unident.	E. Eocene	55	18.6	
65. KR	Italy	Fish unident.	E. Eocene	55	18.7	
66. BB	U.K.	*Squatina prima; St. striata*	E. Eocene	55	17.8	
67. BB	U.K. Oldhaven Beds	*Striatolamia striata*	Paleocene	60	16.5	
68. BB	U.K. Oldhaven Beds	*Striatolamia striata*	Paleocene	60	16.3	
69. BB	U.K. Oldhaven Beds	*Squatina prima; St. striata*	Paleocene	60	15.5	
70. AMNH	N. Mexico	*Lepisosteus sp.*	Paleocene	60		15.3
71. FA	Morocco	*Synodontaspis tingitana*	Danian	62	19.6	
72. FA	Morocco	*Myliobatis sp.*	Danian	62	24.2	
73. AMNH	Wyoming	*Lepisosteus sp.*	M. Paleocene	63		12.3
74. BB	Denmark	*Striatolamia sp.*	Danian	65	19.7	
75. FA	Bolivia	*Pucapristis branisi*	Maastrichtian	68	21.9	
76. FA	Morocco	*Cretolemna maroccana*	Maastrichtian	68	19.3	
77. AMNH	Wyoming	garfish	Maastrichtian	70		12.7
78. LACM	Montana	*Lepisosteid*	Maastrichtian	70		13.4
79. LACM	Calif.	*Plotosaurus tuckeri*	Maastrichtian	70	22.3	
80. LACM	Calif.	*Enchodus*	Maastrichtian	70	22.1	
81. KR	Israel	Teleostid, unident.	Maastrichtian	74	19.8	
82. KR	Israel	*Squatina ? sp.*	Maastrichtian	74	20.3	
83. FA	N. Jersey	*Scapanorhynchus texanus*	Campanian	75	20.2	
84. KR	Morocco	*Lamna biauriculata*	L. Campanian	75	19.5	
85. KR	Jordan	*Squalicorax pristodontus*	Campanian	77	18.4	
86. KR	Israel	*Enchodus bursuaxi*	Campanian	77	20.0	
87. KR	Israel	*Enchodus bursuaxi*	Campanian	77	19.7	
88. KR	Israel	*Enchodus libycus*	Campanian	77	19.1	
89. KR	Israel	*Squalicorax kaupi*	Campanian	77	18.7	
90. KR	Israel	*Lamna biauriculata*	Campanian	77	19.3	
91. FA	Morocco	*Cretolamna appendiculata*	Campanian	75	18.9	
92. AMNH	S. Dakota	Teleostid, unident.	Campanian	77	18.1	
93. LACM	Alabama	*cf. Mawsonia*	Campanian	77	21.3	21.3
94. AMNH	Montana	*Lepisosteus sp.*	L. Cretaceous	80		13.4
95. LACM	S. Dakota (Pierre)	*Platecarpus ictericus*	E. Campanian	83	19.7	
96. LACM	S. Dakota (Pierre)	**Tylosarurus proriger*	E. Campanian	83	18.5	
97. LACM	S. Dakota (Pierre)	*Enchodus petrosus*	E. Campanian	83	19.9	
98. LACM	Kansas (Niobrara)	*Platecarpus ictericus*	Santon.-Campan.	84	19.7	
99. KR	Israel	*Scapanorhynchus sp.*	Santon.-Campan.	84	18.3	
100. KR	Israel	*Scapanorhynchus rapax*	Santon.-Campan.	84	18.6	
101. LACM	S. Dakota	*Ptychodus mortoni*	Santon.-Campan.	85	18.1	
102. AMNH	Kansas	*Ptychodus mortoni*	Santon.-Campan.	85	18.6	
103. KR	Israel	*Scapanorhynchus ? rapax*	Santon.-Campan.	85	18.3	
104. LACM	Kansas	*Inocentrus vulgaris*	L. Santonian	86	18.1	
105. LACM	Kansas	*Squalicorax falcatus*	L. Coniacian	87	18.8	
106. LACM	Kansas	**Tylosaurus*	L. Coniacian	87	18.1	
107. LACM	Kansas (Niobrara)	*Lepisosteus sp.*	L. Coniacian	87	19.3	19.3
108. LACM	Kansas	*Protosphyraena pernicosa*	L. Coniacian	87	19.7	
109. KR	Israel	*Squalicorax falcatus*	E. Coniacian	88	18.0	
110. KR	Sinai, Egypt	*Palaeobalistum ? sp.*	Turonian	90	17.2	
111. LACM	Kansas	*Ptychodus whipplei*	M. Turonian	90	18.0	
112. LACM	Kansas	*Squalicorax falcatus*	M. Turonian	90	19.3	
113. KR	Israel	Teleostid, unident.	Cenomanian	93	17.4	
114. KR	Israel	Shark, vertebra	Cenomanian	95	17.8	
115. KR	Israel	Pycnodontidae, bone	Cenomanian	95	17.9	
116. KR	Israel	*cf. Eubiodectes*	Cenomanian	95	17.8	
117. KR	Israel	*Pachyamia*	Cenomanian	95	17.8	
118. FA	Angola	*Cretolamna appendiculata*	Cenomanian	98	18.8	
119. FA	Texas	*Cretolamna appendiculata*	Albian	103	19.5	
120. FA	France	*Protolamna sokolovi*	Aptian	108	17.2	
121. KR	Israel	Pycnodontidae, tooth	Aptian-Albian	113	17.9	
122. AMNH	N.E. Brasil	*Rhacolepis buccalis*	Aptian	115	19.2	
123. AMNH	N.E. Brasil	*Tharrhias arpinis*	Aptian	115	18.3	
124. KR	Israel	Pycnodontidae, tooth	Berr.-Valangin.	138	18.1	

Table 1. (Continued)

