| | EAST - CENTRAL SICILY | | SOUTHERN ETRURIA, ITALY | | | |
|---|---|---|---|---|---|---|
| | Gornalunga Valley (near Morgantina) | | La Crescenza Valley (10 Km N. of Rome) | | Valchetta Valley (near Veii) | |
| EVENT | Evidence | Date | Evidence | Date | Evidence | Date |
| Erosion | Modern channel on bedrock bordered by deposits of 2 m, flood plain terrace | Present<br>Began ? | Modern channel on bedrock bordered by deposits of 2 m. flood plain terrace | Present<br>Began pre-1534 ? | Modern channel close to bedrock bordered by deposits of 2 m, flood plain terrace | Present<br>Began pre-1534 ? |
| Deposition | 4 to 5 meters of stream deposits | "Medieval" ? | 5 m. of stream deposits bury Roman buildings and road | Post early 3d cent. A.D. to pre-1534 ? | 8 m of stream deposits bury Roman buildings and road | Post 2d century A.D. In part medieval. Ends pre-1534 ? |
| Erosion | Topographic and stratigraphic unconformity | Began post 325 B.C. | Stratigraphic unconformity | Upper limit post early 3rd century A.D., lower limit pre-50 A.D. | Stratigraphic unconformity | Upper limit post 2d century A.D., lower limit pre 1st century A.D. |
| Deposition | 8 to 10 m. of stream deposits | Ended prior to 325 B.C. Began post 8th century B.C. | No Evidence | | No Evidence | |
| Erosion | Topographic and stratigraphic unconformity | Ended post 8th century B.C.<br>Began ? | | | | |
| Deposition | Stream deposits in 17 to 20 m. terrace | ? | | | | |

Fig. 1. Tentative correlation of erosional and depositional events in certain valleys in east-central Sicily and in southern Etruria (north of Rome).

gravelly material overlain by buff to gray, bedded alluvial silts, sands, and clays. Some coarse, sandy alluvium is cross-bedded and in places ripple-marked.

In a number of places, this alluvium overlies structures of late Roman age (*4*), and these give a *post quem* date to the alluviation. Thus, 10 km north of Rome, in the valley of La Crescenza, the old Roman road leading from Rome to Veii is buried beneath 4 m of silt where it crosses the valley bottom. Close by, and exposed in the trench of the modern stream, stands a Roman mausoleum (about A.D. 50), which was built at a level now submerged by 5 m of river silt. Subsequent Roman structures used the already plundered mausoleum to advantage by incorporating it into their structures. A silver coin shows that this site was certainly occupied after A.D. 209. One to 2 m of alluviation occurred between the construction of the mausoleum about A.D. 50 and the later buildings. The later structures are in turn covered by an additional 3 m of stream-laid deposits (see cover photograph).

In the valley of the Valchetta, under the walls of ancient Veii, another excavation also revealed Roman structures buried in silt. A bath, built on a level at least a meter below the modern stream, dates from the 1st century A.D. This structure was added to in the 2nd or 3rd century A.D. From the level of original construction the thickness of subsequent sedimentation measures more than 8 m.

Upstream from this site the Roman road leading across the Valchetta to Veii is also buried in silt and there are other buried structures which were built originally at a level approximating the modern stream. Farther upstream some medieval pottery found in the upper part of the silt indicates that at least the final stages of alluviation were medieval or younger.

On the basis of these two excavations, in two separate valleys, the alluviation in southern Etruria is dated as late Roman Empire or early medieval.

The modern streams in southern Etruria now flow in deep, steep-walled trenches that express a recent period of erosion. As to the question "when did the streams cut down to their present position," no archeological data are immediately available. A map dated 1534, however, suggests that the trenching had been completed by that time (*5*).

The sequence of erosion and deposition just described indicates extensive changes in stream regime during historic time. Casual observation suggests that the erosion and deposition are not restricted merely to the places described in this report. Rather, these events are widely recognizable throughout the Mediterranean Basin, and alluviation and deposition are the rule rather than the exception. From the point of view of human history, the alluvial sequence buries large chapters of human activity. Extensive buildings have been submerged in silt; roads have been drowned out by stream deposits; and cultivation patterns in valley bottoms surely have been destroyed. While alluviation was going on, erosion of material from slopes must have been extensive. The manner in which these processes affected people has yet to be determined. The geologic record, however, suggests that the physical events cannot be ignored in the reconstruction of human history.

The studies have thus far not explained the causes of these events. The data are still insufficient to decide whether the alternate periods of alluviation and erosion are due to the intervention of man in the landscape, whether they are due to natural changes in the environment or climate, or whether they were brought about by some combination of natural and human causes.

