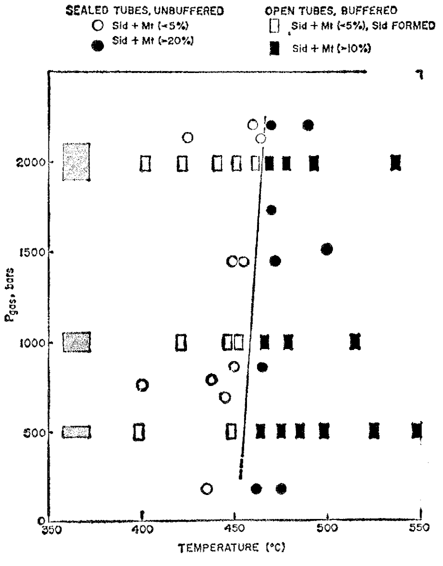

Fig. 1. Experimental results on siderite decomposition to magnetite + graphite. Sealed-tube runs (Rosenberg) shown by circles; buffered open-tube runs (French) shown by rectangles. The solid line indicates the univariant curve for the assemblage, siderite + magnetite + graphite + gas, obtained from the open-tube experiments; virtually the same curve is obtained from the sealed-tube experiments (Table 1). The large rectangles at the left-hand side indicate the experimental uncertainty, ± 7°C and ± 5 percent of the total pressure.

rium could then be demonstrated by two reactions in a single run, either by decomposition of the siderite sample or by growth of siderite from magnetite in the buffer mixture. Equilibrium temperatures were located by (i) production of siderite throughout the entire buffer below the equilibrium temperature, and (ii) production of large amounts of magnetite (in excess of 10 percent of the volume) above the decomposition temperature. The two criteria yielded consistent equilibrium temperatures.

The equilibrium temperatures obtained are compared in Table 1; Fig. 1 shows the experimental data. The temperature uncertainty for each experimental point is probably ±7°C. Agreement between the two sets of data is excellent, particularly above 860 bars, where sufficient data are available. At lower pressures, the apparent close agreement may be conditioned by the small number of sealed-tube experiments.

The agreement between decomposition temperatures determined by two different experimental methods indicates (i) that the temperatures determined do in fact represent equilibrium decomposition of siderite to magnetite and graphite, and (ii) that buffering of f_{O_2} during the sealed-tube experiments is established by precipitation of graphite or carbon from the gas phase.

The equilibrium, siderite + magnetite + graphite + gas, specifies the maximum temperature for stable existence of siderite in an atmosphere of CO_2 + CO (*8*); higher values of f_{O_2} produce lower decomposition temperatures. If graphite is absent, the assemblage, siderite + magnetite + gas, may exist over a temperature interval in excess of 100°C (*8*); this interval may be increased if gas compositions metastable with respect to graphite can be preserved. Therefore, the decomposition of siderite to magnetite cannot be used as an accurate geothermometer unless the value of f_{O_2} is specified independently in some manner, for example, by the presence of additional phases such as graphite.

Studies of metamorphosed sedimentary iron formations (*8*, *10*, *11*) indicate that original siderite in such rocks disappears by reaction with available silica and water to form the iron-amphibole grunerite, $Fe_7Si_8O_{22}(OH)_2$. Temperatures for this reaction must be below those for the decomposition of siderite itself, but they are dependent on the fugacities of both H_2O and CO_2 and have not been experimentally determined. Approximate temperatures of 300° to 400°C have been estimated for the formation of grunerite from geological evidence (*8*, *11*); the estimates are consistent with the upper limit of siderite stability established in this study.

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Fallout from the Nuclear Explosion of 16 October 1964

Abstract. *Measurements of the concentrations of 20 fission products in a sample of rain collected at Fayetteville, Arkansas, on 26 October 1964, yielded two "mass-yield" curves; one for fresh debris from the Chinese nuclear explosion, and another for older debris. The former curve resembled the mass-yield curve for neutron-induced fission of uranium-235.*

A single atmospheric nuclear explosion occurred at Lop Nor in the Takla Makan Desert of China's Sinkiang Province at 7 a.m. (Universal Time), 16 October 1964 and the debris reached Fayetteville, Arkansas, a few days later. We collected a large quantity of rain water on 26 October 1964, 10 days after the explosion, and measured the activities of the fission products.