Source	Locality	Description	Strat. age	Abs. age	$\delta^{18}O$ marine	$\delta^{18}O$ fresh
125. MNH	Spain	*"Anaethalion" vidali*	Berr.-Valangin.	138	18.1	
126. FA	Oman	*Asteracanthus sp.*	L. Jurassic	150	19.7	
127. MNH	France	*Loptolepis coryphaenides*	Toarcian	185	17.3	
128. PO	Feltville Fm.	*Ischypterus*	E. Jurassic	208		17.9
129. FA	S. France	*Hybodus sp.*	Triassic	215		14.2
130. BM	U.K.	*Nemacanthus monilifer*	Triassic (Rhaet.)	215	16.8	
131. BM	U.K.	*Hybodont teeth*	Triassic (Rhaet.)	215	17.0	
132. AT	Italy	*Pholidophorus gervasutii*	Norian	215	17.7	
133. AT	Italy	*Paralepidotus ornatus*	Norian	215	19.6	
134. AT	Italy	*Paralepidotus ornatus*	M. Norian	220	20.2	
135. AT	Italy	*Parapholidophores nybelini*	M. Norian	220	18.0	
136. AT	Italy	*Paralepidotus ornatus*	M. Norian	220	19.9	
137. AMNH	N. Jersey	*Semionotus sp.*	L. Triassic	220		17.0
138. AT	Italy	*Paleobates latissimus*	L. Carnian	228	17.3	
139. AT	Italy	*Ptycholepis scales*	Landinian	232	16.4	
140. AT	Italy	Fish scales	E. Landinian	235	17.9	
141. AMNH	Texas	Xenacanth shark; unident.	Permo-Triassic	245		20.5
142. MNH	France	Fish, unident.	E. Permian	280		15.9
143. FMNH	Nebraska	Arthrodira tooth	Pennsylvanian	300	19.7	
144. BM	Northumberland	*Strepsodus sp.*	L. Carboniferous	315		14.8
145. BM	Northumberland	*Gyracanthus sp.*	L. Carboniferous	315		17.3
146. BM	Ireland	*Psephodus ps.*	E. Carboniferous	350	17.4	
147. AMNH	Quebeck	*Bothriolepis canadensis*	L. Devonian	370		16.0
148. AMNH	Iowa	*Synthotodus trisulcatus*	L. Devonian	370		17.2
149. AMNH	Ohio	*Dinichthys terrelli*	L. Devonian	370	18.2	
150. MNH	Latvia	*Asterolepis*	Devonian	380		16.4
151. BM	Scotland	*Coccosteus cuspidatus*	M. Devonian	380		15.8
152. NHT	Scotland	*Dipterus*	M. Devonian	380		15.5
153. NHT	Scotland	*Coccosteus*	M. Devonian	380		14.3
154. NHT	Scotland	*Homosteus*	M. Devonian	380		18.1
155. BM	N.S.W	Arthrodira	Devonian (Ems.)	390	19.0	
156. MNH	Spitzbergen	Fish, unident.	E. Devonian	400		13.5
157. BM	Shropshire	Acanthodian spine	E. Devonian	400		13.8
158. BM	Shropshire	'thelodont' scales	E. Devonian	400		15.8
159. AGF	Corwallis Is.	Heterostracan fish	Silurian	410	15.9	

* Marine reptiles ($\delta^{18}O_p$ of marine reptiles agrees well with $\delta^{18}O_p$ of fish-KOLODNY and RAAB, 1988)
** Walrus

by the authors and are described in KOLODNY *et al.* (1983) and KOLODNY and RAAB (1988), respectively. Those marked FA are referred to in GRANDJEAN *et al.* (1987, 1988), AT in TINTORI *et al.* 1985), and NHT in TREWIN (1985, 1986). All identifications were given by the contributors, who also supplied us with a stratigraphic age of the fossil and its habitat (marine vs. fresh water). Stratigraphic ages were translated into absolute age by use of the Geologic Time Scale (PALMER, 1983). We aimed at obtaining the best preserved and least cemented teeth and bone samples. These were crushed, dissolved in nitric acid, and bismuth phosphate was prepared from them according to the TUDGE (1960) procedure (see KOLODNY *et al.*, 1983, and SHEMESH *et al.*, 1988, for details). The $BiPO_4$ was dried, fluorinated at 150°C in stainless steel vessels, converted to CO_2, and analyzed mass-spectrometrically. The standard reproducibility of our results is ±0.3 per mil. Throughout this paper we refer to $\delta^{18}O$ of phosphate oxygen as $\delta^{18}O_p$ and to $\delta^{18}O$ of CO_2 derived from apatite as $\delta^{18}O_c$.

The analysis of $\delta^{18}O_c$ and $\delta^{13}C$ in apatite CO_2 was carried out by acid extraction (KOLODNY and KAPLAN, 1970) after all calcite was preferentially dissolved (SILVERMAN *et al.*, 1959). All $\delta^{18}O$ results are reported in per mil with respect to SMOW, and $\delta^{13}C$ in per mil with respect to PDB.

RESULTS AND DISCUSSION

Paleothermometry—$\delta^{18}O_p$ analyses

Table 1 is a summary of a brief sample description, absolute age of the fishes, their localities, identification of their life habitat, and the isotopic composition of oxygen in phosphate ($\delta^{18}O_p$). Table 2 is a similar summary of $\delta^{18}O_c$ and $\delta^{13}C$ in the structural carbonate of apatite. Figures 1, 2, and 3 summarize this information graphically.

Whereas the analytical reproducibility of $\delta^{18}O_p$ is as reported about ±0.3 per mil, it is more difficult to estimate the degree of "geological noise" which

Table 2. Isotopic composition of oxygen and carbon in apatite carbonate and the coexisting phosphate.

Sample*	$\delta^{18}O_p$	$\delta^{18}O_c$	$\delta^{13}C$
Recent			
14. *Salmo*	15.4	20.6	−3.8
Tunus	21.0	32.7	−10.3
Tunus	21.0	37.1	−4.2
Bothus	23.0	25.7	−4.4
Saurida	23.2	24.6	−3.7
Fistularia	23.2	26.2	−3.7
Rhinobates	22.0	26.2	−5.3
Siganus	22.4	26.4	−4.1
Iago	22.1	28.5	−7.0
Pempheris	22.9	28.6	−4.6
Diplodus	22.9	24.7	−7.6
Mustelus	22.7	25.6	
Cottus	9.0	26.0	−6.3
Fossil			
17. Osteichthian	11.3	20.7	−3.7
18. Lepisosteus	21.5	31.5	−0.5
22. Myliobatis	20.9	29.3	−4.3
27. Achtioptorygian	13.7	21.7	−6.7
36. Carcharodon	20.2	29.0	−4.6
62. Amia	11.0	16.3	−5.0
63. Myliobatis	21.3	28.5	−3.3
64. Lamna	18.1	25.9	−2.2
73. Lepisosteus	12.3	17.2	−5.2
77. garfish	12.7	19.8	−2.3
88. Enchodus	19.7	26.4	−3.3
89. Squalicorax	18.7	26.2	−5.1
92. Teleostid	18.1	21.3	−4.7
94. Lepisosteus	13.4	18.0	−1.9
99. Scapanorhynchus	18.3	24.8	−2.3
102. Ptychodus	18.6	23.3	−3.7
103. Scapanorhynchus	18.3	25.0	−1.7
113. Teleostid	17.4	24.2	−3.6
122. Enneles	19.2	26.0	−8.3
130. Nemacanthus	16.8	23.3	−3.5
131. Hybodont	17.0	23.5	−3.4
137. Semionotus	17.0	21.5	−3.3
144. Strepsodus	14.8	21.5	−2.4
145. Gyracanthus	17.3	22.9	−3.8
146. Psephodus	17.4	20.7	−2.8
147. Bothriolepis	16.0	22.1	−3.6
148. Synthotodus	17.2	24.5	−1.6
149. Dinichthys	18.2	21.7	−6.6
151. Coccosteus	15.8	11.6	−12.2
152. Dipterus	15.5	28.2	3.3
153. Coccosteus	14.3	24.4	−0.5
155. Arthrodira	19.0	20.2	−1.2

* For sample number identification, see Table 1.

should be assigned to our data. Two sets of samples may help in such an estimate. Samples 86–89 are all fish bones of Campanian age from the Zefa-Ef'e area in Israel. They come from a narrow stratigraphic sequence, and their $\delta^{18}O_p$ ranges between 19.1 and 20. Similarly, samples 54–59 come from Kpogame in Togo, all of Middle Eocene age, and yield $\delta^{18}O_p$ between 18.5 and 19.6.

