

Table 1. Dates, obtained by carbon-14 dating, of charcoal from one cultural layer of the Anangula site (10).

Laboratory No.	Years ago
I-715	8,425 \pm 275
W-1180	7,660 \pm 300
I-1046	7,990 \pm 230

14 method, are given in Table 1. Living rootlets were present in all samples, and the true ages are probably 10 to 20 percent greater than the ages indicated. Also, geological evidence suggests that the average age obtained by radio-carbon dating is somewhat too young. It is estimated that ash IV, the youngest of the major ashes, is about 5000 years old, for it occurs on the oldest but not the youngest parts of the 10-m storm beach at Nikolski. The age of that beach and of the contemporaneous 3-m beach which borders many parts of the North Pacific today has been estimated, from samples taken at Chaluka (Nikolski), at Cook Inlet, and elsewhere, at about 5500 years (4). Field inspection indicates that weathering of ash IV is less advanced than weathering of the ashes below it to the cultural horizon. Moreover, no bone, shell, or wood has survived in the cultural layer at Anangula, yet such materials are well preserved in the dated midden deposits at Chaluka, the earliest of which were laid down about 5000 years ago in ash IV on top of the 10-m beach. If a date of 8000 years ago were of the right order of magnitude for Anangula, and if only 3000 years separated the two sites, one would expect to see artifacts other than those of stone in the Anangula site and to see less soil formation directly below ash IV. The slightly warmer temperature and presumed reduction in precipitation of the Altithermal (about 5500 years ago) would have increased the depth of oxidation in the ashes underlying ash IV, so direct comparison with present-day soils is difficult. Nonetheless, one expects the soil overlying ash III to represent at least 5000 years and perhaps more. Because the soils below the cultural layer are more weakly developed than those above it, it appears, other things being equal, that the cultural layer must have been deposited somewhat earlier than the mid-point between deglaciation and the present. Deglaciation probably accompanied the abrupt rise in sea level that began between 17,000 and 20,000 years ago, as the ice source was on the

platform that was submerged south of Umnak Island when the sea rose.

Whether the cultural zone is 8000 or as much as 12,000 years old remains in doubt, but clearly the Anangula site is older than any other site recognized in the Bering Sea-Alaska coastal area. Material from Cape Denbigh is distinctly younger, and that of the Campus site near Fairbanks is slightly younger (8). Asiatic affinities are evident, especially in previously unreported angle burins, burin spalls, and core tablets. Also previously unreported are large cores, hammer stones, fragments of a stone dish, and a rubbing stone.

The chance of finding cultural material in this region older than that of Anangula is remote. The rise in sea level caused inundation of most of the earlier home sites, and, in addition, sea-coast erosion during the last 6000 years of high sea levels has been devastating. Sea-cut bedrock platforms, graded to the 3- to 10-m beaches, commonly are 100 to several hundred meters wide. An average rate of lateral erosion of 10 m per century has been estimated for adjacent Unalaska Island (9), and this degree of erosion is probably representative of many places in the Aleutians. Consequently, only those coasts protected from rapid erosion can preserve sites of ancient man. Furthermore, a continuous ice sheet over the Alaska Peninsula during the last major glaciation wiped out any existing traces of early man. Since a major source of ice on the Peninsula was in high mountains, the ice sheet survived later on the Peninsula than on the eastern Aleutian Islands, where the main source was cut off by rising sea level.

Along the Bering Sea-Alaska coast, preservation of sites older than Anangula would have required a very special set of conditions. The most logical place to look for such sites is in the eastern Aleutian Islands.

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References and Notes

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(1961); T. Karlstrom, *Ann. N.Y. Acad. Sci.* **95**, 290 (1961); F. Byers, Jr., *U.S. Geol. Surv. Bull.* **1028-L** (1959), p. 267. Somewhat different conditions existed in the Chukchi Sea north of Bering Strait [G. Moore, *U.S. Geol. Survey Prof. Paper* **400-B** (1960), p. 335], but limitations of space prevent discussion of them here.