The rain sample was collected by means of a sampling system installed on the roof of the Chemistry Building of the University of Arkansas. The rare-earth nuclides were separated by the ion-exchange method with α-hydroxyisobutyric acid (2-methyllactic acid) (*1*). Iodine-131 was isolated from rain water by the ion-exchange method of Sabu (*2*). The radiochemical procedures used for separating the isotopes of strontium, barium, zirconium, cerium, and antimony were reported previously (*3*, *4*). The isotopes of silver, ruthenium, tellurium, and cesium were isolated by the standard methods (*5*).

Tracerlab Low Background Beta-Counting Equipment (CE-14SL) was used for measuring the radioactivity.

Our results are shown in Table 1 and in Fig. 1. By plotting the concentrations of the fission products in rain we obtained two "mass-yield" curves; one for the short-lived nuclides with half-lives less than 2 months (curve *A* in Fig. 1) and the other for the nuclides with longer half-lives (curve *B*). The curve for short-lived nuclides agrees quite well with the general shape of the mass-yield curve for the thermal neutron-induced fission of U^{235} (solid curve designated as $U^{235} + n$ in Fig. 1). Since no nuclear weapons had been tested in the atmosphere for about 22 months before the Chinese nuclear explosion occurred, the short-lived fission products produced prior to December 1962 had completely decayed; the mass-yield curve for the short-lived nuclides therefore represents the fission products resulting from the nuclear explosion in China.

The shape of the mass-yield curve for the long-lived nuclides is not well defined, since only seven experimental points were obtained. Four of the seven nuclides had half-lives ranging from 1.0 to 2.7 years. The arrows pointing upward in Fig. 1 give the magnitude of radioactive decay during the period between December 1962 (the end of U.S.S.R. test series) and October 1964. The concentrations of Sr^{90} and Ru^{106} in curve *B* appear to be about equal, after correction for the decay of Ru^{106}. The concentration of Cs^{137} is greater than that of Sr^{90} by a factor of 2. These facts suggest that the shape of the upper mass-yield curve is similar to that for the fission of Pu^{239}.

Table 1. Fission products in the rain sample collected on 26 October 1964.

Nuclide	Half-life (days, d; years, y; hours, h)		Concentration in rain (10^6 atoms per liter, as of 16 October 1964)	
Sr^{89}	50.4	d	5.9	± 0.6
Sr^{90}	28	y	173	± 17
Zr^{95}	65	d	4.7	± 0.5
Mo^{99}	66	h	4.2	± 0.4
Ru^{103}	40	d	1.8	± 0.2
Ru^{106}	1.0	y	42	± 4
Ag^{111}	7.5	d	0.026	± 0.009
Sb^{125}	2.7	y	15.6	± 3.1
Te^{129}	33	d	0.45	± 0.05
I^{131}	8.05	d	1.5	± 0.2
Cs^{137}	30	y	340	± 34
Ba^{140}	12.8	d	8.9	± 0.9
Ce^{141}	32.5	d	4.5	± 0.5
Nd^{147}	11.1	d	1.0	± 0.2
Pm^{147}	2.5	y	43	± 8
Pm^{149}	53	h	0.29	± 0.06
Sm^{151}	90	y	110	± 20
Sm^{153}	46.7	h	0.10	± 0.05
Eu^{155}	1.7	y	1.5	± 0.3
Eu^{156}	15	d	0.0056	± 0.0010

The shapes of mass-yield curves vary with neutron energies. This is illustrated in Fig. 1 by the trough in curve *A* in the region of mass numbers 110 to 120; this trough is definitely shallower than that in the curve for the thermal neutron-induced fission of U^{235} (solid line in Fig. 1).