SHELDON JUDSON

*Department of Geology, Princeton University, Princeton, New Jersey*

### References and Notes

1. Geologic field work was carried on during May, June, and July 1962, with financial support from the Guggenheim Foundation and the Fulbright Commission. Archeological cooperation was provided by the British School at Rome and by the Department of Art and Archeology, Princeton University. Harold E. Malde gave helpful criticism in manuscript.
2. "Medieval" is used with little chronologic precision as postclassical and pre-Renaissance. Absolute dates of 5th to 15th century may be assigned without doing too much violence to human or physical history.
3. R. Holloway, *Am. J. Archaeol.*, in press.
4. J. B. W. Perkins will report on the archeological excavations of southern Etruria in *Papers of the British School at Rome.*
5. T. Ashby, *Mappa della Compagna Romana del 1547* (Eufrosino della Volpaia, Rome, 1914).

12 February 1963

■

## Xenon Oxyfluoride

Abstract. *The incomplete hydrolysis of* $XeF_6$ *has been used to prepare a xenon oxyfluoride,* $XeOF_4$. *The latter is a clear, colorless liquid, freezing at* $-41°C$. *The infrared and Raman spectra show that the* $XeOF_4$ *molecule has a fourfold symmetry axis. The large Xe—O stretching force constant indicates the Xe—O bond has appreciable double bond character.*

While the hydrolysis of $XeF_6$ has been shown to lead to $XeO_3$ (*1*), less complete hydrolysis of $XeF_6$ has been used to prepare $XeOF_4$. The existence of this compound was noted in the first report of the Argonne National Laboratories on rare gas chemistry (*2*), and was based on the observation of a $XeOF_4^+$ ion occurring in a mass spectrometer record. I report here some details of the preparation of $XeOF_4$ by the hydrolysis of $XeF_6$, note a few of

Table 1. Fundamental vibration frequencies of $XeOF_4$. (Vibrations of symmetry species $B_1$ and $B_2$ are inactive in the infrared for $C_{4V}$ molecular symmetry.) Abbreviations: P, polarized; D, largely polarized; N.O., not observed; s, strong; M, moderate; v, very; $\nu$, stretching vibration; $\delta$, bending vibration.

| Designation | Species | Raman (liquid) ($cm^{-1}$) | Intensity and polarization | Infrared (gas) ($cm^{-1}$) | Intensity | Description |
|---|---|---|---|---|---|---|
| $\nu_1$ | $A_1$ | 920 | 20 P | 926 | s | $\nu$(Xe–O) |
| $\nu_2$ | $A_1$ | 567 | 100 P | 576 | m | $\nu$(X–F) symmetrical |
| $\nu_3$ | $A_1$ | 285 | 2 P | 294 | s | $\delta$(F–Xe–F) symmetrical out of plane |
| $\nu_4$ | $B_1$ | 527 | 40 D | Missing | | $\nu$(Xe–F) antisymmetrical |
| $\nu_5$ | $B_1$ | 233 | 6 D | | | $\delta$(F–Xe–F) antisymmetrical out of plane |
| $\nu_6$ | $B_2$ | N.O. | N.O. | N.O. | N.O. | $\delta$(F–Xe–F) antisymmetrical in plane |
| $\nu_7$ | $E_u$ | | | 608 | vvs | $\nu$(Xe–F) antisymmetrical |
| $\nu_8$ | $E_u$ | 365 | 15 D | 361 | s | $\delta$(F–Xe–O) |
| $\nu_9$ | $E_u$ | 161 | 3 D | | | $\delta$(F–Xe–F) antisymmetrical in plane |

the properties, and discuss the interpretation of the infrared and Raman spectra of $XeOF_4$.

The same circulating loop with the infrared cell in the spectrophotometer beam that was used to study the Xe—$F_2$ reaction and to prepare $XeF_2$ (*3*) was used (without the heated zone) to prepare $XeOF_4$. Xenon hexafluoride was admitted to the loop to nearly saturated vapor pressure at room temperature, about 20 mm-Hg. Air, which had been bubbled through water, was then slowly admitted to the loop while circulation was continued. The absorbance of $XeF_6$ at 520 $cm^{-1}$ was monitored, and the addition of moist air discontinued when the absorbance decreased to about 2 percent of its initial value. In order to avoid the building up of an excessive concentration of HF, the additions were interrupted when the total pressure reached 600 mm-Hg. The mixture of $XeF_6$ and $XeOF_4$ was frozen in the U-tubes chilled to −78°C. The air and much of the HF were then pumped away. After the U-tubes were warmed, the addition of moist air was continued until almost all of the $XeF_6$ had reacted. The $XeOF_4$ product was frozen and the air and HF pumped away. Mass spectrometer scans of this product showed only ions that could be attributed to $XeOF_4$. Yields of $XeOF_4$ have been as great as 80 percent.

Xenon oxyfluoride is a clear, colorless liquid, freezing at −41°C. It is surprising that the vapor pressure of $XeOF_4$ is greater than that of $XeF_6$, being nearly 7.0 mm-Hg at 0°C while the vapor pressure of $XeF_6$ is closer to 3 mm-Hg. It is slightly less reactive than $XeF_6$, being stable for longer times in quartz. It is, however, more reactive than the interhalogens, in that it reacts slowly with polyethylene at room temperature. Since both $XeF_6$ and $XeOF_4$ have their strongest infrared absorption bands near 610 $cm^{-1}$, the weaker 520 $cm^{-1}$ band of $XeF_6$ and the 927 $cm^{-1}$ band of $XeOF_4$ are useful for the analysis of mixtures of $XeF_6$ and $XeOF_4$ which sometimes result from preparations intended to make $XeF_6$ (*4*).