It is significant to note in this context that when Recent fish bones were analyzed (KOLODNY *et al.*, 1983) the spread of $\delta^{18}O_p$ values for six fish specimens of different species from the Gulf of Elat was one per mil (22.3 to 23.3), whereas the spread of $\delta^{18}O_p$ for four specimens of *Sparus aurata* from a single catch from the Bardawil Lagoon was 1.6 per mil (23.6 to 25.2). The difference in noise thus reflects a real difference in the fishes habitat. The Bardawil Lagoon is highly variable both in salinity, water isotopic composition, and temperature, while the Gulf of Elat is a more homogeneous water body.

Hence, it seems safe to assume that the spread of about one per mil observed in different samples from both Togo and Israel reflects, to a large degree, a real environmental variability—either a temperature range of their habitat of a few degrees or a small variation in the isotopic composition (hence salinity) of the sea water. Since no specific information is available on the habitats of the different fossil fishes, such a range should be taken as a rough estimate of the "geological noise" in question.

Figure 1 shows the change of $\delta^{18}O$ in phosphate of marine and fresh-water fishes since the Devonian to the present. The $\delta^{18}O$ can be translated into environmental temperatures by means of the phosphate paleotemperature equation (LONGINELLI and NUTI, 1973a):

$$t\,(°C) = 111.4 - 4.3(\delta^{18}O_p - \delta^{18}O_w) \qquad (1)$$

where $\delta^{18}O_p$ and $\delta^{18}O_w$ are $\delta^{18}O$ of the solid phosphate and the water, respectively. Following estimates of $\delta^{18}O_w$ of pre-glacial ocean water (*e.g.* Savin, 1977) we assume a value of −1 for it. The temperatures calculated by this transformation are shown on the right-hand ordinate axis. The following points may be noted in Fig. 1:

(a) No clear and simple time trend is evident from the plot. The calculated isotopic temperatures for the entire range of 400 My vary between 4 and 35°C.

More detailed examination of the $\delta^{18}O$ variation in the last 150 My (Fig. 2) shows a variation similar to the paleotemperature changes deduced for the same time from the isotopic analysis of foraminifera (SAVIN, 1977). Specifically, the temperature maxima ($\delta^{18}O$ minima) of the Albian (100 My) and the Middle Eocene (50 My) stand out, as do the temperature minimum of the Maastrichtian (70 My), as well as the general cooling trend of the last 100 My. Obviously one cannot expect a perfect correlation between paleotemperature curves like those

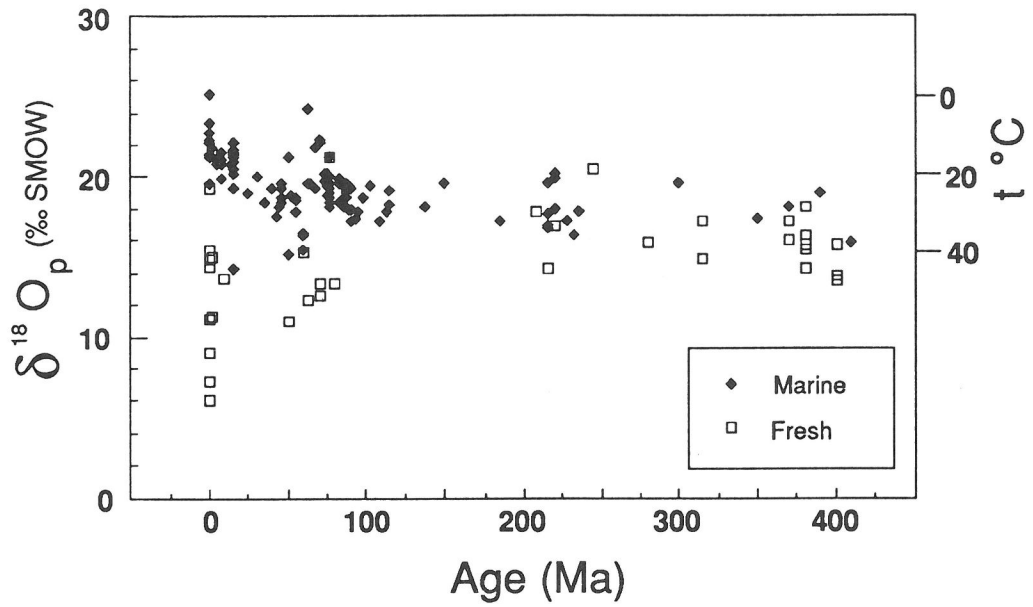

FIG. 1. The secular variation of $\delta^{18}O_p$ in marine and fresh water fishes between the Devonian and the present. The right-hand ordinate denotes temperatures calculated from Eqn. (1), assuming $\delta^{18}O_w = -1$.

of DOUGLAS and WOODRUFF (1981) and that of Fig. 2. In their case the assemblages are benthic and thus record bottom temperatures. These are probably related to a general cooling trend of the high latitudes. Our sample on the other hand includes specimens of different species and genera which cover both a broad geographic range and a wide range of depth habitats, so it is expected to be more noisy. A large part of our samples comes from intermediate latitudes (North America and Europe);

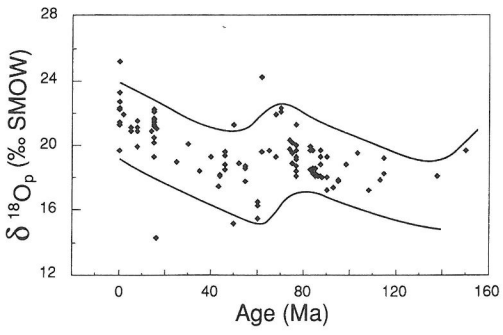

FIG. 2. The secular variation of $\delta^{18}O_p$ in marine fishes in the last 150 My. The envelope marks broad secular temperature trends. Note the general cooling trend in the last 60 My, as well as thermal maxima around 100 My (Albian) and 50–60 My (Eocene), and a thermal minimum around 70 My (Maastrichtian).

