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Volcanic Sunset-Glow Stratum: Origin

Abstract. *Reexamination of the phenomenon of volcanic-dust sunsets, as typified by the Krakatoa event, supports a theory that the scattering layer is produced by the interaction of ozone and sulfur dioxide in much the same manner as is the normal "Junge" aerosol layer at 20 kilometers.*

The phenomenon of volcanic-dust sunsets, such as have been noted after major eruptions of volcanoes, is well known. The extensive observations included in Symon's report (*1*) on the Krakatoa eruption constitute a standard reference work concerning the heights of the glow stratum and ash layer from the most famous eruption of modern times. The eruption of Agung in 1963 has also drawn wide attention to the high-altitude dust that it distributed all over the world. We (*2*) have continued our observations of the height of the scattering layer by the twilight method, and believe that a new interpretation of the dust-layer hypothesis is required by all the evidence now available.

It is rather surprising that the dust layer, as evidenced by the sunset-glow stratum, persists for many years although the particle sizes responsible for the scattering of the sunlight (approximately 1 μ) should have a settling time of the order of 1 year. The Krakatoa sunsets were still being observed after 5 years, when the Symons report went to press, and the Agung sunsets are still conspicuous after 3 years.

It is also surprising that the height of the glow stratum is constant with time after the event, and that separate eruptions produce layers at the same height. One would not expect different volcanoes to eject dust to the same altitude, well above the tropopause, since the violence of eruptions varies widely. The eruption of Agung, for instance, was clearly less violent than that of Krakatoa, yet our heights of 20 to 22 km agree within experimental error with those for the Krakatoa event. There have been several other eruptions in rapid sequence since Agung: in Costa Rica, Iceland, the Philippines, and Indonesia. We believe that our observations show that these minor eruptions have contributed reinforcement of the twilight glows, but we find no evidence of the multiple layers that would be expected if the height of injection of the scattering layer depended on the ballistic or convective mechanics of each event itself.

We suggest that the sources of worldwide effects of volcanic "dust" can be considered as: (i) an initial ash layer that is broadly distributed in height and that settles in the first few weeks or months, and (ii) a more-persistent aerosol layer of chemical rather than ash origin. We believe that the "dust" layer responsible for the persistent twilight-glow stratum results from continual precipitation of sulfates upon nonscattering condensation nuclei.

The sulfates responsible for the "dust" are produced by interaction of atmospheric ozone and the SO_2 that is temporarily augmented by the mass of volcanic gaseous effluent. According to this theory, the glow stratum is not ejected to high altitude by a violent event but results from diffusive mixing of a large injection of SO_2. The origin of the volcanic "dust" aerosol layer therefore appears to be identical with that of the natural sulfate aerosol layer, at 20-km altitude, described by Junge (*3*) and Mossop (*4*), except that the abundance of SO_2 in the case of the volcanic leads to more or larger particles (or to both). Persistence of the enhanced glow stratum after an eruption then depends on constant replenishment of the sulfate-coated particles by chemical means rather than on suspension of particles that were injected during a single event.

The association in our records of dates of stronger glows with polar air masses accords with this hypothesis of sulfate precipitation, since higher concentrations of ozone at the low side of the 25-km ozone maximum are associated with polar air masses. However, one must also remember that under these conditions the sky is very clear, and reddened sunlight of higher-than-normal intensity characterizes the grazing rays.

This hypothesis evokes many interesting questions: what is (i) the global production of SO_2 from volcanoes; (ii) the extent of annual fluctuations in this quantity; (iii) the entire aerochemical reaction chain if the end product is in the form of ammonium sulfate, as in the case of the normal 20-km aerosol layer (*4*); (iv) the global influence of a variable rain of highly hygroscopic particles? It is unfortunate that the U-2 experiments by Mossop were stopped on 15 March 1963 by the eruption of Agung; this event would have provided a wonderful opportunity to examine this hypothesis, even though Mossop's original object, study of extraterrestrial particles, was cut off by the eruption.

