

even slightly before, the mineral substance (Fig. 1, C and D). In the laboratory, even the most friable grains leave an organic "ghost" after dissolution in glutaraldehyde and thus contain organic matter. Yet, intercrystalline organic templates are not seen in the natural etch surfaces. Organic matter is found only as discrete elements, such as pore plates, aperture linings, and films of periostracum. Structurally complex skeletal grains are much weakened by the disappearance of the binding intercrystalline substance.

The sediments contain a range of carbonate phases of varying solubility. Individual particles frequently consist of more than one phase—for example, aragonite and calcite in *Mytilus* shells and a spectrum of magnesian calcites in echinoid skeletons. In the material studied, all varieties of calcite and aragonite are affected by dissolution and thus gradually lost from the sediments. Absolute or relative rates of dissolution are not yet known but exposure experiments are in progress. As a subjective estimate, distinct etch surfaces may form in one or a few years.

In an exposure experiment in the deep sea (3, 7), spheres of optical calcite were etched at a maximum rate of 1 μm per year, whereas specimens of aragonite pteropods and calcite foraminifers were entirely dissolved in 4 months.

Marine calcareous substrates are frequently attacked by boring organisms, such as sponges, algae, and fungi, which remove mineral substance (8). Such bioeroded surfaces are common in the Skagerrak sediments, but they are readily distinguished from etched surfaces; they reflect forms and activities of the excavating organisms, whereas etched surfaces reflect properties of the etched substances.

Shallow marine sediments from supersaturated waters in the Mediterranean Sea and the West Indies, sampled and analyzed in the same ways as the North Sea sediments, do not contain etched grains. During several years of work with warm-sea carbonates, involving hundreds of hours of SEM, I found abundant evidence of precipitation (9) but never an etched surface. It is evident that the two opposite processes, precipitation and dissolution, leave entirely different petrographic records in the sediments.

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References and Notes

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- vestigations related to marine dissolution of carbonates have focused on the conditions in the deep sea. For background, see: R. G. C. Bathurst, *Dev. Sedimentol.* **12**, 362 (1971); A. P. Lisitzin, *Soc. Econ. Paleontol. Mineral. Spec. Publ.* **17** (1972); J. D. Milliman, *Recent Sedimentary Carbonates*, part 1, *Marine Carbonates* (Springer-Verlag, New York, 1974), pp. 223-249; J. M. Edmond, *Deep-Sea Res.* **21**, 455 (1974). From a paleontological point of view, dissolution in shallow seawater may be of no less importance, since the greater part of the fossil record consists of shallow marine sediments.
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4. Standard preparation of material is quick and easy: sediments are separated into Wentworth size grades by gentle wet-sieving, rinsed in distilled water, and air-dried. Dry material is sprinkled onto double-stick adhesive tape on top of SEM stubs and coated with gold, preferably in an ion sputterer. Ordinary, even careless, sedimentological routines will not readily produce accidental etch surfaces.
5. The material was collected at the sediment surface by means of scuba diving, mostly at sublittoral stations with considerable wave and current action. The Skagerrak is a cold marine environment at a latitude of 57° to 59°N. The salinity is 30 to 33 per mil, and the maximum surface water temperature is about 20°C in the summer and about the freezing point in the winter. The carbonate content in the sediments varies from a few percent by weight

in terrigenous sands to over 90 percent by weight in skeletal sands. Aspects of carbonate sedimentation in the area are treated in I. Hessland, *Bull. Geol. Inst. Univ. Upps.* **31**, 1 (1943); E. T. Alexandersson, *ibid.* **3**, 201 (1972); *J. Sediment. Petrol.* **44**, 7 (1974).

