Table 1. Final concentration of dissolved silica of sea water supernatants, change in concentration of dissolved $SiO_2$, weight (milligrams) of dissolved $SiO_2$ released and taken up, and final pH of 1-g ($< 62\ \mu$) mineral samples in 200 ml of silica-deficient and silica-enriched sea water at room temperature. Reaction time was 8850 hours for silica-deficient and 7050 hours for silica-enriched sea water experiments.

| Mineral | Deficient ($SiO_2$ initially 0.03 ppm; pH, 8.18) | | | | Enriched ($SiO_2$ initially 25 ppm; pH, 8.10) | | | |
|---|---|---|---|---|---|---|---|---|
| | Concentration | | Weight (mg) | Final pH | Concentration | | Weight (mg) | Final pH |
| | Final (ppm) | Change (ppm) | | | Final (ppm) | Change (ppm) | | |
| Glauconite | 3.6 | + 3.6 | +0.7 | 6.61 | 7.3 | −17.7 | −3.5 | 6.77 |
| Muscovite | 7.6 | + 7.6 | +1.5 | 7.84 | 14.7 | −10.3 | −2.1 | 7.86 |
| Montmorillonite A | 7.8 | + 7.8 | +1.6 | 7.92 | 14.8 | −10.2 | −2.0 | 7.83 |
| Chlorite | 4.2 | + 4.2 | +0.8 | 7.85 | 16.2 | − 8.8 | −1.8 | 7.91 |
| Kaolinite A | 3.8 | + 3.8 | +0.8 | 7.91 | 17.5 | − 7.5 | −1.5 | 7.75 |
| Kaolinite B | 5.0 | + 5.0 | +1.0 | 7.86 | 17.8 | − 7.2 | −1.4 | 7.69 |
| Illite | 5.7 | + 5.7 | +1.1 | 7.79 | 18.0 | − 7.0 | −1.4 | 7.80 |
| Montmorillonite B | 11.0 | +11.0 | +2.2 | 7.76 | 20.3 | − 4.7 | −0.9 | 7.65 |

filtered through a 0.45-$\mu$ Millipore filter, and several drops of Quatam "D" (*2*) were added to prevent further biologic activity. Solid sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) was added to the sea water so that the concentration of dissolved silica was 25 ppm, and the pH was adjusted to 8.1 with concentrated HCl. Special care was taken to prevent precipitation of a hydroxylated magnesium silicate from the sea water, which, according to results obtained so far, forms when the silica concentration exceeds 26 ppm at a pH of 8.1. A sample of sea water without added minerals was monitored as a control. The containers were continuously agitated on a shaker table for about 10 months; during this time samples were withdrawn and analyzed for dissolved silica (*3*). The final pH of the supernatants was also recorded.

All of the silicate minerals take up dissolved silica. Table 1 gives the amounts of dissolved $SiO_2$ abstracted by the various minerals and the final pH's of the supernatants. The results obtained with the same minerals in silica-deficient sea water also are presented in Table 1. These latter experiments differed from those reported (*1*) only by the fact that the containers were continuously agitated on a shaker table.

Three examples of reaction curves for the experiments on minerals in sea water are given in Figure 1. Apparently all of the minerals have nearly ceased to react. Most of the uptake or release of dissolved $SiO_2$ occurred in less than 6 months. The curves for silica release which are similar to our previous results (*1*), substantiate our earlier conclusions that (i) silicates rapidly release silica to silica-deficient sea water, and (ii) that this release is governed by the formation of an aluminous residue, either an aluminum oxide hydrate or an ill-defined aluminosilicate. In contrast, silica uptake by these same minerals involves the formation of more siliceous materials. Consequently, the curves for silica release and uptake for a specific mineral would not be expected to approach the same steady-state concentration of silica. Also, the uptake of silica by silicates involves the cations in sea water. To substantiate the conclusion that cations are involved in silica uptake, 1-g samples ($< 62\ \mu$) of these same minerals were suspended for 10 months in 200 ml of distilled water containing 25 ppm of dissolved $SiO_2$. Except for chlorite, the minerals abstracted at most only 0.4 mg of dissolved $SiO_2$ from solution.

The siliceous materials formed when aluminosilicate minerals take up dissolved silica are aluminosilicates rather than nonaluminous silicates. As indicated, titration of sea water with dissolved silica results in the precipitation of a hydroxylated magnesium silicate. No other silicates were detected in the titration experiments, and none would be expected. At a pH of 8.1, the concentration of dissolved silica in sea water at equilibrium with this solid is about 26 ppm, and it is higher at lower pH's. We conclude that aluminum must be involved in any reactions that lower dissolved $SiO_2$ below 26 ppm in the pH range of our experiment (6.7 to 8.1).