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3 November 1966

Marine Dolomite of Unusual Isotopic Composition

Abstract. *A piston core taken off of the coast of Oregon in 358 meters of water contained an indurated calcareous layer composed partly of dolomite with a composition* $Ca_{58.7}Mg_{41.3}$. *Dolomites of this chemical composition are typical of the supratidal environment. However, the dolomite has isotopic composition* $\delta O^{18} = 5.8$ *per mille,* $\delta C^{13} = -35.1$ *per mille relative to the Chicago PDB-I standard. The unusual carbon isotope ratio is similar to that of calcites produced as a byproduct of bacterial breakdown of hydrocarbons.*

This report on deep marine dolomites is the first to include a complete study of the samples (*1*). The dolomite that we used came from a piston core taken at 46°03.2′N, 124°45.7′W. This location is 30 nautical miles (56 km) west of the mouth of the Columbia River on the continental slope near the south edge of Astoria Canyon at a depth of 358 m (Fig. 1).

Table 1. Relative percentage of benthonic foraminifers making up 1 percent or more of the sample.

Benthonic foraminifers	Amount in sample (%)
Cassidulina minuta Cushman	52
Cassidulina norcrossi Cushman	18
Uvigerina juncea Cushman and Todd	8
Epistominella pacifica Cushman	6
Eilohedra laevicula Resig	7
Cassidulina californica Cushman and Hughes	2
Epistominella smithi R. E. and K. C. Stewart	2
Trifarina angulosa Williamson	1
Nonionella miocenica Cushman	1

The dolomite was obtained from two similar carbonate layers separated by a layer of pelagic clay 1 cm thick (Fig. 2). The three layers together are 10 cm thick and occur at a depth of 156 to 166 cm in the core. The carbonate is hard and lumpy, similar in appearance to some volcanic ash layers. No layering or bedding is visible within the carbonate layers. The remainder of the core consists of pelagic gray clay interbedded with coarser layers. The coarse layers are mostly fine sand and silt and are distributed irregularly as laminae or lenses. Within the coarse layers there are local concentrations of pyrite and glauconite.

Benthic foraminifera (Table 1) from the clay between the two carbonate layers give evidence of paleobathymetry and age. Other faunas from above and below the carbonate layers, although less complete, contain the same general species suite. Our estimate of paleobathymetry of between 100 and 300 m is based upon modern faunal ranges off the coast of Oregon and elsewhere (*2*).

The fauna is similar to the modern fauna from the same area and is probably no older than Middle Pliocene. This age determination is based upon the absence of typical Late Miocene and Early Pliocene species. The presence of 93 percent left-coiling specimens of *Globigerina pachyderma* Ehrenberg would indicate a Middle Pliocene or Pleistocene age, if we use the zonation of Bandy (*3*) for the Southern California region. The carbonate layers were analyzed by the C^{14} method, but there was no measurable C^{14} activity. This result indicates an apparent age greater than 30,700 years.

Because the carbonate is too fine-grained for petrographic study, we determined the mineralogy by x-ray diffraction. Quartz makes up about 30 percent of the sample and calcite, dolomite, and orthoclase each represent at least 15 percent. Calcite and dolomite are present in equal amounts. The rest of the sample is composed of clay minerals which were removed for a separate x-ray analysis. Montmorillonite makes up 40 percent of the clay fraction, and illite and chlorite each make up about 30 percent. This assemblage is typical of recent pelagic clays off the coast of Oregon (*4*).

Table 2. Isotopic values of carbonates relative to the PDB-1 standard.

Isotope	Mixed carbonate	Dolomite concentrate	Calcite (by calculation)
O^{18}	5.2	5.8	4.6
C^{13}	−38.6	−35.1	−41.0

We ran expanded-scale x-ray scans over the 10 • 4 peaks of calcite and of dolomite with $NaCl$ and CaF_2 as internal standards. The dolomite peak was at 2.917 Å, which indicates a composition of $Ca_{58.7}Mg_{41.3}$ (*5*). The 10 • 4 calcite peak was at 3.012 Å, indicating a calcite composition of $Ca_{92.5}Mg_{7.5}$. Carbonates with these compositions are common in shallow water and supratidal environments (*6*). No similar carbonates have been reported from the deep sea.