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Volcanic Twilights from the Fuego Eruption

Abstract. *Striated twilight glows have been observed since 26 November 1974 in New England, indicating the spread of stratospheric dust earlier observed over Arizona. Similar photometric results were obtained from New Mexico and Florida, and twilights in Puerto Rico showed features not hitherto measured. Letters and verbal reports indicate the source to be eruptions of Fuego Volcano in Guatemala between 13 and 23 October 1974.*

Meinel and Meinel (1) noted on 9 and 16 November 1974 colorful twilight glows while flying near the tip of Baja California. Since 21 November, they have observed red twilights and bluish-ashen daylight skies over southern Arizona. The dust stratum, which Meinel and Meinel estimate to be at an altitude of about 19 km, was attributed to eruptions, between 13 and 23 October 1974, of Fuego Volcano (14.5°N, 91°W) in Guatemala. I observed the dust twilights near Boston, Massachusetts, and have obtained measurements from a small network of twilight photometers. This network had been set up to study the latitudinal dependence of seasonal variations of twilights under the then existing background conditions of stratospheric aerosol.

The twilights in the Boston area in the spring of 1974 exhibited a constant or even decreasing color ratio (the ratio of red, wavelength $\lambda = 0.77 \mu\text{m}$, to green, $\lambda = 0.50 \mu\text{m}$) after sunset; in June a very slight purple coloration reappeared, probably in the course of the usual seasonal variation. From June until 23 November, most twilights were inconspicuous and ended (at a solar depression angle of 7° to 8°) with a

watery, yellow-orange seam at the solar horizon. However, on 2 November as light cirrus clouds became invisible during twilight, all photometric and visual aspects of a weak volcanic twilight remained. The morning twilight of 11 November also had characteristics suggestive of volcanic conditions.

On 26 November, A. B. Meinel informed me about the dust event, and, as the cloud cover had just cleared up, a few grayish streaks of haze (2° by 10° wide and slightly tilted to the left) were easily visible above the sun at an elevation angle of 15°, 40 minutes before sunset. Many finer streaks appeared, became pinkish at a solar depression angle of 4°, and disappeared later. A golden glow with a red edge was seen the next morning, and, soon after, the eastern sky was covered with a pink film, everywhere billowy and streaked. As the color ratios of some of the photometric measurements before and after the intrusion of the dust show (Fig. 1), the intensity of the glow was exceptionally strong early on 7 December (Fig. 1c), when the sky seemed to be on fire but with hardly any streaks, and early on 11 December, when the sky was very streaked. Although the

horizon always (in the absence of distant clouds lifting the earth shadows) shows the red volcanic glow up to 1 hour after sunset, the stratospheric dust layer apparently was not dense enough at this time to produce a visible secondary purple coloration as after the eruption of Krakatoa Volcano in Indonesia (2, p. 399). However, the purple coloration is readily evident in the measured color ratios (Fig. 1, b and c) and in color slides. In cloud-shadowed twilights, the colors are less developed but the ripple structure, which may indicate a wavy surface (due to wind shear or inversions) of aerosol layers, can still be seen. The daytime sky near the sun was often slightly striated, but an assessment of the probably barely detectable extinction of the stratospheric veil was not yet possible because of a lack of very clear weather.

Color ratios of twilight photometry in Florida (29.7°N, 82.3°W) and Sacramento Peak, New Mexico (32.7°N, 105.8°W), showed prevolcanic conditions similar to those at Boston. At Sacramento Peak twilight enhancement took place between 27 October and 4 November. The same change in the color ratio as a function of solar depression angle, but with a relatively weak afterglow, was derived from Florida twilight records of 23 and 29 November after a longer break between measurements. However, very unusual twilights were recorded in Puerto Rico (19°N, 67°W) starting on 19 November (Fig. 2) (the last normal twilight was observed on 30 October). In these twilights, the green intensity between a solar depression angle of 2° and 3.5° did not decrease steadily as in all other twilights, and near-infrared (and red) intensities even showed a slight peak at a solar depression angle of ~3.5°. This feature, probably indicative of the great altitude and small vertical extension of a dense aerosol layer, vanished between 3 and 10 December. Although the course of the change in the color ratios with solar depression angle (inset in Fig. 2) was not much different from that near Boston, a considerable decrease in the sky radiation near sunset in Puerto Rico (as indicated in Fig. 2) implies a much larger amount of volcanic aerosols in the tropical stratosphere. Although the twilights observed from Boston to Florida were in general agreement with those measured in the Northern Hemisphere for some years after the 1963 eruption of Agung Volcano in Bali, those in Puerto Rico should be compared with Australian twilights of 1964–1965 (3).

