Glacial-Holocene Transition in Deep-Sea Carbonates: Selective Dissolution and the Stable Isotope Signal

Abstract. *The oxygen and carbon isotopic signals of planktonic Foraminifera from closely spaced samples from two box cores taken in the western equatorial Pacific change through the glacial-to-Holocene transition as a result of several factors, one of which is the Holocene dissolution pulse starting about 12,000 years ago and reaching full force shortly after. The onset of dissolution comes shortly after the maximum rate of deglaciation but well before the maximum drop in fertility in upper waters. The effect of dissolution is 20 to 30 percent of the amplitude of isotopic change in* Globigerinoides sacculifer, *at the depth of the present lysocline.*

There are two fundamentally different methods for determining the amplitude of the temperature fluctuations in the Pleistocene ocean. The first depends on the proportions of planktonic species with various temperature preferences, as found within the sediment (*1*, *2*). The second is based on the proportion of the isotopes ^{16}O and ^{18}O within the shells of planktonic Foraminifera (*3*, *4*). Both methods have their pitfalls (*5*, *6*). Among other things, the results of both methods are affected by the amount of differential dissolution experienced by the planktonic assemblage analyzed.

We are concerned here with the magnitude of the effect of differential dissolution on the oxygen isotope signal, and with the usefulness of this effect in the study of carbonate dissolution. Berger has considered this dissolution effect earlier (*7*), reasoning that the selective removal of thin-walled and highly porous variants within the same foram species would enrich the assemblage with thick-walled and terminal forms. These thick-walled forms build much of their shells within deeper and colder water than the more open-structured ones and, therefore, are isotopically heavy (*8*). Berger suggested that the apparent isotopic temperatures could be changed by several degrees Celsius through this mechanism. Savin and Douglas (*9*) have adduced evidence that this is indeed so, by comparing the isotopic composition of individuals of the same foraminiferal species in surface samples from shallow and deep cores. They found enrichment of ^{18}O in the samples from the greater depths, which they ascribed to selective removal of isotopically light variants. However, at least some of their samples come from an area where Pleistocene sediments are exposed on the seafloor at and below 4000 m (*10*). Thus, there is doubt about the exact significance of their data: the increased ^{18}O in the surface samples from these greater depths may reflect the presence of material produced during the last glacial.

Although our results cannot entirely remove this doubt, they do confirm the conclusion of Savin and Douglas that partial dissolution increases the ^{18}O content in a species population (*11*). In addition, they allow an appraisal of when the dissolution effect became important, in relation to other oceanographic events during deglaciation. We also demonstrate an analogous effect of dissolution in the δ^{13}C signal.

Our measurements were made on box core material recovered from the Ontong-Java Plateau in the western equatorial Pacific (*12*). In this area, the glacial-to-Holocene temperature difference is thought to be small, about 2°C (*2*). Two box cores were selected, out of 20, for the present study: ERDC Bx 92 (2°14′S, 157°00′E; 1597 m) and ERDC Bx 128 (0°01′S, 161°26′E; 3732 m). The shallower core, Bx 92, was taken from well above the lysocline (*13*) and there are no signs of dissolution other than in pteropods (*14*). Specimens of pink *Globigerina rubescens* (a planktonic foram species which is common and very susceptible to solution) are present throughout this core. In contrast, the deeper core, Bx 128, taken from within the lysocline, has experienced considerable dissolution within the period represented by the uppermost 14 cm; however, below 14 cm, pink *G. rubescens* appear in traces and become quite abundant below about 18 to 20 cm.

The rise of the compensation depth of pink *G. rubescens* during the transition from glacial-to-Holocene time confirms earlier suggestions of increased Holocene dissolution in the Pacific (*10*, *15*). The total rise from the lowest to the highest level comprises somewhat more than 1 km (*14*).

The average sedimentation rates of Bx 92 and Bx 128 appear to be rather similar, judging by both the preservation stratigraphy and the isotopic signals (~1.8 cm per 1000 years). Winnowing by bottom currents is indicated at the shallow site on top of the Ontong-Java Plateau (Bx 92: 52 percent sand; Bx 128:

Table 1. Average oxygen and carbon isotope values (per mil) of two foraminiferal populations from two box cores. Numbers in parentheses are the numbers of independent determinations.