indeed, the young (post-Eocene) cooling trend resembles more the high latitude trend detected by SHACKLETON and KENNETT (1975), not the equatorial warming of DOUGLAS and SAVIN (1975). It is likely that when single species fish assemblages from limited geographic areas are sampled through geologic time, a more self-consistent paleothermometric pattern would emerge. A modest beginning in this direction was the study of KOLODNY and RAAB (1988). That study dealt with Cretaceous to Eocene fish remains from the southern Tethys and arrived at temperature curves which show similar trends to previous estimates, though the absolute temperatures are consistently higher than those from contemporaneous carbonates. In fact, the temperature estimates which are derived from $\delta^{18}O_p$ measurements are in considerably better agreement with climate model simulations for the Cretaceous-Eocene (MANABE and BRYAN, 1984) than the previous estimates based on $\delta^{18}O$ of planktonic foraminifera (CROWLEY, 1991).

The isotopic composition of pre-Cretaceous marine fishes does not sharply deviate from the pattern of younger age. The $\delta^{18}O_p$ values remain within the rather narrow limits of 17 and 20. This variation is translated into a temperature range of 35 to 20°C, respectively. The very few samples with $\delta^{18}O$ outside this range will be dealt with separately, below.

(b) No case has been detected where $\delta^{18}O_p$ of a

fresh-water fish fossil is higher than that of a contemporaneous marine fish. Obviously this is the result of the basic relationship between sea water and meteoric water (EPSTEIN and MAYEDA, 1953), the latter being the distillation product of the former. The observed relationship suggests, however, that the analyzed fishes did not undergo significant, post-depositional, isotopic exchange, at least not to the degree that their original, depositional signature would have been erased. The last conclusion might have been doubted in view of the fact that the difference between marine and fresh-water fishes is significantly larger for recent fish than it is for ancient, *e.g.*, Devonian fossils (Fig. 1). This could be interpreted as resulting from increased isotopic exchange for the old fossils. However, in such a case, there is no reason why in some instances marine fossils would not exchange to a degree that they became more ^{18}O depleted than their fresh-water contemporaries. Similarly, fresh-water fishes may become more ^{18}O enriched than marine fossils of the same age. In fact, a slight overlap between marine and fresh-water values is permitted; the Pleistocene fossil gar *Lepisosteus spatula* from Florida (sample #18) has $\delta^{18}O$ of 21.5, which is within the lower range of marine values. Such an isotopic composition is easily understood for a fish from a low latitude, where meteoric water is "heavy," and was even heavier during the Pleistocene (mean present-day Florida rain has a $\delta^{18}O$ of -2 to 0; YURTSEVER and GAT, 1981), and evaporation is intensive.

(c) The range of fresh-water fossil fishes $\delta^{18}O_p$ is much narrower than that of Recent fishes. The first isotopically, very light fishes are of Pleistocene age. This observation of a change in the range between the present and the bulk of the fossil record may be compared with the essentially similar spread (though changing values) of the marine fishes (Fig. 1). We shall deal with this observation below.

In two cases the isotopic analyses of marine fossil fishes are "misbehaved" in the sense that they show surprisingly low $\delta^{18}O$ values:

(1) Samples 67, 68, and 69 are Tertiary sharks *Squatina* and *Striatolamia,* with unexpectedly low $\delta^{18}O$. This regularity applies to several specimens of *Striatolamia striata* and *Sq. prima,* whereas closely related *Striatolamia macrota* and *Myliobatis* have normal values, similar to other fossils of the same age. Table 3 summarizes 40 analyses of $\delta^{18}O$ of sharks and stresses the aforementioned differences. One may speculate that the ^{18}O depletion is a species-related feature resulting in the disequilibrium ^{18}O depletion ("vital effect") or that it is their bone structure which makes some sharks more sensitive to diagenesis or that some feature of their habitat makes those species more likely to undergo fresh-water diagenesis (see discussion below).

Table 3. $\delta^{18}O_p$ of sharks from the Cretaceous—Tertiary (*Squatina-Sq., and Striatolamia—S.*).

Squatina sp. S. striata, Sq. prima.	*S. macrota*	*Myliobatis*
14.2	18.1	18.1
14.6	17.9	19.3
17.8	18.8	18.6
17.9	17.2	17.4
15.4	18.5	18.4
15.7	17.7	20.1
19.0	18.3	18.2
15.4	19.1	17.5
15.3	19.2	20.5
16.8	18.7	18.8
17.3	18.8	18.0
18.0	18.1	
16.3		
15.3		
16.5		
14.9		
15.6		
Average: 16.2	18.3	18.6

(2) Sample 129 is a Triassic *Hybodus* from South France. Its $\delta^{18}O$ is 14.2, clearly not a marine value. This sample has been studied by GRANDJEAN *et al.* (1987). They found here an extremely high $^{87}Sr/^{86}Sr$ ratio (0.708629), much too high for Triassic sea water, a non-seawater REE pattern and a low Sr content (425 ppm). The bulk REE pattern has been confirmed by GRANDJEAN and ALBARÈDE (1989) who analyzed this sample by an ion probe and showed a clear enrichment in the middle REE. Such pattern is interpreted by Grandjean and her co-workers as reflecting deposition in estuarine or near shore conditions. Although GRANDJEAN *et al.* (1987) identify the fossil as marine, MACFARLANE (1923, pp. 192–193) claims that in the Triassic *Hybodus* was ". . . at least partially if not wholly freshwater," and ". . . wavering between a lake and sea environment." Even if the *Hybodus* in question spent most of his life in sea water, fresh-water early diagenesis could have affected its final isotopic composition. The Triassic *Hybodus* has also been studied by FTIR spectroscopy (SHEMESH, 1990). Of all analyzed fossil fishes it showed the second highest crystallinity index, suggesting its severe recrystallization.

Thus, in both of these cases we raise the possibility that it is fresh-water early diagenesis which altered $\delta^{18}O$ of the "misbehaved" fossils.

Both GRANDJEAN *et al.* (1987) and SHAW and WASSERBURG (1985) interpret geochemical signals recorded in fossil fish bones and teeth as reflecting depositional environments. Their approach is principally based on mass balance considerations. Thus GRANDJEAN *et al.* (1987) suggest that because the bulk of the REE in apatitic fossils should be acquired by the fossil early diagenetically, soon after death, some transitional carrier phase (oxyhydroxides, organic debris?) is required. Very fast (postdepositional) REE enrichment is indicated also by the combined REE and U-Th isotopic studies of BERNAT (1975). Such reasoning does, however, not demand that the addition of REE must occur on the sea-floor. If a marine environment is replaced by fresh water while a marine fish bone undergoes diagenesis, *i.e.,* if it undergoes transformation to carbonate fluorapatite (CFA), it may acquire both a low $\delta^{18}O$ of its phosphate oxygen and an unpredictable REE signature depending on the nature of the sediments within which it is buried. We shall return to this discussion below.