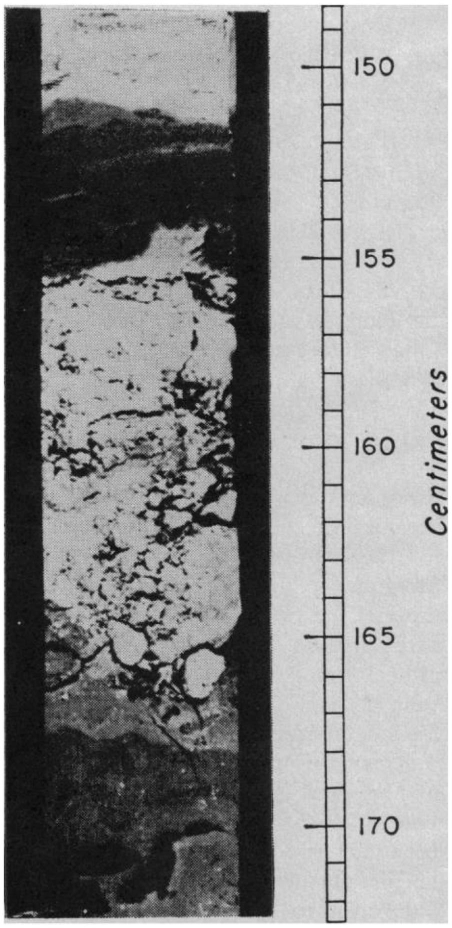

Fig. 2. Portion of core 6508-C-14 containing the carbonate layers.

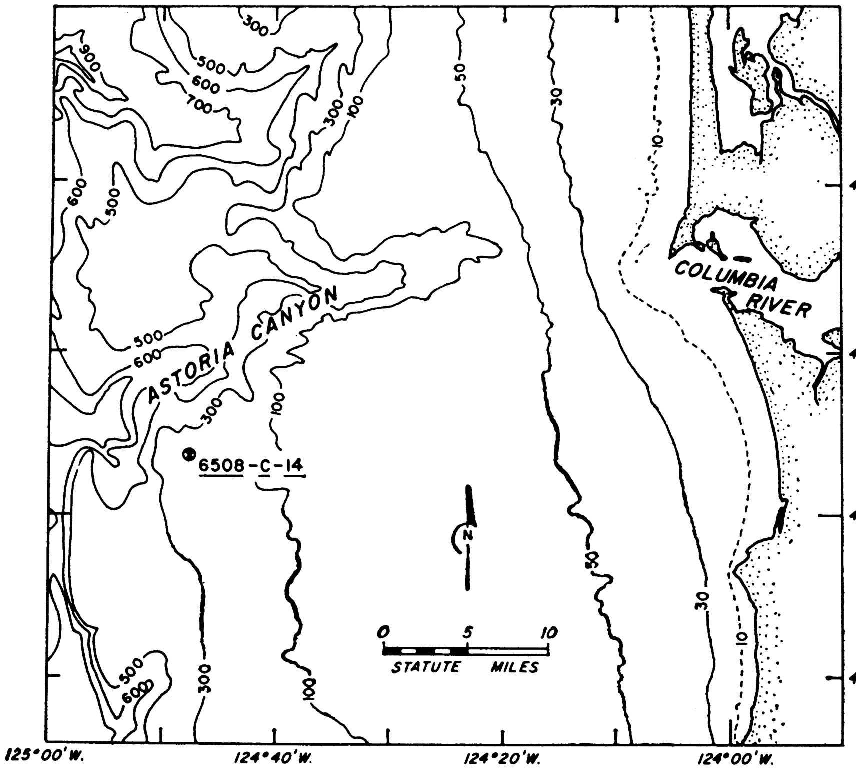

Fig. 1. Location of core 6508-C-14 and bathymetry of the area.