5. W. S. Laughlin and G. Marsh, *Am. Antiquity* **20**, 27 (1954).
6. Black was accompanied by C. Turner and G. Boyd on a project supported by National Science Foundation grant G-24148 (1962-63).
7. The excavations were made by A. McCartney, M. Yoshizaki, and R. Nelson under the supervision of W. Laughlin, who studied the site in 1962 and 1963. Black examined the excavations and completed the geologic study in 1963 [See W. S. Laughlin, *Science* **142**, 633 (1963)]. The work was supported by National Science Foundation grant GS-136 (1963-64), by the Research Committee of the Graduate School, University of Wisconsin, and by the Wenner-Gren Foundation for Anthropological Research.
8. This is the interpretation of M. Yoshizaki, Director, Department of Archeology, Hakodate City Museum, Hakodate, Hokkaido, Japan.
9. H. Drewes *et al.*, *U.S. Geol. Survey Bull.* **1028-S** (1961), p. 665.
10. The U.S. Geological Survey date was based on a smaller-than-normal sample, and dilution with dead carbon was required to provide enough bulk for counting.

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Xenon Tetroxide: Preparation and Some Properties

Abstract. *Xenon tetroxide is a yellow solid at low temperature. It has a vapor pressure of about 25 mm-Hg at 0°C. It is unstable at room temperature. The infrared spectrum of the vapor shows it to have tetrahedral symmetry.*

The existence of a gaseous tetroxide of xenon has recently been established in this laboratory by mass spectrometric analysis of the gas that evolves when sodium perxenate reacts with concentrated sulfuric acid (1). This compound has now been prepared in amounts up to 100 mg by reaction of sulfuric acid with sodium or barium perxenate. Some preliminary vapor pressure measurements and a study of the infrared spectrum of the gas have been made.

The perxenate salts, Na₄XeO₆ and Ba₂XeO₆, were prepared by methods described (2). The salts were dried in a vacuum desiccator, but may have contained water of hydration. The sulfuric acid was reagent grade, boiled to remove traces of water.

Amounts of salt up to 500 mg were loaded into the glass (Pyrex) side-arm attached to a glass bulb containing about 5 ml of the acid. The bulb was connected by a glass U-tube to a metal vacuum line. The system was evacuated and the salt and acid were mixed

either by adding the acid to the salt or vice versa. The U-tube was cooled with liquid nitrogen while the reaction was taking place. The course of the reaction was checked from time to time by closing the valve to the pump and noting whether or not an increase in pressure occurred in the manifold. In a satisfactory experiment no pressure increases were observed, indicating the absence of oxygen. After the mixture of acid and salt had stopped bubbling, the pale yellow solid (XeO_4) which had condensed in the glass trap cooled with liquid nitrogen was purified by sublimation into the manifold, where it was collected in a trap cooled with dry ice.

The best yields of XeO_4 (34 percent) were obtained when the reaction took place slowly. The most satisfactory method was to add the salt slowly to the acid that was cooled to -5°C . In general, higher yields were obtained when barium perxenate rather than the more finely divided sodium perxenate was used. If the reaction took place too vigorously, it was accompanied by flashes of fire, producing chiefly xenon and oxygen and only negligible amounts of tetroxide.

Vapor pressure measurements were made by slowly warming the metal trap and then by reading pressures on a monel bourdon pressure gauge at various temperatures up to 0°C . Only on one occasion could the sample be warmed to 0°C . Usually decomposition to elemental xenon and oxygen occurred before the sample reached 0°C . This decomposition could be violent, and in one case it caused a welded seam on a nickel U-tube to be blown open. The observed vapor pressures were 3 mm at -35° , 10 mm at -16°C , and 25 mm at 0°C . The products of decomposition were analyzed by a mass spectrometer and were identified as xenon and oxygen. Three analyses on separate samples gave $\text{Xe}:\text{O}_2$ ratios of 0.546, 0.427, and 0.467 indicating the formula XeO_4 .