Depth (cm)	*G. sacculifer*		*P. obliquiloculata*		Depth (cm)	*G. sacculifer*		*P. obliquiloculata*	
	^{18}O	^{13}C	^{18}O	^{13}C		^{18}O	^{13}C	^{18}O	^{13}C
	ERDC Bx 92					*ERDC Bx 128*			
0.7	−1.98	1.95 (3)	−1.19	1.15 (3)	8.5	−1.82	(1)	−1.26	1.01 (2)
2.2	−2.10	2.00 (2)	−1.32	1.11 (2)	9.5	−1.71	1.53 (2)	−1.30	1.04 (2)
4.3	−2.11	2.06 (2)	−1.35	1.12 (2)	10.5	−1.69	1.78 (2)		
6.8	−1.86	2.18 (2)	−1.11	1.03 (2)	11.5	−1.63	1.78 (2)	−1.21	1.04 (2)
8.2	−1.98	2.13 (2)	−1.14	1.19 (2)	12.5	−1.65	1.81 (2)	−1.09	0.95 (2)
9.8	−1.99	2.15 (3)	−1.18	1.20 (3)	13.5	−1.65	2.02 (2)	−1.15	1.11 (2)
11.7	−2.07	2.01 (2)	−1.03	1.12 (2)	14.5	−1.49	2.10 (2)	−0.95	0.95 (2)
13.3	−1.94	2.07 (1)	−1.19	0.94 (2)	15.5	−1.55	1.91 (2)	−0.88	0.86 (2)
14.7	−1.89	(1)	−1.22	1.10 (2)	16.5	−1.60	1.83 (2)	−0.74	0.93 (2)
16.7	−1.83	2.00 (2)	−0.95	1.08 (2)	17.5	−1.46	1.81 (2)	−0.80	1.01 (2)
18.3	−1.87	1.84 (2)	−0.94	0.79 (2)	18.5	−1.32	2.00 (2)	−0.75	1.00 (1)
20.3	−1.61	(2)	−0.79	1.07 (1)	19.5	−1.29	1.75 (1)	−0.80	1.00 (2)
21.8	−1.56	1.96 (2)	−0.72	0.88 (1)	20.5	−1.54	1.75 (1)	−0.85	0.96 (2)
23.3	−1.58	2.16 (2)	−0.77	0.95 (2)	21.5	−1.32	1.85 (3)	−0.55	1.04 (2)
24.5	−0.95	1.79 (1)	−0.43	1.01 (2)	22.5	−1.31	1.74 (2)	−0.56	1.03 (2)
25.2	−1.28	(1)	−0.18	1.02 (2)	23.5	−1.11	1.76 (1)	−0.73	1.04 (1)
26.7	−1.12	1.68 (2)	−0.21	1.11 (2)	24.5			−0.66	0.99 (1)
28.2	−0.85	1.56 (1)	−0.21	1.12 (2)	25.5	−1.09	1.81 (1)	−0.47	1.09 (2)
29.5	−0.75	1.81 (1)	−0.11	1.17 (2)	26.5	−1.19	1.89 (1)	−0.45	0.96 (1)
30.2			−0.16	1.19 (1)	27.5	−1.53	1.65 (1)	−0.55	(1)
31.8	−1.01	1.91 (2)	0.05	0.88 (2)	28.5	−1.09	1.77 (1)	−0.60	(1)
33.2	−0.94	1.88 (5)		1.04 (1)	29.5			−0.43	1.07 (1)
34.5			−0.14	(1)	30.5	−0.94	1.95 (1)	−0.09	1.20 (2)
					32.5	−1.	1.67 (1)	0.05	1.43 (1)
	ERDC Bx 128				33.5	−1.20	1.50 (2)	−0.01	1.27 (2)
0.5			−1.21	1.26 (2)	34.5	−0.73	2.10 (1)	−0.14	(1)
1.5			−1.19	1.29 (2)	35.5			0.03	1.34 (3)
2.5	−1.82	(1)	−1.24	1.16 (2)	36.5	−0.78	(1)	−0.02	1.39 (2)
3.5			−1.06	1.19 (2)	38.5	−0.89	1.86 (1)	−0.16	1.36 (2)
4.5			−1.15	1.24 (2)	39.5	−0.87	2.07 (1)	−0.04	2.05 (1)
5.5	−1.83	1.59 (2)	−1.20	1.17 (2)	40.5	−0.80	1.54 (1)	−0.39	1.34 (1)
6.5	−1.89	(1)			41.5	−0.60	1.75 (1)	−0.50	1.34 (1)
7.5	−1.79	1.99 (2)	−1.24	1.27 (2)	42.5	−0.88	1.91 (1)	−0.30	1.23 (1)