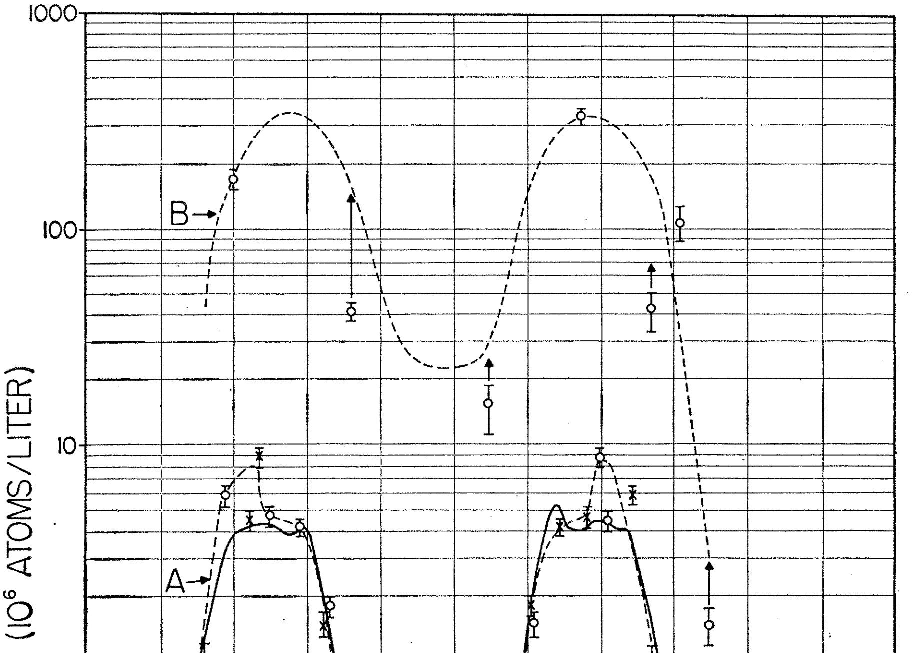

Fig. 1. Fission products in the sample of rain collected on 26 October 1964 at Fayetteville, Arkansas. The concentrations of the radionuclides in rain are expressed in terms of 10^6 atoms per liter of rain as of 16 October 1964 (the date of the nuclear explosion). The lower curve *A* (dashed line) is for the short-lived nuclides with half-lives less than 2 months; the top curve *B* (dashed line) is for long-lived nuclides with half-lives longer than a year. The arrows pointing upward indicate the magnitude of decay of the long-lived nuclides since December 1962. The curve given by the solid line is for the thermal neutron-induced fission of U^{235}.

Another noteworthy deviation of the curve *A* from the mass-yield curve for the fission of U^{235} occurs at mass numbers 89 and 140. This may be explained by the fact that Sr^{89} and Ba^{140} both have gaseous precursors:

$$\mathrm{Br}^{89} \xrightarrow[4.5\ \mathrm{sec}]{\beta^-} \mathrm{Kr}^{89} \xrightarrow[3.2\ \mathrm{min}]{\beta^-} \mathrm{Rb}^{89} \xrightarrow[15\ \mathrm{min}]{\beta^-} \mathrm{Sr}^{89} \xrightarrow[50.4\ \mathrm{days}]{\beta^-} ;$$

$$\mathrm{Xe}^{140} \xrightarrow[16\ \mathrm{sec}]{\beta^-} \mathrm{Cs}^{140} \xrightarrow[66\ \mathrm{sec}]{\beta^-} \mathrm{Ba}^{140} \xrightarrow[12.8\ \mathrm{days}]{\beta^-} .$$

These fission products of mass numbers 89 and 140 remain in gaseous state for some time after the fallout particles begin to form and hence Sr^{89} and Ba^{140} would tend to become enriched in smaller particles. This means that Sr^{89} and Ba^{140} would be depleted in larger particles, which are deposited preferentially as a local fallout in the vicinity of the nuclear test site. Smaller particles may tend to remain in the atmosphere for a longer period, traveling longer distances and then being deposited at greater distances from the test site. The phenomenon of the atmospheric fractionation of nuclear debris is well known (*4*, *6*).

The area in Fig. 1 below the mass-yield curve due to the Chinese nuclear explosion adds up to approximately 200 × 10^6 atoms, whereas the area below the mass-yield curve due to older debris adds up to at least 10,000 × 10^6 atoms. Thus the percentage of the contribution from the Chinese bomb to the total fallout of the fission products in the rain collected on 26 October 1964 is of the order of a few percent.