In conclusion, certain common silicates take up dissolved silica from silica-enriched sea water. This uptake involves the cations in sea water, and is governed by the formation of ill-defined aluminosilicates. The experimental concentrations of dissolved $SiO_2$ of silica-enriched or silica-deficient sea water after reaction with silicates are the same as, or very near, the concentrations of dissolved $SiO_2$ in the oceans. The duration of our experiments (about 10 months) is comparable to the average interval of exposure to sea water of suspended materials brought to the oceans by streams. We conclude that silicates are a major control of the silica concentration of the ocean, and other chemical species (*4*).

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9 January 1967

## Single Fallout Particles and Zirconium-95 from the Chinese Nuclear Explosion of 9 May 1966

Abstract. *Daily fluctuations of the number of single fallout particles and activity of zirconium-95 in the ground-level air were measured at Fayetteville (94°W, 36°N), Arkansas, for a period of about 3 months after the Chinese nuclear explosion of 9 May 1966. We found a cyclic pattern of variations for both zirconium-95 and fallout particles; this indicated that they were airborne for a long period and traveled far. Apparently, some of the particles circled the world more than once.*

The fallout of highly radioactive single particles has occurred in Japan for the past several years (*1*), and we have recently studied mass-yield distributions of the fission products in some of the particles collected in Japan and also at Fayetteville, Arkansas (*2*). We have measured the variations of the number of single fallout particles and $Zr^{95}$ activities in the ground-level air at Fayetteville.

The air-filter samples were obtained by a Gelman Hurricane air sampler with a flow rate of 140 $m^3$ per hour. The filter was IPC 1478 (cellulose-type). Samples were collected (for 24 hours on consecutive days) on the roof of the chemistry building (about 12 m above ground level) at the University of Arkansas.

After the autoradiographic exposure was made of each air-filter sample, the filter was dissolved with a mixture of fuming $HNO_3$, $HClO_4$, and HF, and carriers (10 to 20 mg each of Zr, Sr, Ba, Ce, and Cs) were added and equilibrated during the process of dissolving. Zirconium was separated from this fission-product mixture as barium fluozirconate (*3*). A modification of this procedure was used (*4*) to obtain zirconium in the final form as zirconium tetramandelate. Tracerlab low-background beta counting system (CE-14SL) was used for radioactivity measurements.

The data for $Zr^{95}$ are expressed (Fig. 1) in terms of its activities as of 9 May 1966, when the nuclear device was exploded at Lop Nor (90°E, 40°N), Sinkiang Province, China. The general pattern of daily fluctuation of the number of single particles in the air was similar to that of $Zr^{95}$, which has a half-life of 65 days. The first wave of particles and $Zr^{95}$ reached Fayetteville about 1 week after the nuclear explosion. It was followed by a sudden decrease of the particles and $Zr^{95}$ about 25 May. After a small peak was observed on 30 May, the second big wave reached Fayetteville early in June.

