

Table 2. Heat treatment of stishovite at 1 atm pressure. The bulk color of the samples changed from grey to white with the presence of a large amount of amorphous material. A, amorphous, C, cristobalite, Q, quartz, S, stishovite, W, weak. For comparison, data from the literature is included. *a*, Synthetic stishovite of Stishov and Popova [*Geokhimiya* No. 10, 837 (1961)]. *b*, Natural stishovite, Fahey (11).

Temp. (°C)	Time (hr)	Results		R.I. aggre- gate*
		X-ray	Microscopy	
1100	18	C + Q	Q + A + C	—
1100	2	C + Q	Q + A + C	—
1060	0.5	C	A	1.456
1040	0.1	A	A	1.456
750	0.1	A	A	1.480
750	0.2	A	A	—
650	0.2	W S	S	1.500
500	0.2	S	S	—
425	3.5	S	S	1.740
350	70	S	S	1.783
350	0.2	S	S	—
130	0.5	S	S	—
900 (<i>a</i>)	6.0	C + A	—	—
498 (<i>b</i>)	165	A + S	—	1.557

* R.I. of starting stishovite aggregate (1.793 average).

noteworthy whether it arises from an SRO phase directly from the coesite or from an intermediate quartz phase. Under dry conditions, cristobalite crystallized from silica glass powder only after heating ½ to 1 hour at 1300°C (9). We observed no growth of cristobalite from quartz (–325 mesh) by these high-temperature x-ray methods after exposure for 10 hours at 1200°C, and only 5 percent after an additional 6 hours at 1250°C.

All the experiments on stishovite were conducted with a natural stishovite (3) supply that weighed 20 mg (10). The individual experiments, on 1- to 2-mg samples which were contained in platinum envelopes, were limited to static runs at different temperatures followed by rapid quenching. The data in Table 2 show that the stishovite differs markedly from the coesite in metastable persistence. It withstands exposure at 425°C for a few hours, but becomes completely amorphous to x-ray diffraction methods after heating less than 5 minutes between 650° and 750°C. Judging from the change of the aggregate refractive index, stishovite breaks down slowly at 350°C and much faster at 425°C. At lower temperatures the stishovite should be more resistant to change, obvious in its persistence in the crushed sandstone of the Arizona Meteor Crater formed thousands of years ago. At higher temperatures and longer heating times (½ to 18 hours) crystallization of quartz (in the stability field of tridymite) in the presence of the SRO phase is again observed. Although cristobalite is the

first to be observed by x-ray diffraction it is barely evident microscopically after 18 hours at 1100°C whereas quartz can be detected microscopically after 2 hours. No evidence of a transient formation of coesite from the much denser stishovite has as yet been found.

In Fig. 2, we attempt to summarize schematically some of the results obtained and to offer a probable interpretation. Coesite apparently forms a "dense," fine grained SRO phase, which then is converted to quartz. In the case of stishovite it is inconceivable that the rutile-type structure (where the coordination number is 6) could avoid the SRO stage and indeed there is direct evidence for the formation of the SRO and subsequent conversion at low temperatures. That the refractive index of the SRO phase rapidly approaches that of silica glass, may be a manifestation of a high disordering tendency of the coordination change, not involved in the case of coesite. The relative amounts of the various phases formed in any particular run might be explained on the basis of the competing reactions stishovite (or coesite) → SRO, SRO → quartz, quartz → SRO, and SRO → cristobalite with widely differing activation energies (12).

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References and Notes

1. A. C. D. Chaklader and A. L. Roberts, *J. Am. Cer. Soc.*, **44**, 35 (1961).
2. W. Ostwald, *Z. Physik. Chem.*, **22**, 306 (1897).
3. S. M. Stishov, S. V. Popova, *Geokhimiya* No. 10, 837 (1961); C. B. Sclar, A. P. Young, L. C. Carrison, C. M. Schwartz, *J. Geophys. Res.*, **67**, 4049 (1962).
4. E. C. T. Chao, J. J. Fahey, J. Littler, E. J. Milton, *ibid.*, **67**, 419 (1962).
5. F. Dachille and R. Roy, *Z. Krist.*, **111**, 451 (1959).
6. L. Coes, *Science*, **118**, 131 (1953).
7. R. Roy and E. F. Osborn, *J. Am. Chem. Soc.*, **71**, 2086 (1949).
8. H. A. McKinstry, dissertation, Pennsylvania State University, 1960.
9. R. Rieke and K. Endell, data cited by R. B. Sosman in *The Properties of Silica* (Chemical Catalog Company, 1927), p. 99.
10. The stishovite was obtained from the U.S. Geological Survey through the courtesy of E. C. T. Chao. The sample had been concentrated from the crushed sandstone of the Arizona Meteorite Crater.
11. J. J. Fahey, abstracts, Annual Meeting Geol. Soc. Am. (1962), p. 49; and personal communication.
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Xenon Fluorides: Fluorine-19 Nuclear Magnetic Resonance Spectra