We now consider several cases in Table 1, which deserve special attention:

Questionable marine fishes. Two samples have been marked in Table 1 as both marine and fresh water (93, 107). We followed this procedure for those cases where our paleontological information was not unequivocal, identified by our contributor as "? fresh water" or "? marine." Such is the case with the Mid-Campanian coelacanth identified as *Mawsonia.* It had been marked as "? fresh water" when contributed by J. D. Stewart. It comes from a marine unit in Alabama, which also contains terrestrial dinosaurs. Such coelacanths have tended to be fresh water or near shore where previously discovered (J. D. STEWART, written comm.). Cretaceous coelacanths are also known from shallow marine deposits (CARROLL, 1988, p. 148). $\delta^{18}O$ of the phosphate oxygen in the *Mawsonia* bone is 21.3, clearly a marine value.

The gar *Lepisosteus* from the Coniacian Niobrara Fm. is similarly identified; gars are usually fresh water, occasionally brackish, rarely in marine water (NELSON, 1976, p. 63). Even the Pleistocene *Lepisosteus spatula* from Florida, which was discussed above, was not necessarily a purely fresh-water fish; it is euryhaline, and while it generally spends its time in large river systems it may also be found in coastal waters (L. ROE, written comm.). The *Lepisosteus* in case here, comes however from the same unit in the Smoky Hill Chalk Member of the Niobrara Fm. and from the same locality in Trego County, Kansas, as two clearly marine fishes—the pelagic shark *Squalicorax* and *Protosphyraena.* The $\delta^{18}O_p$ value of the gar is intermediate between its two, clearly marine, neighbors. Hence, the simple conclusion from the isotopic analysis of the *Mawsonia* and *Lepisosteus* is that both fishes were marine in the Cretaceous. Our suggestion that early diagenesis of apatitic fossils involves practically complete dissolution-recrystallization (see below), casts some doubt on such a simple solution. If that suggestion is correct, then a fresh-water fish which drifted into the sea sank there to the floor, and became fossilized might not be distinguishable from a marine fish which is found in the same assemblage. The decision as to whether a certain species was fresh water or sea dwelling in the geological past must in such cases be resolved by using additional, often field, evidence. Thus the re-occurrence of *Mawsonia* and *Lepisosteus* with marine $\delta^{18}O_p$ values would serve as a strong support to our suggestion that indeed both these fishes were marine in the Cretaceous.

The Holost *Pachyamia* from the Cenomanian of Israel is an analogous case (# 117). Again, this is a fish presently known to be related to fresh water species (Y. KHALIFA, pers. comm.), but again, it is isotopically undistinguishable from the clearly marine fossils of *Eubiodectes* and the Pycnodontidae (samples 114, 115, 116) which occur in the same area. In this case there seems to be independent paleontological evidence (S. WENZ, pers. comm.) that the Pachyamia was indeed a marine fish in the Cretaceous.

Isotopic analysis of inoceramids. The interpretation of Cretaceous paleotemperatures and paleosalinities has been severely complicated by the seemingly conflicting results of the isotopic analysis of carbon and oxygen of inoceramids, oysters, baculites, and other cephalopods from the Campanian and Maastrichtian Pierre Shale of the Western Interior Seaway. TOURTELOT and RYE (1969) were the first to find that inoceramids had generally much lower $\delta^{18}O$ values (as low as −9.5 PDB) than did the cephalopods. Whereas their results were confirmed by several investigators (SCHOLLE and KAUFFMAN, 1975; SCHOLLE, 1977; PRATT 1984, 1985; ARTHUR *et al.,* 1985; WRIGHT, 1987) the interpretation of the discrepancy varied between explaining it by a "vital effect" (TOURTELOT and RYE, 1969) to referring the ^{18}O depletion in inoceramids to fresh-water influx (PRATT, 1984, 1985; ARTHUR *et al.,* 1985). Accordingly, the paleogeographical interpretations varied: RYE and SOMMER (1980) suggested that the Western Interior Seaway has been brackish to normal in its salinity, whereas WRIGHT (1987) used practically the same data to claim a stratified water body in the Interior Seaway. Sample

104 offers a case to re-examine the $\delta^{18}O$ values in inoceramids from a different angle. We analyzed here an Inoceramus together with the fish often found living inside its shell, the *Inocentrus vulgaris*. Whereas the inoceramid we analyzed yields a low $\delta^{18}O$ value (−7.9 PDB, not in Table 1), the fish shows a perfectly normal $\delta^{18}O_p$ (18.1 SMOW). Hence, we must conclude that both the Inoceramus and the co-habitant fish lived in normal seawater at normal marine temperatures; apparently the inoceramids did not record their environment properly. The initial explanation of TOURTELOT and RYE (1969) seems to be in agreement with our data.

Two sites of oxygen in apatite; $\delta^{18}O_p - \delta^{18}O_c$

Practically all low temperature, sedimentary apatites (phosphorites, apatitic fossils) are francolites, or carbonate fluorapatites (CFA). The location of the carbonate in the CFA lattice of phosphorites is apparently mainly governed by the distorted $(CO_3 \cdot F)^{-3}$ tetrahedron replacing a tetrahedral PO_4^{-3} ion (BORNEMAN-STARYNKEVITCH and BELOV, 1940; ALTSCHULER *et al.*, 1952; BACQUET *et al.*, 1980). The status of the carbonate ion in bone is much less clear and is still largely unsolved (LOWENSTAM and WEINER, 1989, p. 152; NEWESELY, 1989). The main difficulty with carbonate-containing bone apatites is deciding whether the carbonate forms an integral part of the crystal structure or is external to it, *i.e.* adsorbed on the surface of the crystals or in a separate phase. If the carbonate ions replace ions in the structure, it probably occurs in two sites: one in which it replaces hydroxyl and a second site where it substitutes for phosphate ions (NEWESELY, 1989). It is during diagenesis and aging that the poorly ordered, phosphatic bones are transformed into the much better ordered CFA structure.