The fundamental vibration frequencies of $XeOF_4$ have been obtained from the Raman spectrum of the liquid, observed by George Begun of Oak Ridge National Laboratory, and from the infrared spectrum of the vapor. They are listed in Table 1. The entire vibrational spectrum, including Raman line polarizations and infrared band contours, is in accord with a structure having the $C_{4v}$ symmetry, and in many details resembles the $IF_5$ (*5*) and $BrF_5$ (*6*) vibrational spectra. The identifications given in Table 1 are based on this symmetry. The very prominent Q branch of the 927 $cm^{-1}$ infrared band indicates, by itself, the $XeOF_4$ must be very nearly a symmetrical top molecule. The intensity of the infrared band $\nu_2$, the Xe—F symmetric stretching vibration, is less than the intensity of $\nu_1$, the Xe—O stretching vibration. The relative intensities are comparable with those in $BrF_5$. This may be taken as evidence that there is no sizable Xe—F vibrational component parallel to the symmetry axis. Thus, the structure is probably similar to the $BrF_5$ structure. It would appear that the $XeOF_4$ structure may not differ greatly from a square pyramid with the Xe atom close to the plane of the four fluorine atoms and the oxygen atom at the apex.

The force constants have been computed for the idealized 90° bond angles. The Xe—F stretching constant (3.21 millidyne/Å) is about 12 percent greater than the 2.85 md/Å value found for $XeF_2$ (*2*). The Xe—O stretching constant is more than double this, 7.11 md/Å, a very large value indicating appreciable double bond character to the Xe—O bond. This stretching constant is about 25 percent larger than the value 5.66 md/Å pertaining in $XeO_3$ (*7*) where the short 1.76 Å XeO distance indicates appreciable double bond character.

*Caution:* The dangerously explosive $XeO_3$ can be as readily prepared by the hydrolysis of $XeOF_4$ as by the hydrolysis of $XeF_6$.

*Note added in proof.* At the Conference on Noble Gas Compounds, 22–23 April 1963, C. L. Chernick, H. H. Claassen, H. H. Hyman, J. G. Malm, P. Plurien, L. A. Quarterman, and I. Sheft reported the preparation of $XeOF_4$ by the hydrolysis of liquid $XeF_6$. H. H. Claassen, C. L. Chernick, and J. G. Malm reported the vibrational spectrum which they also interpreted in terms of the $XeOF_4$ structure given in this report.

D. F. Smith

*Technical Division, Oak Ridge*
*Gaseous Diffusion Plant,**
*Oak Ridge, Tennessee*

### References and Notes

1. D. F. Smith, *J. Am. Chem. Soc.* **83**, 816 (1963).
2. C. Chernick *et al., Science* **138**, 136 (1962).
3. D. F. Smith, *J. Chem. Phys.* **38**, 276 (1963); P. A. Agron *et al., Science* **139**, 842 (1963).
4. E. E. Weaver, Bernard Weinstock, and C. P. Knop, in their report on $XeF_6$ [*J. Am. Chem. Soc.* **85**, 111 (1963)], note the broad band of $XeF_6$ at 520 $cm^{-1}$, which they incorrectly assert is not associated with any of the xenon fluorides, $XeF_2$, $XeF_4$, or $XeF_6$. They then attribute the $XeOF_4$ bands $\nu_4 + \nu_7$ at 1150 $cm^{-1}$, and $\nu_2 + \nu_7$ at 1189 $cm^{-1}$, to $XeF_6$. These bands do not occur in the $XeF_6$ spectrum.
5. R. C. Lord, M. A. Lynch, W. C. Schumb, E. J. Slowinski, *J. Am. Chem. Soc.* **72**, 522 (1950).
6. C. V. Stephenson and E. A. Jones, *J. Chem. Phys.* **20**, 1830 (1952). The force constant analysis given there for $BrF_5$ has been applied with only trivial modifications to $XeOF_4$. See also R. S. McDowell and L. A. Asprey, *J. Chem. Phys.* **37**, 165 (1962) for the infrared spectrum.
7. D. M. Templeton, Allen Zalkin, J. D. Forrester, and S. M. Williamson [*J. Am. Chem. Soc.* **83**, 817 (1963)] have shown $XeO_3$ to have a pyramidal structure with 103° bond angles and 1.76-Å bond length. My observation of the infrared spectrum of $XeO_3$ gives $\nu_1 = 770$ $cm^{-1}$, $\nu_2 = 311$ $cm^{-1}$, $\nu_3 = 820$ $cm^{-1}$, $\nu_4 = 298$ $cm^{-1}$, which, when combined with the structural information, permits the evaluation of the force constants.

* Operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

22 April 1963