Since it still is not possible to infer accurately the amount of stratospheric dust from twilight measurements, we may turn to other types of measurements already available. Lidar measurements made by

McCormick and Fuller (4) at Hampton, Virginia (37°N, 76.4°W), on 26–27 November showed two strong dust layers, centered at 16 and 20-km, which were much weaker two nights later. However, both McCormick and Fuller (4) and Fernald (5) at Boulder, Colorado, observed the strong layers again in early December.

From the Hampton lidar data of 26 November, I estimate that the optical thickness of the stratospheric dust is $\tau_a \approx 0.025$

at $\lambda = 0.50 \mu\text{m}$. Indeed, solar radiance measurements at this wavelength at Sacramento Peak (2830 m) show an increase in the minimum value of τ_a (including low-altitude turbidity) from 0.03 in early November to 0.055 or more afterward, indicating a possible reduction of vertical transmission by about 2.5 percent. Lidar data from Mauna Loa Observatory, Hilo, Hawaii (19.5°N, 155.6°W) (6), indicate that the dust cloud was much denser at times.

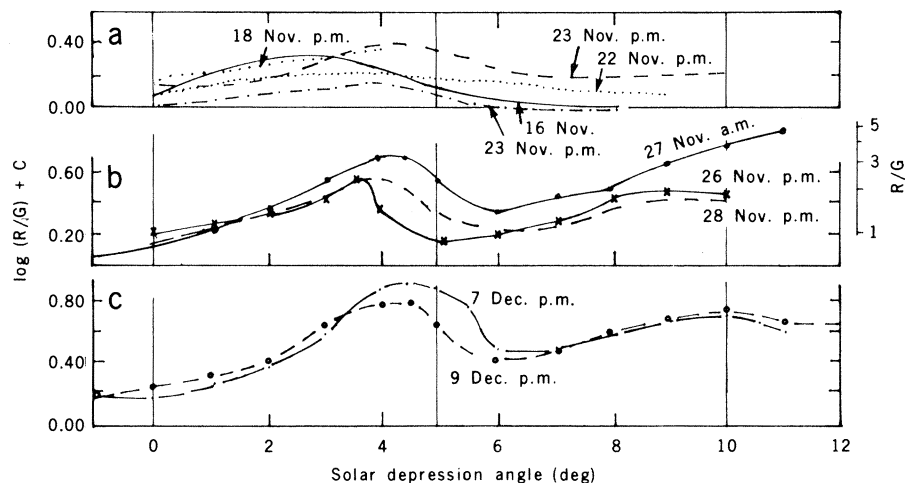


Fig. 1. Color ratios (the ratio of red, R , at $\lambda = 0.77 \mu\text{m}$ to green, G , at $\lambda = 0.50 \mu\text{m}$) plotted as a function of the solar depression angle for twilights at Lexington, Massachusetts (42.5°N, 71.3°W), before (a) and after (b and c) the intrusion of volcanic dust; elevation angle, 20°.