The occurrence of structurally bound carbonate within the apatite lattice opened the possibility of using the isotopic composition of both the oxygen and the carbon in this carbonate as isotopic thermometers and/or tracers (KOLODNY and KAPLAN, 1970; MCARTHUR *et al.*, 1980, 1986; BENMORE *et al.*, 1983; GLENN *et al.*, 1988). SHEMESH *et al.* (1983, 1988) made use of the simplicity of analytical separation between the oxygen in PO_4^{-3} ($\delta^{18}O_p$) and the one in CO_3^{-2} ($\delta^{18}O_c$) and treated these two coexisting(?) sites as two cogenetic oxygen-bearing phases. It was found that $\delta^{18}O_p$ is very well correlated with $\delta^{18}O_c$. This correlation has been explained as reflecting, at least in part, post-depositional isotopic exchange between the two oxygen-bearing phases. The possibility has also been explored that the linear correlation and its slope reflect non-equilibrium exchange conditions, under which the carbonate oxygen has been altered by an aqueous phase more significantly than its phosphate oxygen counterpart.

On Fig. 3 we plot the variation with age of both $\delta^{18}O_p$ and $\delta^{18}O_c$. Also shown are the values of $(\delta^{18}O_p + 9.5)$, which is a good approximation of the expected value for $\delta^{18}O_c$, if it behaves similarly to a carbonate (both the carbonate paleotemperature equation of EPSTEIN *et al.*, 1953, and Eqn. 1 have a similar slope, with different intercepts; see discussion in SHEMESH *et al.*, 1983). As evident from Fig. 3, in some Cenozoic fish $\delta^{18}O_c$ is indeed close to the $(\delta^{18}O_p + 9.5)$ values. In many other cases, however, especially in the older fish fossils, $\delta^{18}O_c$ is considerably lower than the expected value, thus suggesting its lower resistivity to post-depositional isotopic alteration.

The good correlation between $\delta^{18}O_p$ and $\delta^{18}O_c$ which is observed in phosphorites is absent in living fish (Fig. 4). Whereas the phosphate oxygen reflects well the temperature and the water isotopic composition of the environment in which the fish lived, $\delta^{18}O_c$ has apparently no relation to these parameters. Neither are the isotopic compositions of the two oxygens in living fish-bones related to the "expected" $[\delta^{18}O_p = \delta^{18}O_c - 9.5]$ straight line. An analogous plot of data from fossil fishes (Fig. 5) shows a somewhat better correlation between $\delta^{18}O_p$ and $\delta^{18}O_c$. Almost all points plot to the left of the $[\delta^{18}O_p = \delta^{18}O_c - 9.5]$ straight line. Thus, the relationships depicted on Fig. 5 can be explained by a shifting of the carbonate towards lower $\delta^{18}O$ values by post-depositional interaction with meteoric water. In the above reasoning we consider the plot of Fig. 5 as intermediate between the initial conditions of living fish (Fig. 4) and the "end point" towards which such an assemblage is altered—that of a strong correlation between $\delta^{18}O_p$ and $\delta^{18}O_c$ as expressed by the phosphorite relationship.

The proposed changes in $\delta^{18}O_p$ and $\delta^{18}O_c$ of fish apatite upon fossilization require that the bone mineral undergoes a thorough mineralogical reorganization. Several lines of evidence support such an assumption: SHEMESH (1990) observed a sharp difference between the infrared spectra of bones of living and fossil fish. He attributed these differences to the recrystallization of carbonate-hydroxy-apatite into francolite (CFA). Several studies of REE in apatitic fossils (SHAW and WASSERBURG, 1985; GRANDJEAN *et al.*, 1987, 1988; GRANDJEAN and ALBARÈDE 1989) stressed the dramatic increase of REE concentration in fish bones from very low levels in apatite from living animals to hundreds of parts per million in fossils. The enrichment occurs

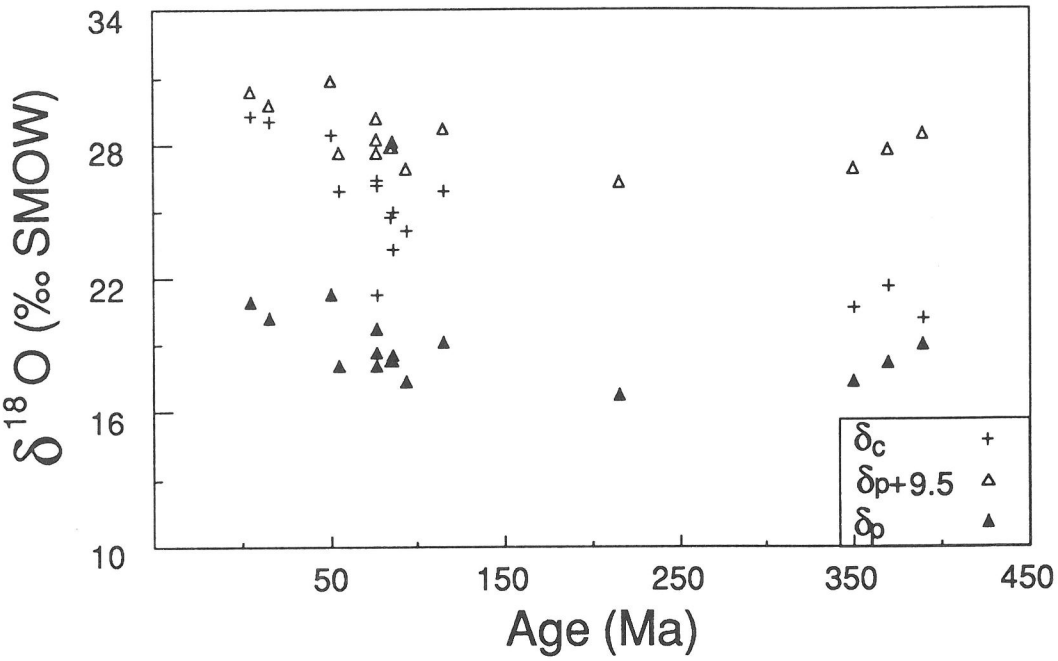

FIG. 3. The secular variation of $\delta^{18}O_p$ and $\delta^{18}O_c$ in fossil marine fishes. Empty triangles mark estimates of $\delta^{18}O_c$ from $\delta^{18}O_p$ ($\delta^{18}O_c$(est) = $\delta^{18}O_p$ + 9.5). Note the good agreement between the estimated and measured $\delta^{18}O_c$ for young fishes, and the divergence between the two values (due to alteration) for older samples.

apparently very rapidly after the sinking of the fish debris to the sea floor. All these changes suggest that upon sinking to the sea floor, fish fragments undergo dissolution and replacement recrystallization. In effect *every fossil fish is a pseudomorph after a fish bone,* the original phase being hydroxy apatite and the replacing one—francolite (CFA). It is quite likely that during that replacement the isotopic composition of oxygen both in the carbonate and the phosphate of apatite are re-equilibrated. Possibly the recrystallization is bacterially mediated (SOUDRY and CHAMPETIER, 1983) so as to reset $\delta^{18}O_p$. Fossil fish fragments may yield $\delta^{18}O_p$ values which reflect the habitat of the fishes because in most cases organisms die and are buried (and fossilized) in environments which are not dissimilar