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Mars: The Origin of the 3.58- and 3.69-Micron Minima in the Infrared Spectra

Abstract. *The 3- to 4-micron spectra of Mars, recorded with the 200-inch telescope in 1958, were reexamined in order to ascertain whether the minima at 3.58 and 3.69 microns are due to telluric HDO molecules. Solar spectra obtained at Denver and water vapor abundances derived from radiosonde flights during the observing period were used. There seems to be a correlation between the intensities of the 3.58- and 3.69-micron features and the amount of telluric water vapor in the optical path. An important corollary is that there is no evidence for attributing these spectral features to Mars.*

In 1956 and 1958, one of us (Sinton) detected spectral features in the 3- to 4-μ spectra of Mars (*1*, *2*). With an infrared spectrometer on the 200-inch (500-cm) Hale telescope at Mount Palomar these features appeared to be more pronounced for the dark than for the bright areas and were identified as minima at 3.43, 3.56, and 3.67 μ. These minima are significant because they are in the general region where organic C-H bonds absorb, so that, taken together with other observations of Mars, they strongly suggest that life is present on the dark areas; this was the tentative interpretation at that time. The assignment was modified by Colthup (*3*), who concluded that the 3.67-μ minimum had to be due to an aldehyde C-H, and most probably to acetaldehyde (CH_3CHO). At the same time Sinton reexamined the original spectra and changed the minima to 3.45, 3.58, and 3.69 μ, with a probable error of ± 0.02 μ (*4*). The origins of these bands were further investigated at Berkeley by Rea *et al.* (*5*). Rea *et al.* were not satisfied with previous interpretations but could find no new attractive possibilities and reluctantly concluded: "At present we know of no satisfactory explanation of the Martian bands."

This was the situation until recently when similarity between the 3.58- and 3.69-μ bands and those of D_2O-HDO-H_2O mixtures was noted by Shirk *et al.* (*6*). In particular, these workers believed the spectra could best be reproduced by a gas mixture in which the D/H ratio is approximately one. This represents a phenomenal enrichment of deuterium over the D/H ratio of less than 1 : 4500 for the interstellar medium (*7*) and demands an explanation. Shirk *et al.* raised the possibility that extensive fractionation had occurred during the escape of H and D atoms from the planet's gravitation field, but they presented no calculations to indicate that this is a plausible mechanism. Moreover, no mechanism was advanced to explain the preferential location of water vapor over the dark areas. Because of these factors, we regard the identification of the 3.58- and 3.69-μ minima with Martian water vapor having a D/H ratio near one as improbable.

However, this proposal did suggest to Rea that the explanation may lie in our own atmosphere. It has been known for many years that the ν_1 band of HDO (the O-D stretching vibration) is present in solar spectra with *P*, *Q*, and *R* minima at about 3.75, 3.67, and 3.57 μ, respectively (for example, see *8*, *10*). To determine whether this telluric HDO could be the source of the absorption at 3.58 and 3.69 μ in the spectra of Mars we conducted the following investigation.

We remeasured the original infrared spectra obtained at Mount Palomar and estimated for all of the spectra the percentage absorption at 3.58 and 3.69 μ. In doing this we had to make a more-or-less subjective estimate of the background envelope, the curve which would be observed for no absorption. This could introduce errors of a few percent, so that absorptions of this magnitude are not very meaningful. If the absorption was estimated to be less than the noise, it was given a value of zero.

The next step was to obtain solar spectra which could be used for comparison. Fortunately, during 1954–55 D. M. Gates had spent several days at the University of Denver (elevation 1615 m) recording solar spectra with a double-pass Perkin-Elmer model 112 monochromator equipped with a NaCl prism. The resulting widths of the spectral slits were less than those used by Sinton, but the difference was much less than for the high resolution spectra in the solar atlases (*8*). In addition, Gates's spectra were obtained for a wide range of zenith angles with a resulting broad range of precipitable water vapor in the path. The actual amount of water vapor could also be calculated for each spectrum with the aid of the peak or integrated intensities of the near-infrared water-vapor bands which were