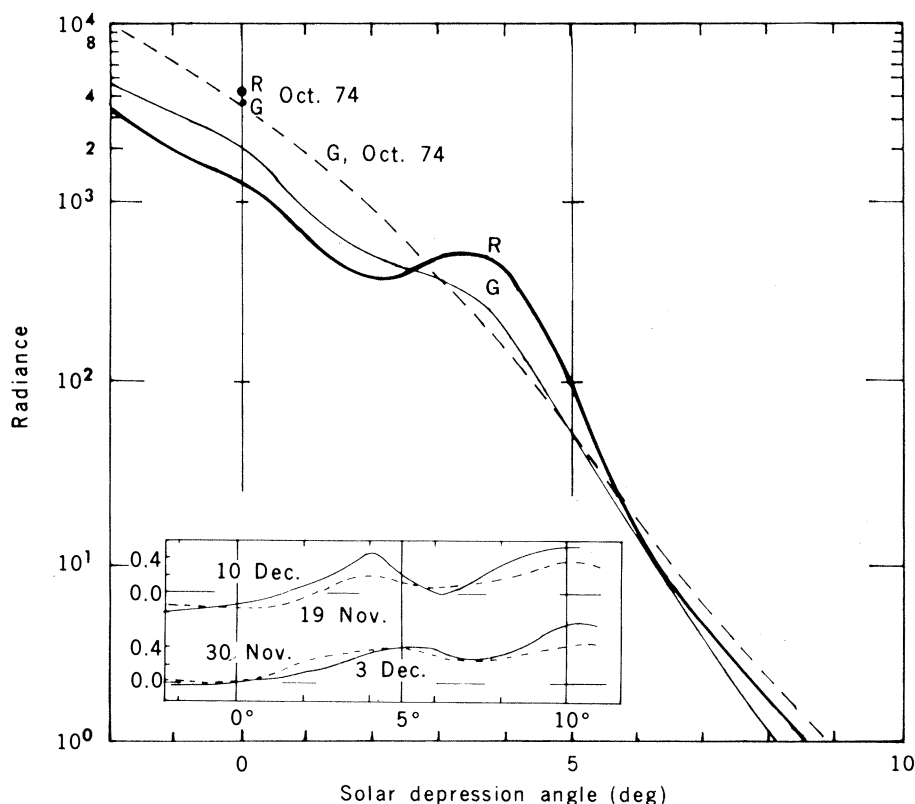


Fig. 2. Twilight radiance (in arbitrary units) at Puerto Rico in red light (R , $\lambda = 0.77 \mu\text{m}$, heavy solid line) and green light (G , $\lambda = 0.50 \mu\text{m}$, light solid line) in unusual volcanic conditions and in green light in prevolcanic conditions (dashed line); elevation angle, 20°. The inset shows the R/G color ratios ($\log R/G$) as a function of the solar depression angle for volcanic conditions.

With respect to the size distribution of the volcanic dust, Meinel and Meinel (1) reported seeing a silvery disk around the sun while the dust veil was still visible in the daytime. I also noted a wide white disk shortly before sunset when the lower troposphere was shielded from sunlight by dense cirrus clouds at the horizon. Both observations strongly suggest an aerosol scattering function characteristic of power law size distributions.

The twilight data presented here indicate that stratospheric aerosol existed over New Mexico and probably on discrete dates over New England by early November 1974, a few days before the strong sky phenomena were noted by Meinel and Meinel (1) over Mexico. The activity of Fuego Volcano continued into November, but the stratospheric dust may have originated from one or more of the strong ash eruptions which took place between 13 and 23 October, especially during the night of 17 October. "Ash has been carried at least 200 km to the north and west" (7). The dust obviously rose higher than suspected. A glance at the upper air chart for 50 mbar $\approx$ 20 km clearly shows that dust at this level would first have been carried west, probably to Hawaii, where the northernmost patches could have turned north around a small semipermanent high and entered the westerlies. In fact, a high dust cloud was observed at Mauna Loa Observatory starting on 26 October and measured by lidar at 19.5 km (6). Owing to probable spread over a large altitude range, the movement of the ash clouds in this period may have been quite complex. Indeed, a west-southwesterly circulation over the United States by early November makes it possible that the sightings mentioned earlier of weak volcanic twilights during that period were caused by patches of Fuego dust.