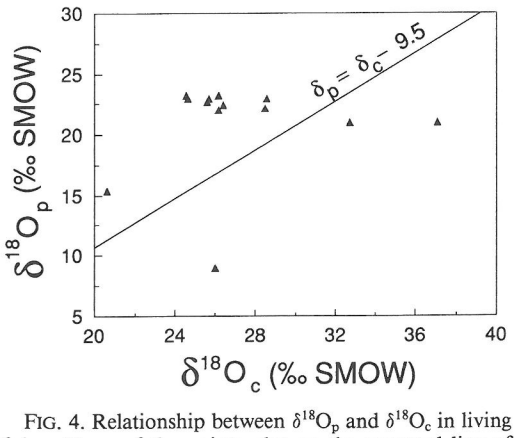

FIG. 4. Relationship between $\delta^{18}O_p$ and $\delta^{18}O_c$ in living fishes. None of the points plot on the expected line of $\delta^{18}O_p = \delta^{18}O_c - 9.5$.

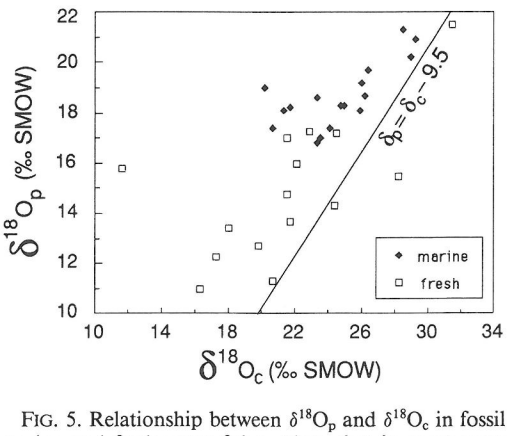

FIG. 5. Relationship between $\delta^{18}O_p$ and $\delta^{18}O_c$ in fossil marine and fresh-water fishes. Note that in most cases measured $\delta^{18}O_c$ is lower than expected from the ($\delta^{18}O_p = \delta^{18}O_c - 9.5$) relationship.

to their life environments. In oscillating or schizohaline environments on the one hand, and at river mouths on the other, one may, however, expect cases in which a marine fish would undergo recrystallization in fresh water or vice versa. In our listing of "misbehaved" fossils we cite several such possibilities (the Tertiary sharks *Squatina* and *Striatolamia,* the Triassic *Hybodus,* the Cretaceous *Pachyamia*).

The variation of $\delta^{18}O_c$ with time (Fig. 3) also demonstrates the susceptibility of oxygen in the carbonate site of apatite to isotopic alteration. Whereas the changes in $\delta^{18}O_p$ are a rather smooth function of age, $\delta^{18}O_c$ fluctuates sharply. A similar conclusion is suggested by comparing $\delta^{18}O_p$ and $\delta^{18}O_c$ of two specimens of *Coccosteus* from the Middle Devonian of Scotland (samples 151 and 153, Table 2). The two samples show a rather small difference in their $\delta^{18}O_p$ values (15.8 vs. 14.3) whereas the respective $\delta^{18}O_c$ are almost 13 per mil apart (11.6 and 24.4, respectively).

Freshwater fishes

The Orcadian Basin fishes. Three fossils (samples 152–154) come from the very well-studied Fish-Beds of the Orcadian Basin (Achanarras and Weydale) in Scotland (TREWIN, 1985, 1986). The habitat of these fishes has been interpreted as rather large, more than 65 m deep, post-orogenic fresh-water lakes. The fish mass mortality has been explained as being caused by hydrogen sulfide poisoning; the high H_2S content of the bottom water is also the suggested cause of the scarcity of bottom dwelling fishes as compared to the abundance of surface water dwellers. Thus, the very abundant *Dipterus* and *Coccosteus* (samples 152 and 153) were both swimming in the upper waters of the lake (TREWIN, 1986), whereas *Homosteus* (154) is interpreted as a bottom feeder. Indeed, the $\delta^{18}O_p$ values of the fish bones are 14.3 and 15.5 for the two surface swimmers, and 18.1 for the *Homosteus.*

Scotland was located between 20 and 30°S of the Devonian equator (SMITH *et al.,* 1973). The Orcadian lakes were fed by waters from the surrounding mountains. TREWIN (1986) notes that "the landscape of the Devonian landmass was still mountainous," but the accompanying sketch suggests rather low mountains (see sketch in TREWIN, 1985, 1986). The isotopic composition of the Devonian lake water may be constrained within narrow limits. In fresh-water lakes density stratification depends only on the temperature-depth gradient. One can hence assume that the difference in $\delta^{18}O_p$ between bottom dwelling fish and surface dwellers (paleontologically identified) depends only on temperature difference at constant $\delta^{18}O_w$. From Eqn. (1) $\delta^{18}O_w$ can be derived for any given temperature. The lower limit for $\delta^{18}O_w$ is calculated from $\delta^{18}O_p$ of the bottom dweller *Homosteus* assuming a temperature of 4°C (the lowest bottom temperature of any fresh-water lake, HUTCHINSON, 1957). The upper limit can be estimated from $\delta^{18}O_p$ of the surface dwellers and an assumption that the temperature of the upper water body was 37°C. Hence, $\delta^{18}O_w$ of the Orcadian water was within the limits of $-7 < \delta^{18}O_w < -3$. Conditions can be further constrained. Near-freezing winter temperatures have probably prevailed within land masses even during the more "equable" stages of Earth history (SLOAN and BARRON, 1990). Hence, bottom water temperature was close to 4°C, and $\delta^{18}O_w$ was closer to the lower estimate of −7. If one assumes $\delta^{18}O_w = -6$ (SMOW), then the estimated temperatures would be higher by about 4°C. Accordingly, the temperature of the water in which the surface dwellers lived was between 20 and 15°C. The emerging set of conditions is rather typical of a vertical temperature distribution in temperate lakes during summer stratification and stagnation (HUTCHINSON, 1957). The relationships between the three Orcadian fishes are thus in good agreement with the expected values and do not suggest post-depositional alteration.

The young and isotopically light fishes. The broader range of $\delta^{18}O_p$ in young fresh-water fishes could also be interpreted as a result of late, post-depositional changes. There is, however, no reason why fish bones which were formed with a broad range of $\delta^{18}O_p$ should converge to a narrower one with time. Moreover, $\delta^{18}O_p$ of pre-Cretaceous fresh-water fish is higher than about +12, whereas in younger fossils values as low as +6 are reached. Such a pattern is not to be expected if all samples underwent increasing post-depositional re-equilibration with time.