Abstract. Chemical shifts have been measured for liquid XeF_2 , XeF_4 , XeOF_4 , and XeF_6 , and F^{19} - Xe^{129} spin-spin coupling constants for XeF_4 and XeOF_4 . The data are in accord with reported structures and are similar to values in the literature for chemical shifts of fluorides of neighboring elements.

The F^{19} nuclear magnetic resonance spectra of XeF_2 , XeF_4 , XeOF_4 , and XeF_6 were obtained with a Varian high-resolution spectrometer operating at a fixed frequency of 56.4 Mc/sec. The samples were placed in quartz capillary tubes, each containing about 10 mg of a xenon compound.

No signals were obtained with solid XeF_2 or XeF_4 . A single broad peak was observed for both solid and molten XeF_6 . Molten XeF_2 gave a broad peak barely visible above the background noise. Liquid XeF_4 and XeOF_4 both gave spectra consisting of two lines symmetrically distributed about a stronger center line.

The center line results from F atoms bonded to the zero-spin isotopes of xenon. The two outside lines result from the spin coupling of F^{19} with Xe^{129} (spin ½). The F^{19} spin coupling with Xe^{131} (spin 3/2) should produce four lines with a spacing three tenths that of the Xe^{129} interaction and areas 10 percent of the center line of the spectrum. These peaks were not observed; however, even a small relaxation broadening effect due to the quadrupole moment of Xe^{131} would make these small peaks blend into the background.

The experimental data obtained in this study, together with a similar measurement (1) for a solution of XeF_4 in HF are presented in Table 1.

The spectra of XeF_4 and XeOF_4 both indicate the magnetic equivalence of the

Table 1. Chemical shifts (δ) and spin coupling constants (J) for xenon fluorides: (l, liquid; s, solid).

Compound	Temp. (°C)	δ (ppm)*	J (cy/sec)†
XeF_2 (l)	132	~600‡	
XeF_4 (l)	114	445	3836
XeF_4 (in HF)§	Room	450	3860
XeOF_4 (l)	26	329	1127
XeF_6 (s)	26	330	
XeF_6 (l)	56	340	

* Chemical shift from $F_2 \equiv 0$. † F^{19} - Xe^{129} spin-spin coupling constant. ‡ Estimate from scope trace. § Data from (1).

Table 2. Spin-spin coupling constants for fluorides of Xe, Sb, and Te.

Compound	Cycles per second		Reference
	J	J'	
Xe ¹²⁹ F ₄	3836	13040	This work
Xe ¹²⁹ OF ₄	1127	3830	This work
Sb ¹²¹ F ₆	1937	7610	(5)
Te ¹²⁵ F ₆	3688	10980	(6)

four fluorines in each of the compounds. This is in agreement with the square planar structure reported for XeF₄ (2) and the fourfold-symmetry axis shown by the Raman and infrared spectra of XeOF₄ (3).

The chemical shifts (δ) for the four compounds are in a logical order; the higher numbers indicate a greater degree of shielding of the F¹⁹ nuclei. The δ values seem to bear closest resemblance to those of the iodine fluorides (4).

Table 2 shows spin-spin coupling constants (J) for fluorides of Xe, Sb, and Te (M). The J values have been adjusted whereby $J' = J_{MF} (\gamma_F/\gamma_M)$, to compensate for the difference in magnetogyric ratios (γ) of the nuclei. It is reasonable to expect XeF₄ to have a larger J value than XeF₆, as is true of

other series of fluorine compounds (6). Assuming a J' value for XeF₆ comparable to that for TeF₆, the J' value for XeF₄ does not seem out of line. Data for compounds analogous to XeOF₄ are not available.