25 percent sand). This loss of fines as a result of winnowing in Bx 92 (and possibly some gain of fines in Bx 128) apparently roughly balances the loss of material by dissolution in Bx 128.

Samples for isotopic analysis were taken from each core at close intervals. In the analysis of the foraminiferal shells by mass spectrometry we followed standard procedures (*16*). The average difference of duplicate runs is near 0.1 per mil for both $\delta^{18}O$ and $\delta^{13}C$.

The results of our oxygen isotope analyses are given in Table 1 and are summarized in Fig. 1, together with information on faunal stratigraphy and ^{14}C dates (both for Bx 92 only). The majority of the isotopic data points represent average values for duplicate determinations.

The isotope data must be considered against the background of faunal variation within the core. Two types of stratigraphic signals are evident: one related to changes in fertility, the other to changes in preservation since the last glacial (Fig. 1, A and B). The "fertility" signal is based on the ratio of *Neogloboquadrina dutertrei* to *Pulleniatina obliquiloculata*, the former being recognized as a species associated with equatorial upwelling. The preservation signal is based on the abundance of (aragonitic) pteropod fragments in Bx 92 and on that of *G. rubescens* in Bx 128 (where no pteropods are preserved). The segment of maximum preservation (and apparently also of maximum fertility) almost coincides with the segment of maximum change in the oxygen isotope signal of Bx 92.

Comparison of the oxygen isotope curves (Fig. 1C) within cores, between two different species, *Globigerinoides sacculifer* and *Pulleniatina obliquiloculata* (hereafter referred to as *sacc.* and *Pull.*, respectively), shows an ecological effect. Comparison between cores shows a depth effect, that is, dissolution.

The signals derived from *Pull.* and *sacc.* differ by about 0.8 per mil, which is equivalent to a difference in apparent (isotopic) temperature of about 3°C. The signals are parallel, demonstrating that either species can be used to reflect the change in $\delta^{18}O$ associated with deglaciation, between 16,000 and 10,000 years ago. Shackleton and Opdyke (*4*) used *sacc.* to describe glacial-interglacial fluctuations in this area of the Pacific. The similarity in range and shape of the signal of a *Pull.*, a deep-living form, to that of the shallow-water *sacc.* supports their argument that the signal in this area is caused mainly by changes in water chemistry rather than temperature. If it were temperature, the *sacc.* signal should be somewhat amplified, since the temperature effects in *sacc.* would presumably be greater than in *Pull.*

The general range of $\delta^{18}O$ (about 1.3 per mil) is in accord with earlier determinations of the glacial effect, recently critically reviewed by Berger and Gardner (*5*). Considering the effects of mixing, the true maximum range of the glacial effect on the oxygen isotopic composition of the water may be considerably larger than suggested in recent estimates (*17*) or a marked temperature effect may indeed be present, or both (*18*).

