Comments and Communications

Volcanism—A Contributing Factor to Major Change in Sea Level

We know that during the Tertiary there were considerable changes in the level of the sea. We know, also, that the Tertiary was a period of active and extensive volcanism. From the bottom of the Pacific alone there have been poured out millions of cubic kilometers of lava, and the total outpourings on the bottoms of the seas are vastly greater than is generally believed. The number of submarine masses exceeds those that reach the surface and are marked as islands on maps. Perhaps some single masses have displaced more than 50,000 km^3 of water, and the volcanic outflow in the Hawaiian area alone may amount to 500,000 km^3.

With only our present inadequate surveys and data on which to base opinions, it is very difficult to arrive at anything more than a very rough approximation of the amount of displaced water. It should be left to the geophysicists to calculate the probable rise in sea level caused by this displacement, but it appears possible that volcanic activity has displaced enough water to raise the level of the sea as much as 500 m—perhaps more, even if generous allowance is made for compensating subsidence. If such a theory can be substantiated, then answers to some of our perplexing problems connected with sea level changes may be at hand.

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Antiquity of Man in America Demonstrated by the Fluorine Test

The fluorine content of Miocene horse bones from Florida has been reported in Science (**112**, 620 [1950]). Investigations are currently being conducted also on the fluorine content of putatively ancient human and associated extinct animal bones from the same state (personal communications from R. F. Heizer and E. H. Sellards). It is hoped that fluorine tests will decide the questions of contemporaneity and relative antiquity of such disputed specimens as Melbourne man and Vero man.

As was pointed out in the article referred to, the fluorine test for relative antiquity is not new. Some of the investigations upon which it is based were carried out in France during the early part of the 19th century. Revival of interest in the procedure is due in the main to Kenneth Oakley, of the British Museum (Natural History), who has provided new datings for such famous Old World specimens as Piltdown man, Swanscomb man, and Galley Hill man.

Considering the ready acceptance of Oakley's findings and the present industrious application of the test to American problems, it is astonishing that the fluorine dating of the Natchez human pelvic bone published in *The American Naturalist* (**29**, 301, 439, 719) by Thomas Wilson in 1895 has gone unrecognized. If Hrdlička knew of this publication when he wrote his *Skeletal Remains Suggesting or Attributed to Early Man in North America* (*Bur. Am. Ethnol., Bull. 33* [1907]), he failed to mention it. This might be expected because Wilson's conclusions are contrary to those of Hrdlička. The latter concluded on morphological grounds that the Natchez pelvic bone was that of a recent Indian, whereas Wilson concluded from the fluorine content that this bone was as ancient as an associated *Mylodon* bone.

Beginning in 1881, Thomas Wilson spent 5 years in the consular service in Belgium and France. After this he traveled and studied in Europe for 2 more years, and in 1887 he succeeded Charles Rau as curator of prehistoric archeology in the U. S. National Museum. These biographical facts undoubtedly explain his interest in the early French efforts to interpret the fluorine content of human bone. He found the experiments of Adolphe Carnot of Paris particularly illuminating and devoted considerable space in his own paper to their translation.

Although the fluorine test was known to other American anthropologists (*Science,* **21**, 262 [1893]), Wilson alone seems to have had the imagination to apply it to a problem in American prehistory. His reasons for utilizing the Natchez bone were probably (1) the publicity given this specimen a short time before by the geologist Leidy, and (2) the willingness of the Academy of Natural Sciences in Philadelphia to furnish samples for testing.

A first sample was tested for fossilization by W. F. Hildebrand, a chemist of the U. S. Geological Survey stationed in the National Museum. He found that "the human bone is in a higher state of fossilization than is that of the Mylodon."

A second sample was tested for fluorine by R. L. Packard, a Washington chemist working in the Museum laboratory. Commenting on Packard's report, Wilson points out that

> the fluorine in the Mylodon was 0.28, in man 0.38. . . . A reference to [Carnot's] tables will show that for modern bones the average as calculated from twelve specimens, is 0.058. By the same table the Quaternary bones were shown to be 0.36. [He goes on to say that the test] . . . shows two things, (1) that . . . the bones under present consideration, the man and the Mylodon, are substantially of the same antiquity, and (2) . . . their antiquity is about midway between the modern bones and those of the Quaternary geologic epoch.

Failure to recognize this finding may be due to the ambiguous title under which it was published: *"On the Presence of Fluorine as a Test for the Fossiliza-*

tion of Animal Bones." In any case, for 55 years anthropology has been deprived of an important objective argument in favor of the antiquity of man in America.