Oxygen and carbon isotopes were determined in the carbonate of the total sample and in a dolomite concentrate obtained by leaching out the calcite with 5-percent acetic acid. Acetic acid leaching does not introduce isotopic exchange. The isotopic values relative to the PDB-I standard are given in Table 2. Independent determination of the calcite and dolomite values by the phosphoric acid double-extraction method (*7*) could not be used because the reaction rates of calcite and high-calcium dolomite are almost identical. Therefore, the δO^{18} and δC^{13} (*8*) of the calcite were estimated by calculation using the x-ray diffraction result which indicated equal amounts of dolomite and calcite. When calcite is dissolved with acetic acid considerable dolomite is dissolved. If the original sample contained a spectrum of dolomites whose reactivity to acid is correlated with isotopic variations, then the dolomite isotopic composition in Table 2 would be that of the least reactive dolomite, and the calculated calcite isotopic composition would be in error.

The values for calcite and dolomite, though similar, are significantly different. These differences may or may not be real. Sharma and Clayton (*9*) have shown that the δO^{18} values of ideal dolomites should be corrected by subtracting 0.8 per mille to account for a difference in behavior of dolomite and calcite when prepared by the phosphoric acid method. However, O'Neil (*10*) has shown that this correction does not apply when dealing with high-calcium dolomites.

If we apply the oxygen isotope paleotemperature equation (*11*) to the calcite data (assuming a water δO^{18} of 0.0 per mille), we get a temperature of −0.3°C. Present-day water temperatures at the locality are about 5°C. Experimental data (*7, 12*) and studies of hydrothermal dolomite (*13*) suggest that dolomite may concentrate O^{18} relative to calcite by as much as 7 per mille at 25°C. This would allow a calculated isotopic temperature as high as 20°C for the dolomite. However, most synsedimentary pairs of dolomite and calcite which are presumed to have formed at earth surface temperatures do not exhibit the predicted difference in oxygen isotope composition. This observation has led some workers to conclude that such dolomites form without establishing isotopic equilibrium (*14*).

The δC^{13} values of −35.1 and −41.0 are very unusual. Recent carbonate sediments have δC^{13} values ranging from 2.0 to −3.0 per mille (*15*), although individual sediment contributors can have values as negative as −8.0 per mille (*16*). Ancient marine limestones range from 2.0 to −6.0 per mille and rarely have values as negative as −12.0 per mille (*17*). The only carbonate values which are as negative as the material studied here are samples of calcite from the cap rock of salt domes (*18*). Cap rock calcite is believed to originate as a by-product of sulfate reduction by bacteria. The origin of the carbonate carbon is CO_2 derived from the oxidation of the petroleum hydrocarbons which serve as a source of energy for the bacteria. The fact that petroleum is depleted greatly in C^{13} (δC^{13} from −15 to −35 per mille) and the fact that C^{12} atoms are selectively metabolized by the bacteria account for the highly negative C^{13} values (C^{13} from −25 to −55 per mille) found in the cap rock calcite (*18*). Among possible sources of the carbon in the Oregon carbonates, only petroleum and natural gas have sufficiently light carbon isotope ratios. However, it is possible that some combination of a nonhydrocarbon source of light carbon and bacterial selectivity during oxidation might have produced the unusually light carbon in this material. If the carbonate formed from a source of carbon other than normal seawater, the absence of C^{14} activity may not be an indication of age. If a bacterial metabolic process was involved in the formation of the calcite and dolomite, then the oxygen isotope data may indicate nonequilibrium conditions and have no paleotemperature significance.

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$$\int \frac{(O^{18}/O^{16})(\text{sample})}{(O^{18}/O^{16})\text{std}} - 1 \times 1000$$

Standard is PDB-I; precision is ±0.1 per mille.

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Superconductivity and the d-Shell

Abstract. *The various isotope effects on the superconducting transition temperature of* Mo_2B *and* W_2B *have been measured. Together with resistivity data they indicate that the* d-*shell forms a highly stable electron configuration for molybdenum and tungsten. This leads to an understanding of high superconducting transition temperatures.*

We have experimental evidence from isotope effects and normal state resistivities that tungsten, though being a transition element, behaves essentially like a nontransition element with respect to superconductivity, that is, the *d* electrons do not substantially take part in the phenomenon. The resulting conclusion, to consider the superconductivity of W as that of a nontransition element, seems at first