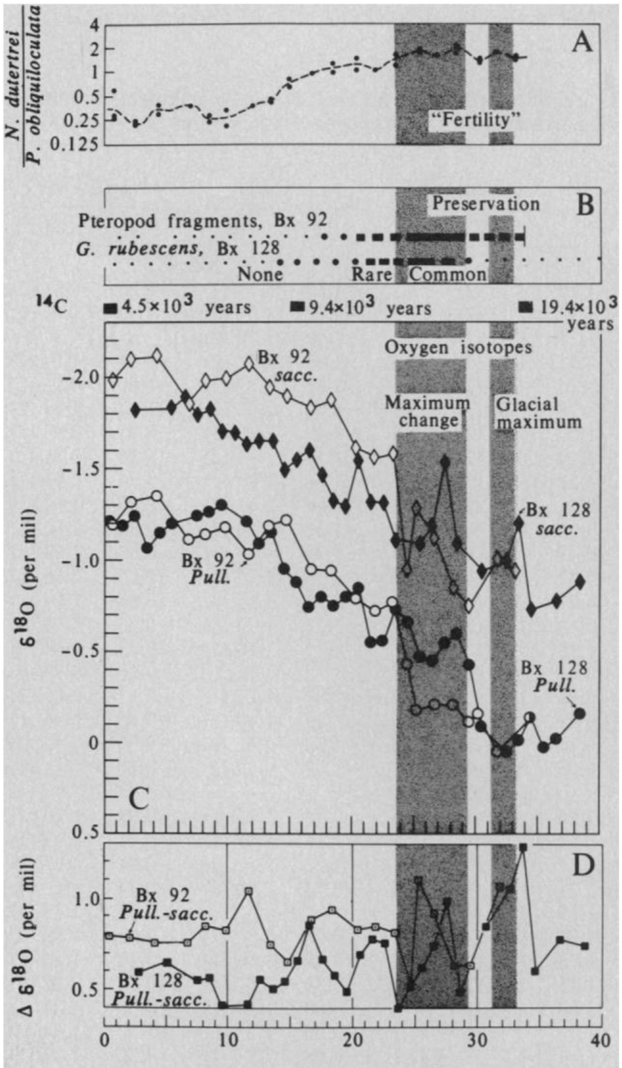

Fig. 1. Faunal stratigraphy and oxygen isotopic composition of the planktonic Foraminifera *Globigerinoides sacculifer* and *Pulleniatina obliquiloculata* in box cores ERDC Bx 92 (1597 m) and ERDC Bx 128 (3732 m). The ^{14}C dates refer to Bx 92 [see (*21*)]. (A) Ratio of *Neogloboquadrina dutertrei* to *Pulleniatina obliquiloculata* (< 295 μm) in Bx 92, interpreted as a "fertility" signal. (B) Distribution of easily dissolved particles (pteropod fragments in Bx 92, *Globigerina rubescens* in Bx 128). (C) Oxygen isotope stratigraphies. (D) Differences between the $\delta^{18}O$ values of *P. obliquiloculata* (*Pull.*) and *G. sacculifer* (*sacc.*) in Bx 92 and Bx 128, as a function of depth in the core.

The difference between the *Pull.* and *sacc.* signals is noticeably decreased in the Holocene record of Bx 128, with respect to the same difference in Bx 92 (Fig. 1D). We interpret this discrepancy as an effect of the Holocene dissolution pulse, starting some 12,000 years ago (compare Fig. 1, B and D).

The highly resistant species *Pull.* is apparently unaffected by the Holocene dissolution in Bx 128. The decrease of the difference between the oxygen signals of *Pull.* and *sacc.*, by about 0.3 per mil, is almost entirely due to a change in composition of the *sacc.* assemblage, that is, a removal of the isotopically lighter shells. The range of composition of the initial population, of course, has to be at least twice the possible shift by selective destruction, that is, 0.6 per mil. The isotopically lighter shells are made in relatively warm, less dense waters, and are constructed to be lightweight, that is, open-structured and porous. The relationship between porosity and water temperature is well known and has been used for paleoclimatic interpretations (*19*). That the more porous foraminifera are more easily dissolved is also well established through field observations and, more recently, through laboratory experiments (*20*).