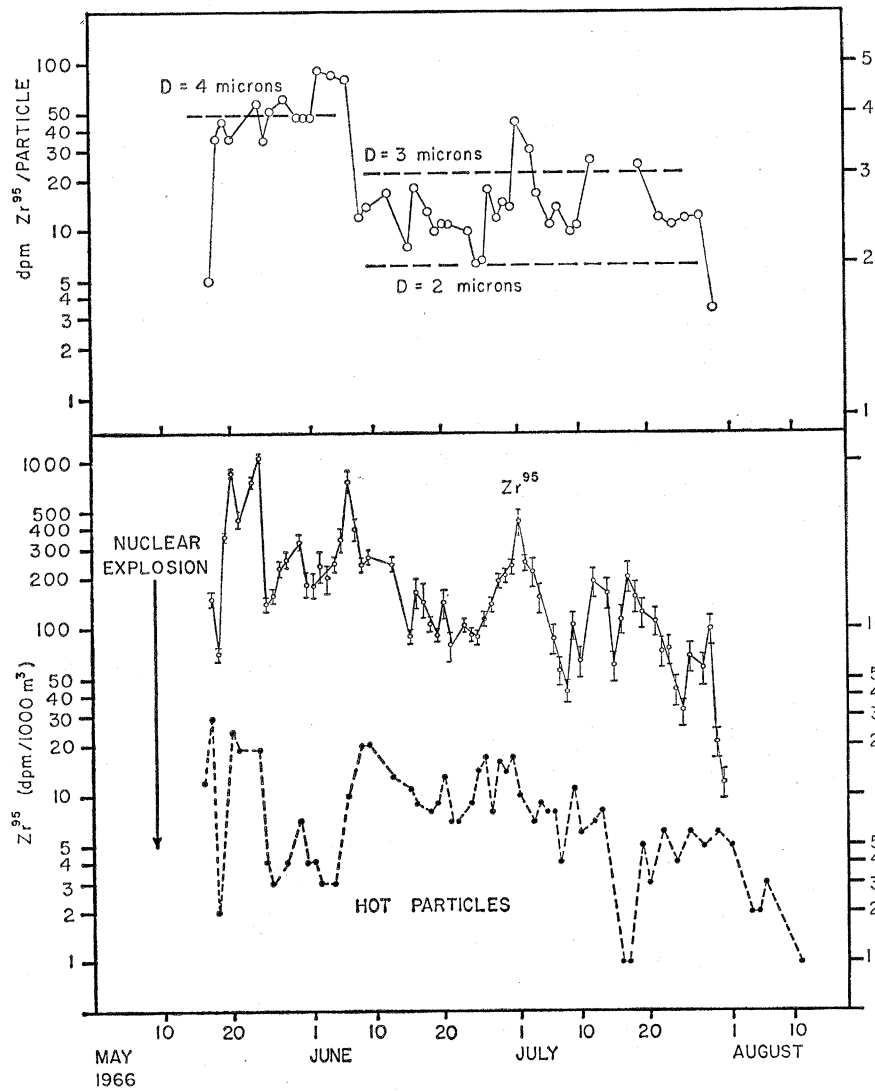

Fig. 1. Daily variations of the number of single fallout particles and $Zr^{95}$ in the ground-level air at Fayetteville, Arkansas. Top: Calculated mean diameters of particles.

During June, both the number of particles and $Zr^{95}$ activities showed a general decrease, reaching a minimum about 20 June. During July, a similar trend was repeated; a gradual decrease of the number of particles and $Zr^{95}$ reached a minimum shortly before 20 July. The cyclic pattern of the variations of $Zr^{95}$ activities and the number of particles in the air at ground level suggested that the debris from the nuclear explosion had circled the world several times. Similarly, the data (obtained after the nuclear explosion of 14 May 1965) for the ratios of strontium and cerium isotopes showed that the debris traveled eastward and circled the world within approximately a month (*5*).

The fact that the average number of single particles in the ground-level air apparently remained rather high for almost 3 months suggests that many of these single particles may have traveled to a great height as well as over a great distance.

Measurements of the ratios of $Sr^{89}$ to $Sr^{90}$ in rainwater collected at Fayetteville indicated that a considerable fraction of the debris from the nuclear explosion of 9 May 1966 had entered the lower stratosphere (*6*). Some of the particles might have traveled at the speed of the jet stream and hence were able to circle the world faster than those particles that traveled in the troposphere. This may explain some of the small peaks (those of 30 May, 20 June, and 9 July) in Fig. 1.

The amounts of $Zr^{95}$ in two single particles collected in Osaka, Japan, and one particle collected at Fayetteville shortly after the nuclear explosion of 9 May 1966 were (*2*): Osaka No. 1 (16-$\mu$ diameter), 3900 ± 800; Osaka No. 2 (13-$\mu$ diameter), 1500 ± 300; Fayetteville No. 1 (6-$\mu$ diameter), 190 ± 40 disintegrations per minute of $Zr^{95}$ (as of 9 May 1966) per particle.

These data provide the simple relationship

$$x = (0.80 \pm 0.15) \cdot D^3 \qquad (1)$$

where $x$ represents disintegrations of $Zr^{95}$ per minute per single particle (9 May 1966), and $D$ is the diameter of the particle in microns (Fig. 1). The average diameter of particles observed during May was about 4 $\mu$. The average size of the particles apparently decreased to about 2 to 3 $\mu$ in June and July, but it remained fairly constant until the end of July.

Volatile fission products and those with gaseous or volatile precursors were depleted in single particles (*1*, *2*). Hence, such products of fission as $Sr^{89}$ with a precursor of $Kr^{89}$ (3.2 min) were expected to behave quite differently from the refractory fission products, such as $Zr^{95}$. Because of the similar half-lives of $Sr^{89}$ and $Zr^{95}$ (50.4 and 65 days, respectively), their ratio of production was expected to be approximately unity. The ratio of $Sr^{89}$ to $Zr^{95}$ in the ground-level rain at Fayetteville was 1.2 on 20 May, but it increased to 5.2 on 29 May, during the period when the number of single particles reached a minimum. The ratio of $Sr^{89}$ to $Zr^{95}$ in rain returned to 0.7 on 6 June. These results demonstrate the phenomenon of atmospheric fractionation of the products of fission and show that the highly radioactive single fallout particles are important in the process of transport of the nuclear debris.