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The Formation of Free Alkoxy (RO·) Radicals in Solution

Many investigators,[1] on the basis of indirect evidence, have postulated the formation of alkoxy (RO·) free radicals in the course of the decomposition of hydroperoxides by ferrous salts. Direct evidence of the formation of such radicals in the aqueous phase has been obtained by carrying out the decompositions in the presence of butadiene. The products identified are accounted for by reaction sequences of the following type.

$$\mathrm{ROOH + Fe^{++} \rightarrow RO\cdot + FeOH^{++}} \qquad (1)$$

$$\mathrm{RO\cdot + H_2C{=}CHCH{=}CH_2 \rightarrow ROCH_2CH{=}CHCH_2\cdot} \qquad (2)$$

$$\mathrm{2ROCH_2CH{=}CHCH_2\cdot \rightarrow (ROCH_2CH{=}CHCH_2{-\!-})_2} \qquad (3)$$

The yields of dimer vary somewhat with the nature of the hydroperoxide decomposed. With butadiene the best yield (85%) was obtained by decomposing *t*-butyl hydroperoxide; decomposition of α-cumyl hydroperoxide and hydrogen peroxide yielded, respectively, 65% and 30% of the dimeric products.

Butadiene forms, in addition to the dimer formulated in equation 3, smaller amounts (15–20%) of isomeric products—probably $\mathrm{[ROCH_2(H_2C{=}CH)CH{-\!-}]_2}$, together with some $\mathrm{ROCH_2CH{=}CHCH_2CH(CH{=}CH_2)CH_2OR}$. These isomeric products have been separated from the principal dimeric product $\mathrm{[(ROCH_2CH{=}CHCH_2{-\!-})_2]}$ by fractional distillation under reduced pressure.

The carbon-hydrogen content and the molecular weight of the principal dimer are consistent with the empirical formula given above. Evidence of structure has been obtained by ozonolysis and oxidation to succinic acid (isolable to the extent of 80% of the calculated amount), and by hydrogenation and subsequent hydrolysis of the saturated diether. These procedures gave the 1,8 glycol, which was identified by conventional methods.

It is of interest that, when hydroperoxide decomposition is carried out in the presence of a polyamine (e.g., triethylenetetramine) and traces of an iron salt, the butadiene product formed is of the type $\mathrm{ROCH_2CH{=}CHCH_2OH}$.[2] This fact suggests that, under the specified conditions, the intermediate free radical (formed as indicated in equation 2) reacts with the hydroperoxide.

$$\mathrm{ROCH_2CH{=}CHCH_2\cdot + ROOH \rightarrow ROCH_2CH{=}CHCH_2OH + RO\cdot} \qquad (4)$$

Additions of alkoxy free radicals to isoprene, to simple 1-alkenes, and to allyl alcohol have also been studied. They will be reported in detail in the near future.

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[1] For leading references see: Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, **15**, 763 (1950).

[2] These experiments were carried out with E. H. White.

Formation of Colloidal Sulfur

THE recent article by Akiya, Nomato, and Okui (*Science*, **112**, 463 [1950]) concerning the effect of ultrasonic waves and nitrous acid on the production of colloidal sulfur prompts the writer to report on some work done at the University of Wisconsin by C. H. Sorum and the undersigned.

The kinetics of the reaction between thiosulfate ion and nitrite ion in dilute aqueous acid were studied, using the change in pH with time and the change in thiosulfate ion concentration with time. The rate law was found to be

$$\frac{-d[\mathrm{S_2O_3^=}]}{dt} = k[\mathrm{NO_2^-}]^{1.0}[\mathrm{S_2O_3^=}]^{0.2}[\mathrm{H^+}]^{2.0}.$$

Since both iodine titer and hydrogen ion concentration decreased in the course of this reaction, indicating the formation of $\mathrm{S_4O_6^=}$, it is hard to reconcile these data with the conclusions of the authors of the above-mentioned article (for their mechanism would hold if the iodine titer and hydrogen ion concentrations increased).

In our studies, the reaction was observed to take up hydrogen ions quite rapidly in acid solution, for the half-life of the reaction at pH 4.0 is less than 1 min. The formation of elemental sulfur is dependent on the concentrations of thiosulfate ion and hydrogen ion, a fact well demonstrated by the work of La Mer and co-workers (Kenyon and La Mer, *J. Colloid Sci.*, **3**, 163 [1949] and preceding papers). If one assumes the following stoichiometry,

$$\mathrm{2HNO_2 + 2S_2O_3^= + 2H^+ \rightarrow S_4O_6^= + 2NO + 2H_2O},$$

a simple and consistent explanation for the retardation of colloidal sulfur formation by nitrous acid is obtained.

The yellow color, which was ascribed to an unstable intermediate in the first-mentioned article, was observed in our kinetic investigation. Since the rate of its appearance qualitatively followed the reaction rate law for thiosulfate oxidation, we feel it is probably nitrogen dioxide formed by oxygen and nitric oxide.

If desired, further details may be obtained from the writer, or from the thesis filed in the library of the University of Wisconsin at Madison, Wisconsin. As much work remains to be done before a satisfactory mechanism can be postulated, we are not planning any publication of our material at this time.

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