The nuclear magnetic resonance spectra observed so far fail to reveal any major difference between the xenon compounds and compounds of their analogous neighbors in the periodic table (7).

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References and Notes

1. T. H. Brown, E. B. Whipple, P. H. Verdier, *Science* **140**, 178 (1963).
2. J. H. Burns, P. A. Agron, H. A. Levy, *ibid.* **139**, 1208 (1963).
3. Private communication, D. F. Smith, Technical Division, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee.
4. H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.* **19**, 1259 (1951).
5. W. G. Proctor and F. C. Yu, *Phys. Rev.* **81**, 20 (1951).
6. E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.* **81**, 1084 (1959).
7. The compounds used were prepared by D. F. Smith, Technical Division, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tenn. This paper is based on work performed for the U.S. Atomic Energy Commission by Union Carbide Corporation.

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Burns and Other Skin Lesions: Microcirculatory Responses in Man during Healing

Abstract. *Morphological changes in the cutaneous microcirculation during wound healing have been studied by capillaroscopy in man. In experimental and accidental burns, abrasions, and lacerations, in addition to the anticipated revascularization by the deeper dermal vessels, a distinctive pattern of response by the surrounding papillary capillaries was consistently observed. This appears to be a general phenomenon in healing of skin lesions and suggests the possibility that a potent capillary-attracting factor may be produced within the injured tissue.*

Mechanical and thermal injury to the skin or any other vascularized tissue results in profound changes in the minute blood vessels supplying the damaged area. To discern the relationship of these changes either to the specific pathogenesis of the lesion or the generalized reparative response of the human cutaneous vasculature, the reaction of the microcirculation to experimentally produced skin lesions was followed during both the acute and healing stage.

The general structure of such changes can easily be observed by capillaroscopy, and this technique was used to study experimental lesions produced by burn, laceration, and abrasion in the forearm skin of volunteers. It was antic-

ipated that major changes would be seen only within the injured area itself; however, striking and unexpected vascular changes occurred during healing in capillaries in the area surrounding the lesions. These changes proved to be a distinctive, reproducible response which was observed during healing of all the experimental lesions. This response has also been detected in a number of other skin lesions.

Lesions were produced on the ventral surface of the forearm. This area is conveniently studied by capillaroscopy, and the structure of its microcirculation is well-known. The keratin was stripped with cellophane tape to afford a clearer view of dermal vessels, and oil and a

cover slip were applied to the lesions to reduce surface reflection. These lesions were observed microscopically and photographed (black and white film) with a 25 mm microtessar lens (1, 2).

Stripped and unstripped areas of the keratin were burned with a heated platinum wire 1 mm in diameter and several millimeters long. To make the degree of burn roughly constant, we waited 5 seconds after the wire ceased to be visibly red hot before inducing the burn. The depth of the burns was approximately constant and on histological examination the burns were entirely within the upper dermis. Lacerations and abrasions, extending into the superficial dermis and resulting in mild bleeding, were produced with a razor. The lesions were observed closely with the capillaroscope and photographed frequently. Accidental burns and lacerations were observed as well.

The response of the microcirculation after acute injury and the time sequence of changes during healing were similar in all experimental lesions as well as in accidental ones.

A typical sequence in one burn is shown in the illustrations. The area to be burned is marked with ink (corners of Fig. 1a). Ten minutes after application of the heated wire, a coagulum has formed in the area (Fig. 1b). The coagulum darkens and enlarges and forms the usual eschar. At day 3 (Fig. 1c) the area seems to have widened, and a horizontal orientation of the surrounding capillaries appears, though in the figure it is difficult to see because of the eschar. By day 6 (Fig. 1d) the eschar loosens and the horizontal inwardly-directed capillaries are more easily seen. The surrounding pattern is more obvious at day 8 (Fig. 1e), and by day 10 the eschar has come off and the vascular tufts growing up from the deeper dermal vessels into the burned area are revealed (Fig. 1f). The edges of the healing burn are supplied by the surrounding undamaged capillaries that have turned horizontally and have grown a short distance into the margin of the burn. Capillaries farther out from the edge also tilt horizontally, but the slant decreases with distance from the site of the burn. Vessels growing up from below into the center of the burned area continue to branch and appear to sprout new capillaries (Fig. 1g, day 20). The surrounding pattern of horizontally oriented capillary loops disappears slowly over a long period as