It must be stressed that the broad range of $\delta^{18}O_p$ of young fresh-water fishes reflects a broad sampling scheme; thus, the most ^{18}O-depleted samples are fishes from Lakes Baikal, Lake Inari in Finland, and a lake in Idaho. We shall now consider the expected change with latitude of $\delta^{18}O$ values in a solid authigenic precipitate—carbonate or phosphate. The isotopic composition of oxygen in rain-water changes regularly with latitude, altitude, distance from the coast, and intensity of precipitation. An early set of worldwide data has been analyzed by DANSGAARD (1964) who showed that $\delta^{18}O$ of precipitation is linearly correlated with the annual

mean surface air temperature. Actually this correlation is a combined summary of the so-called latitude, altitude, and amount effects, and the suggested change is one of 0.69 per mil per one °C. The DANSGAARD (1964) relationship has been strongly influenced by high latitude stations, whereas JOUZEL *et al.* (1987) noted that the relationship essentially vanishes at high temperatures. A multiple linear regression analysis of a larger data set suggested to YURTSEVER and GAT (1981) that for continental areas $\delta^{18}O$ decreases by about 0.1 to 0.15 per degree latitude, and since temperature decreases with increasing latitude, $\delta^{18}O$ decreases by about 0.25 to 0.4 per mil per °C. The best fit suggested by YURTSEVER and GAT (1981, p. 116) is given in Eqn. (2):

$$\delta^{18}O_w = -11.99 + 0.338t \qquad (2)$$

where $\delta^{18}O_w$ is the weighted mean average isotopic composition of precipitation water, and t is average monthly temperature at the collection site. The isotopic composition of the solid should not change with latitude similarly with $\delta^{18}O_w$, since both $\delta^{18}O_c$ and $\delta^{18}O_p$ are related to temperature by an expression of the type of Eqn. (1). In both cases $\delta^{18}O$ of the solid ($\delta^{18}O_s$) is related to t by a function of the type

$$t = A - 4.3(\delta^{18}O_s - \delta^{18}O_w). \qquad (3)$$

For both apatite and calcite the slope of Eqn. (3) in the low temperature region is −4.3; *i.e.*, $\delta^{18}O$ will *increase* by 1/4.3 = 0.23/°C. By combining Eqns. (2) and (3) one obtains the expected change of the isotopic composition of a solid precipitated from a meteoric water body as a function of the average air temperature in the area where that water body exists:

$$\delta^{18}O_s = 0.10t - 12 + A/4.3 \qquad (4)$$

where A is the same constant as in Eqn. (3). Thus the $\delta^{18}O$ of calcitic or apatitic shells varies rather little with latitude (or surface temperature). The present-day air surface temperature gradient between the equator and latitude 70° of about 30°C would result in a $\delta^{18}O$ range in apatite (or calcite) of about 3 per mil. In the case of Cretaceous or Eocene climates, when the Equator-to-Pole surface temperature gradients were substantially reduced to perhaps one-half the present-day gradient, (BARRON, 1983; SLOAN and BARRON, 1990), this would result in an even smaller variation in the oxygen isotopic composition of shells and skeletons.

The narrow range of $\delta^{18}O_p$ of pre-Pleistocene fishes should hence be considered as largely confirming our expectations. It is the very ^{18}O depleted fish fossils of young geological age that require explanation. The explanation may be provided by another regularity of the isotope systematics of the hydrological cycle, which has been referred to (YURTSEVER and GAT, 1981) as the altitude effect. Rain at the cool, high altitudes is depleted in ^{18}O in comparison to coastal rains. In the present post-orogenic period, when high altitudes are abundant, many water bodies (such as lakes) in low regions get their water supply from water in the mountains. Such water bodies are then characterized by "too light" water in comparison with the values expected from surface temperatures. Thus, at Lake Baikal the average monthly surface temperature is about 10°C; hence, the expected $\delta^{18}O_w$ would be about −8.5 to −9. In fact $\delta^{18}O$ of Lake Baikal water is about −16, as the source of water is from rain falling upon the surrounding (up to 3000 m high) mountains (the Barguzin Range, the Sayan) not upon Lake Baikal itself, hence the very low $\delta^{18}O$ values of Lake Baikal fish bones (+6 to +9). They were deposited from a combination of both ^{18}O-depleted and warm waters.

If high standing mountains are a relatively short-lived phenomenon in Earth history, and if most of Phanerozoic time has not been post orogenic, then it should not be surprising that for most of that time the range of $\delta^{18}O_p$ in fossil fishes is indeed rather narrow. Following that logic the ^{18}O-depleted fishes between 70 and 50 Ma ago (samples 62, 73, 77, 78) from Wyoming and Montana may reflect conditions which followed the Laramide orogeny.

The above discussion is not an attempt to deny that part of the difference in the spread of $\delta^{18}O_p$ values may be due to a bias in sampling: in present day conditions we know there is a Lake Baikal; hence, one goes and samples it. In the geological past such sampling is much less likely. On the other hand, the opposing effects of temperature of precipitation and water composition upon $\delta^{18}O_p$ (and $\delta^{18}O_c$) should make the observed pattern less surprising.

SUMMARY

Isotopic analysis of oxygen in the phosphate of fossil marine and fresh-water fish is apparently the best paleo-environmental recorder among sedimentary phosphates. Fish are clearly a better recorder than phosphorites. This has been demonstrated by the isotopic analysis of phosphorites and fish from the Miocene Monterey Formation of California (KASTNER *et al.*, 1990). The $\delta^{18}O_p$ values for phosphorites from the Monterey (14.9 to 20.8)

are significantly lower and have a larger range than those of Miocene fish bones from the same and related formations (19.9 to 21.5). Thus, the temperatures which are indicated by fish bone analysis are both lower and "more reasonable" than the temperatures derived from the analysis of phosphorites.

The range of temperatures indicated by the isotopic analysis of $\delta^{18}O_p$ in phosphorites seems clearly too high for surface or bottom temperatures of ancient seas and lakes (SHEMESH *et al.*, 1988; KOLODNY and LUZ, 1991). They are, however, quite acceptable as burial-diagenetic temperatures or temperatures of incipient metamorphism. In contrast, the temperatures indicated by fish-bone analysis are compatible with what might be expected from surface environments.

When discussing our results above, we stressed the problems one encounters upon critical examination of our data. These include the possibility of diagenetic changes, "vital effects," and possible long-range preservation problems. Thus, it is quite clear that $\delta^{18}O_p$ in fishes is not an *ideal* recorder. On the other hand it is quite possible that it is the *best* recorder presently available. The final judgment on how good it is in comparison with other paleothermometers will have to wait until a sufficiently large data base is available for inter-calibration.

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