During 18 months of lidar observations at Mauna Loa Observatory, no clouds were observed above the tropopause prior to 8 October 1974. Since this was 1 week before the Fuego eruptions became violent, Fegley and Ellis (6) discuss the possibility that the dust layer, which was weaker and 2 km lower than the Fuego clouds observed later, may have been caused by high-altitude aircraft. However, I also noted stratospheric dust in New Mexico in mid-October 1974. From jet altitude, a few distant haze streaks at an elevation angle of about 10° were seen in the afternoon of 15 October for 30 minutes until descending to El Paso. I also saw during twilight of the same day faint spotty dust clouds which probably were in the stratosphere. In the dusk of the next day while at Sacramento Peak, I noticed a very distant dust seam appearing at the horizon and turning red;

its estimated altitude is 18 km. A relation of these phenomena to Fuego dust is very unlikely, but they indicate that the dust cloud observed over Hawaii by early October may not have been a local event.

It is likely that a substantial amount of Fuego dust will remain in the tropical stratosphere, which for some time—as probably with the Agung dust—may act as an aerosol source for higher latitudes, where residence times are known to be shorter. At any rate, traces of the Fuego dust should still be detectable in 1976 or 1977.

Note added in proof: Continued twilight photometry at Puerto Rico, Sacramento Peak, and Lexington showed color ratio amplitudes of about 6 until February. By May, the amplitudes had decreased to 3 at Puerto Rico and to 2 at the mid-latitude stations and thus were still higher than the spring values during the years before the Fuego eruption. Lidar data from Mauna Loa Observatory, Hawaii (6, 8), and Virginia (9) indicate that the volcanic dust load in this latitude range generally was constant until at least March and April, respectively. Light-scattering calculations based on the lidar dust layer profiles gave good agreement with the twilight observations. Spreading of the dust to lower alti-

tudes since early spring explains the abatement of twilight colors. Fuego twilights were noticed in Europe during the winter and in Alaska during February.

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Amino Acid Composition of Proteins: Selection against the Genetic Code

Abstract. *Distribution of amino acids in 68 representative proteins is compared with their distribution among 61 codons of the genetic code. Average amounts of lysine, aspartic acid, glutamic acid, and alanine are above the levels anticipated from the genetic code, and arginine, serine, leucine, cysteine, proline, and histidine are below such levels. Arginine plus lysine account for 11.0 percent of codons and aspartic acid plus glutamic acid account for 11.3 percent; thus the average charge is roughly neutral.*

Most proteins are complex sequences of amino acids. The few exceptions are proteins that consist of short repetitions, such as the "antifreeze" proteins (1) and the silk fibroins. Leaving these special proteins aside, we have been interested in the frequency of occurrence of amino acids in the genetic code as compared with their average levels in proteins (2). The code has 61 codons for amino acids. A protein with one amino acid per codon would have the following composition: Ala₄Arg₆Asn₂Asp₂Cys₂Gln₂Glu₂Gly₄His₂Ile₃Leu₆Lys₂MetPhe₂Pro₄Ser₆Thr₄Tyr₂TrpVal₄ (3). We find that the average distribution of some, but not all, amino acids in proteins differs in important respects from these proportions.

Large numbers of amino acid replacements accumulate in proteins during evolution. This becomes evident when homol-

ogous proteins in different species of living organisms are compared. This process results from point mutations in DNA, and we shall assume for purposes of argument that the process should lead to a tendency for codons for amino acids to approach the proportions found in the genetic code (2).

The internal milieu of cells is approximately neutral in terms of pH. In accordance with this, the average charge of most proteins is approximately neutral; that is, they are zwitterionic with, on the average, roughly equal numbers of positively and negatively charged side chains at physiological pH. The genetic code contains twice as many codons for the basic amino acids arginine plus lysine as for the acidic amino acids aspartic plus glutamic acids.

Of course, some proteins, such as cytochrome c, are basic, and others such as ferredoxin are acidic. The basicity of a pro-