The timing of the change in the difference between $\delta^{18}O$ of *Pull.* and *sacc.* is of interest, since it denotes the onset of appreciable dissolution. This factor is a much more sensitive measure of the onset of dissolution than the percentage of carbonate, for example. Since Bx 128 is as yet undated, whereas Bx 92 is dated by ^{14}C (*21*), assignment of a date to dissolution events depends on correlation between the two cores. We have already mentioned that the Holocene sedimentation rates of the two cores appear to be similar: the *Pull.* curves follow each other rather closely. Winnowing in Bx 92 and dissolution in Bx 128 presumably subtract about similar amounts of sediment from the original supply. Allowing for some minor differences in sedimentation rate between the two box cores, it appears that a clear divergence between *Pull.-sacc.* separation values develops at about 20 cm (Fig. 1D), which corresponds to 12,000 years ago, according to the ^{14}C dates.

It appears that the onset of strong dissolution closely follows an earlier period of unusual preservation (Fig. 1B). The flipover from unusual preservation to pronounced dissolution is an excellent stratigraphic marker. It occurred between 13,000 and 12,000 years ago. The dissolution effects appear to have reached full force about 12,000 years ago and to have hardly diminished since. The glacial effect on the oxygen isotope signal had its maximum rate of change somewhat earlier than the onset of the dissolution effect. The change in isotopic composition of both *Pull.* and *sacc.* in Bx 92, which is due to the introduction of meltwater, is most visible between 28 and 23 cm, that is, between about 16,000 and 13,000 years ago. The maximum meltwater effect, in terms of a low salinity layer, would be expected at the end of this period. The faunal transition in Bx 92, which is due to changes in the fertility of the surface waters, occurs from 22 to 12 cm (~13,000 to 8,000 years ago) with a maximum change at 14 cm (9,000 ^{14}C years ago) (see Fig. 1A).

The sequence of deglaciation events, as recorded in our box cores, would appear to be as follows: (i) marked introduction of meltwater immediately after maximum glaciation, with a maximum rate between 14,000 and 13,000 years ago, (ii) a sudden increase in dissolution at depth, immediately after the main dumping of the meltwater (*22*), reaching full force at about 12,000 years ago, and (iii) a decrease in fertility throughout the transition period but with a maximum change near 9,000 ^{14}C years ago. Deconvolution of the benthic mixing process is necessary to obtain a more detailed chronology and to ascertain the amplitude of the meltwater effect (*23*).

That dissolution effects precede changes in fertility has been suggested by Pisias *et al.* (*24*). However, their suggestion that deglaciation follows rather than precedes these events is not supported by the present analysis, which is in agreement with the opposite proposition (*25*). Additional studies in areas of high sedimentation rates are necessary to determine the chronology of oceanographic events during deglaciation, which is of the utmost importance to paleoceanography (*26*).

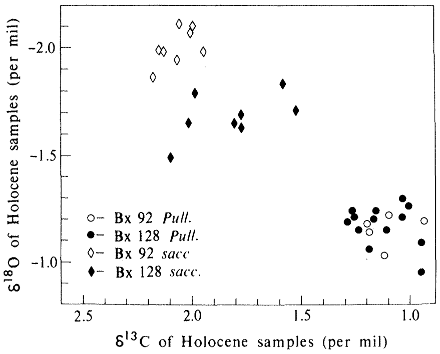

Fig. 2. Oxygen versus carbon isotopes of *Pulleniatina obliquiloculata* (*Pull.*) and *Globigerinoides sacculifer* (*sacc.*) in the Holocene portions of Bx 92 and Bx 128. Note the congruency in *Pull.* and the discrepancy in *sacc.* values, interpreted as an effect of differential dissolution.

One conclusion of our results is that dissolution-affected Pleistocene oxygen isotope sequences based on *G. sacculifer*, such as the one by Shackleton and Opdyke (*4*), cannot be simply interpreted in terms of variation in the isotopic composition of seawater (that is, sea level changes) and constant sedimentation rates (*27*). In addition to introducing another variable to an already complicated picture, however, we also offer a new tool. Once the ecologic difference in the oxygen isotope signals of *Pull.* and *sacc.* is established as a function of time (in shallow cores), deviations from this difference become a sensitive tool for determining the degree of dissolution experienced by sediments deposited at greater depths.