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## Ultraviolet Stellar Spectroscopy on Gemini 11

Abstract. *Objective-prism and objective-grating spectrograms were obtained in six star fields during the Gemini 11 mission. The grating spectra show absorption lines in the 2000 to 3000 angstrom wavelength region of Canopus and Sirius and provide ultraviolet-energy distribution data for approximately 50 stars. Many prism spectra show the Balmer discontinuity due to hydrogen and two absorption features probably due to ultraviolet iron multiplets.*

During the 2-hour standup EVA (extravehicular activity) of Gemini 11 on 14 September 1966, astronauts C. Conrad and R. Gordon photographed ultraviolet stellar spectra in six regions of the sky. Objective-grating spectra with a dispersion of 180 Å/mm were obtained in regions centered on $\lambda$ Scorpii, Canopus, and $\epsilon$ Orionis, and objective-prism spectra with a dispersion of 1500 Å/mm at 2500 Å were obtained in regions centered on Antares, $\lambda$ Scorpii, and $\iota$ Orionis. The limiting magnitude for the 2200 to 2600 Å region of early B-type stars on well-guided 2-minute exposures is about $V = 5.0$ with the grating and about $V = 6.5$ with the prism.

The grating spectra show resolved absorption lines in the middle-ultraviolet spectra of Canopus and Sirius, the first time that lines have been observed in this wavelength region in stars other than the sun (*1*). The spectrum of Canopus (Fig. 1) shows the very strong Mg II resonance doublet at 2799 Å, the weaker Mg I resonance line at 2852 Å, the 2882 Å line of Si I, and several broad features which are mostly identifiable as blended features of Fe I and Fe II. The ultimate lines of Fe II near 2400 Å are especially strong. The broad absorption feature near 2530 Å is probably a blend of the ultimate lines of Si I with Fe I. The absorption feature near 2620 Å probably contains the ultimate lines of Mn II as well as a strong multiplet of Fe II. Variations in focus, together with field distortions and only moderate resolution of wavelength (about 15 Å), make precise measurements of wavelength difficult. However, the above identifications are generally confirmed by the close similarity of the Canopus ultraviolet spectrum to that of the sun (*2*).

The spectrum of Sirius shows the Mg II doublet as well as the lines of the hydrogen Balmer series. As expected, no lines are resolved in the middle-ultraviolet spectra of the B stars observed in Scorpius and Orion.

Grating spectra of 99 stars are identifiable in three regions photographed. The film has a photometric calibration,

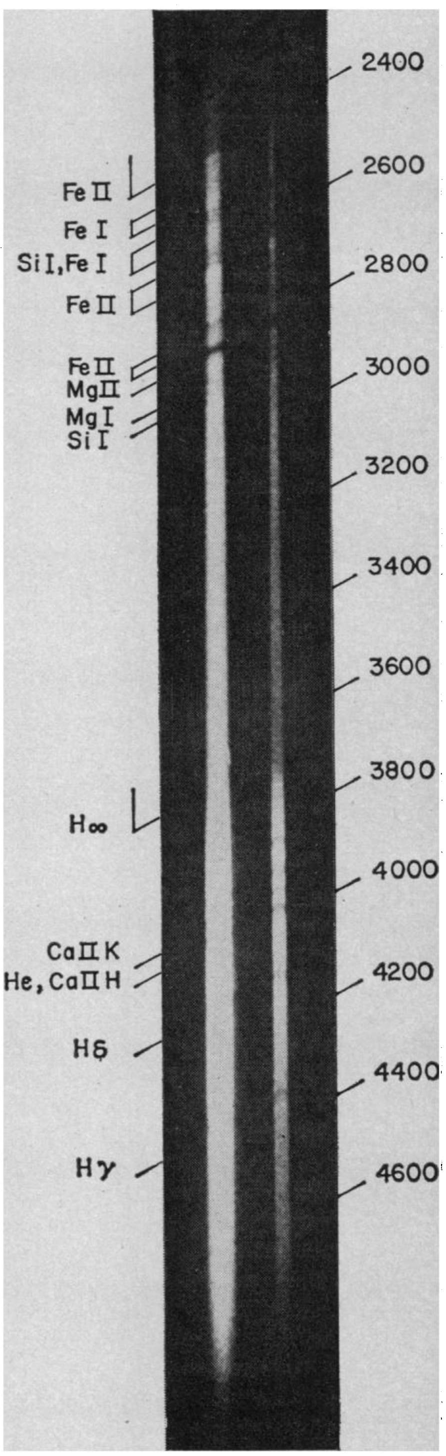

Fig. 1. The spectrum of Canopus. A wavelength scale is given to the right; ions with strong lines are listed to the left. The double spectrum was caused by sudden spacecraft motion during exposure.