It would appear that the gaseous tetroxide can be handled somewhat readily at temperatures as high as room temperature; some decomposition may

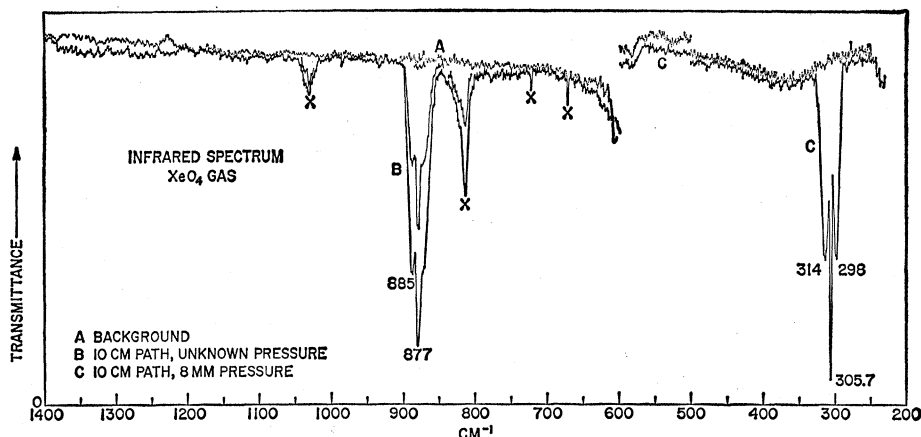


Fig. 1. Infrared spectrum of XeO_4 gas.

occur, possibly giving rise to xenon trioxide and oxygen as well as xenon and oxygen. The condensed phase appears to be more difficult to deal with and samples have exploded at temperatures as low as -40°C .

Gaseous samples of XeO_4 could be manipulated so that the infrared spectrum of the XeO_4 gas was obtained without great difficulty; nickel cells having either silver chloride or polyethylene windows were used. Stability of the gas in the cell was not consistent, and apparently depended on the previous conditioning of the walls and windows. In one instance the cell was left in the Beckman IR-7 instrument for $1\frac{1}{2}$ hours at room temperature. During this time the peak absorbance of the band at 305.7 cm^{-1} changed from 1.08 to 0.81, indicating that 25 percent of the sample had disappeared either by decomposition or reaction. In other instances the whole sample disappeared in a few minutes. Several bands were observed which could be attributed to a nonvolatile impurity in view of their persistence even after the cell was evacuated. Based on their frequency some of the bands could be attributed to XeO_3 .

A tracing of the spectrum obtained is given in Fig. 1. The two intense bands are definitely due to XeO_4 , and the weaker ones marked with an \times are due to impurities, judging by their varying intensity from one sample to another. Frequencies for maxima of P, Q, and R branches may be given for both bands: PQR, 298, 305.7, 314 and 870, 877, 885.

If the XeO_4 molecule has only two infrared-active fundamentals, as our data indicate, it must be a tetrahedral molecule of symmetry T_d , which is in agreement with the structure predicted

by Gillespie (3) prior to the discovery of this compound. For such molecules there are four fundamentals. All are Raman-active, but only two are infrared-active. The triplet structure of our two observed bands, with each branch of approximately equal intensity, also fits the tetrahedral model. From the spacing of 16 cm^{-1} between the P and R branches one can calculate a rough value of bond length, the result being 1.6 \AA with an uncertainty of 0.1 or 0.2 \AA for the Xe—O bond length in XeO_4 . For comparison, XeO_3 solid has an Xe—O bond length of 1.76 \AA (4).

Further, it is instructive to compare frequencies with the tetrahedral OsO_4 molecule and $[\text{IO}_4]^-$ ion, the latter being isoelectronic with XeO_4 . The close correspondence between the infrared-active fundamentals of XeO_4 and $[\text{IO}_4]^-$ lends strong support for the tetrahedral structure.

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7. We thank L. F. Krout for the mass spectrometric analysis. This report is based on work performed under the auspices of the AEC.

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Table 1. Frequencies (ν) of fundamentals.

Mole- cule	ν_1	ν_2	ν_3	ν_4	Refer- ence
XeO_4	?	?	877	305.7	This work
$[\text{IO}_4]^-$	791	256	853	325	5
OsO_4	971	328	960	328	6