We have also determined the ratios of ^{13}C to ^{12}C within *Pull.* and *sacc.* (Table 1). The $\delta^{13}C$ signal is affected by differential dissolution in a way analogous to $\delta^{18}O$ (Fig. 2). The tests precipitated in shallower water, which dissolve more easily, contain a higher proportion of the heavier isotope than the ones formed at depth (*28*). The reason is that the $^{12}C/^{13}C$ ratio has a nutrient type profile, because ^{12}C is preferentially removed from surface waters by the settling of organic matter rich in ^{12}C and is liberated at depth through the oxidation of organic matter. Thus, surface water is relatively depleted in ^{12}C whereas the water of the oxygen minimum is enriched (*29*). Upon dissolution, the open-structured ^{13}C-rich tests are preferentially removed and the remaining tests will yield a lowered $\delta^{13}C$ value for the species. In our data, the effect is about 0.3 per mil, for the particular degree of dissolution studied. In this case, too, an intraspecific range of at least twice this value, that is, 0.6 per mil, is implied.

The use of the $\delta^{13}C$ values of calcareous plankton has been proposed as an indicator of paleofertility (*30*). Indeed, the $\delta^{13}C$ values of *sacc.* tend to be higher in the Holocene part of Bx 92 than in the glacial one (Table 1), presumably as a result of a decrease in the $^{12}C/^{13}C$ ratio of the bicarbonate in the surface water, parallel to a decrease in nutrients. It will be well to keep in mind the effect of dissolution as one limitation on the interpretation of changes in the carbon isotope signal of planktonic Foraminifera, in cores raised from greater depths.

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13. The lysocline is at a depth of 3500 to 3700 m in this region [see M. N. A. Peterson, *ibid.* **154**, 1542 (1966); F. L. Parker and W. H. Berger, *Deep-Sea Res.* **18**, 73 (1971); M. J. Valencia, *Pac. Sci.* **27**, 290 (1973); J. M. Resig, V. Buyannanonth, K. J. Roy, *Deep-Sea Res.* **23**, 441 (1976)].
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16. Samples were removed from the cores at 1-cm intervals and subjected to a treatment with Calgon solution and ultrasonic vibration to disaggregate the particles and provide clean foraminiferal specimens. The samples were washed through a series of sieves, and individual foraminifera were hand-picked from the size fraction greater than 295 μm. Approximately 0.5-mg amounts of prepared samples were reacted with

100 percent phosphoric acid at 50°C in an "in-line" vacuum system connected to a mass spectrometer (V. G. Micromass model 602C). After measuring the isotopic composition of the released CO_2 against that of a known CO_2 reference gas, we calculated the oxygen and carbon isotopic values for the samples with respect to Pee Dee belemnite (per mil) by the usual proce-d[illegible] [H. Craig, *Geochim. Cosmochim. Acta* **12**, 133 (1957)]. The reference gas was calibrated against standard National Bureau of Standards sample NBS-20 limestone treated in the same way as the samples. The analytical precision expressed as $1 - \sigma$ (where σ is the standard deviation) for NBS-20 standard carbonate was 0.06 per mil, and the average difference between 60 duplicate foraminiferal samples was calculated at 0.12 per mil for $\delta^{18}O$ and 0.11 per mil for $\delta^{13}C$.

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22. A low salinity layer covering the ocean as a consequence of glacial melting and a consequent buildup of CO_2 and increase in carbonate dissolution was proposed by L. V. Worthington [*Meteorol. Monogr.* **8**, 63 (1968)].
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Biochemical Identification of Homogentisic Acid Pigment in an Ochronotic Egyptian Mummy

Abstract. *Roentgenograms of an Egyptian mummy, dating from 1500 B.C., showed extensive calcification of the intervertebral discs and articular narrowing in both hip and knee joints. Biopsy cores from the right hip showed parallel black zones in the region of the articular surfaces, leading to a clinical diagnosis of ochrinosis. The black pigment was extracted, analyzed, and compared to an air-oxidized homogentisic acid polymer. The two substances apparently were identical. The chemical evidence thus confirms the clinical finding of ochronosis, an autosomal recessive disorder. This is, so far as known, the earliest verified case of this disorder.*

Ochronosis is a hereditary disorder in which arthritic symptoms appear in affected individuals because of the accumulation of a black pigment in cartilagenous and fibrous tissues (*1*). The formation of the black pigment has been linked to the metabolism of phenylalanine and tyrosine. The enzyme homogentisic acid oxidase is absent, and the normal degradation product of tyrosine accumulates. The homogentisic acid in turn undergoes oxidative conversion to quinone derivatives, and these polymerize to form the pigment. This disease has been suspected in Egyptian mummies because of characteristic roentgenographic findings (*2*). Although the black pigment has also been ascribed to the materials used in the process of mummification, the mummies were preserved by dehydration, usually with inorganic salts. Hence, this origin for the pigment appeared to be unlikely. A mummy with apparent arthritic symptoms and black pigment accumulation was available to us, and we have therefore carried out chemical studies to ascertain whether the pigment is related to homogentisic acid. This report is believed by us to be the first documentation by modern biochemical methods of a genetic disease in early civilized man.

The mummy Harwa served as a custodian of a granary in Egypt at approximately 1500 B.C. His cause of death is unknown. Roentgenograms suggest that he was in his early thirties. As is usual with many bodies in ancient Egypt, the internal organs were removed prior to mummification. For the past 60 years the mummy has been exhibited in the Field Museum of Natural History in Chicago. It was lent for study to Northwestern University Medical School.

The body was in a good state of preservation with only the face exposed. Roentgenograms of the entire body revealed extensive calcification in all of the intervertebral discs without secondary arthritic features (Fig. 1). Articular narrowing was present in both hip joints and both knee joints. With the use of fluoroscopic control with a Steinman pin, a percutaneous Craig needle biopsy of the right hip was performed.

The tissue obtained was two com-

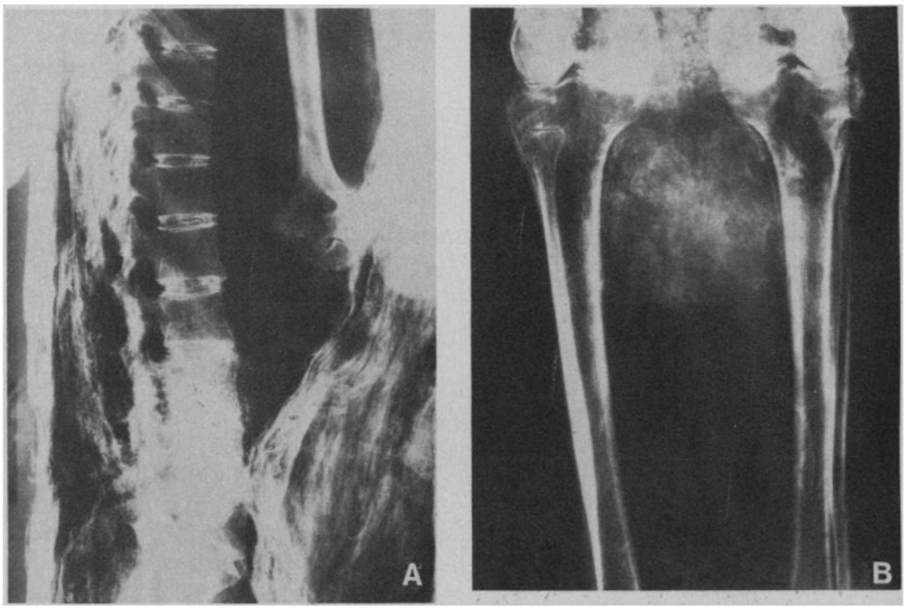

Fig. 1. (A) Lateral roentgenogram of thoracolumbar spine demonstrating calcification of each intervertebral disc. (B) Anterioposterior roentgenogram of the legs showing marked joint space narrowing at the knees bilaterally.