second principal pyroxene band in this wavelength region is particularly sensitive to changes in the Ca and Fe content.

It is possible, however, that the Vesta band at 0.9 μ may result from two minerals. For example, enstatite (0.90 μ) combined with a few percent olivine (1.04 μ) could yield a combination band at 0.915 μ. However, this possibility seems to be ruled out by the shape of the reflectivity curve of Vesta in the visible spectral region, as we discuss below.

We interpret the sharp decrease in reflectivity below 0.4 μ to be a charge-transfer band. Only the long-wavelength side of this band is shown. The band is typical of pyroxenes and of other iron-bearing minerals. Unfortunately, the band does not allow further insight into the pyroxene composition.

The structure of the Vesta curve between 0.4 and 0.7 μ is somewhat ambiguous because of the differences between the data from Chile and Mount Wilson. The general flattening of the curve in this region is clear, and there is a band center somewhere between 0.5 and 0.6 μ. A broad, weak absorption between 0.5 and 0.6 μ is characteristic of pigeonites but not of the orthopyroxenes or orthopyroxene-olivine mixtures, which, in addition, also have steeper curves. The most probable band assignment is Ti^{3+} which gives a broad band near 0.5 μ. Other bands in this spectral region arise from Fe^{2+} and Fe^{3+} on octahedral sites. However, these bands are usually too weak to be resolved in diffuse reflected light.

If we consider the Vesta curve as a whole, the best comparison is with a magnesian pigeonite that contains minor amounts of titanium. Orthopyroxene plus a small amount of olivine or calcic clinopyroxene could account for the 0.915-μ band, but the spectrum of this mixture is in poor agreement with the Vesta curve between 0.5 and 0.6 μ and drops too abruptly toward the ultraviolet.

The strength of the 0.9-μ absorption band ($\sim$30 percent) is in itself important. Studies of the Apollo 11 lunar samples have suggested that the abundance of opaque materials on the lunar surface has depressed the absorption band strength for lunar surface material as viewed through telescopes from the earth (*8*, *9*). Thus it appears that Vesta's surface is relatively free of such opaque materials. A silicate surface of this sort should have a visible albedo considerably higher than that of the lunar surface, perhaps in the range of 30 to 40 percent.

We have compared the Vesta curves with laboratory curves for Apollo 11 samples, chondrites, and basaltic achondrites (Figs. 3 and 4). The curves for chondrites do not flatten between 0.5 and 0.6 μ, because of the dominance of orthopyroxene structure, and therefore do not compare well with the curve for Vesta. The lunar samples and the basaltic achondrites with calcic pyroxenes have the major band at 0.93 μ or longer wavelength. However, the basaltic achondrites with predominant pigeonite have the main band as low as 0.925 μ and show an excellent agreement with the other features of the Vesta curves (Fig. 3). The discrepancy of 0.01 μ in the position of the main band is just within the error range when one compares the telescope and laboratory data. Although the visible region of the reflectivity curve very quickly drops below an acceptable level as the content of orthopyroxene is increased, the band could be slightly shifted to shorter wavelengths if a slightly more orthopyroxene-rich specimen were selected.

We conclude that the surface of Vesta is similar in composition to certain basaltic achondrites. Furthermore, the mineralogy of this asteroid appears to be distinctly different from that of other meteorite types and from samples of the lunar surface at the Apollo 11 landing site. Determination of Vesta's spectrum from 1.1 to 2.5 μ would help to confirm our conclusions; a band should exist centered near 2.0 μ. Also, additional spectral reflectivity measurements of other asteroids would yield further information on the heterogeneity of the asteroids and on their relationship to meteorites.

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Chlorophyll Derivatives in Middle Eocene Sediments

Abstract. *Chloroform extracts of middle Eocene brown coal were made; the chlorophyll derivatives obtained were separated chromatographically. The visible light spectrum, chromatographic behavior, HCl number, infrared spectrum, and mass spectrum of one of the pigments extracted is indicative of methyl pheophorbide a. This is the oldest occurrence of fossil phorbins reported.*

Green-colored angiosperm leaves were reported in 1931 by Weigelt and Noack (*1*) from middle Eocene brown coals of the Geisel valley near Halle, East Germany. Weigelt and Noack identified several chlorophyll derivatives from crude extracts of these green fossil leaves and their associated brown coals. A reinvestigation of this material by modern techniques of chromatography and spectrophotometry has made possible a more precise separation and identification of the green pigmentation of this material.

The material examined in this study was collected from the Neumark-Süd open pit brown coal mine in the Geisel valley near Halle, East Germany. Only a small number of the angiosperm leaf impressions in the Geisel valley brown coal are green; they are most often dark brown to black with a few scattered light-brown to white-colored leaf impressions present. The color of the green leaves varies considerably from light to dark. These leaves are impressions only; no cellular structure is preserved. The green coloration is visible only on the surface of the leaf impressions. Apparently as the leaves decayed specific compounds abundant in the brown coal were concentrated in the sites the leaves had occupied and thus colored the leaf impressions.

A sample of fossil lignite containing green-colored leaf impressions from this deposit was examined as follows: the surface of the material was extracted with chloroform for a few minutes to remove any contaminants which might have been picked up by the material between the time of collection in the field and testing in the laboratory. The material had been kept at between 0° and 5°C insofar as possible during this interval.

The material was then divided into two portions and extracted as follows. (i) One portion was ground in a ball mill with chloroform and then filtered to remove the solid material; (ii) the other was ground with a mortar and pestle and extracted with chloroform in a Soxhlet apparatus. The material was then fractionated by descending flow paper chromatography, with 30 percent chloroform in heptane as the eluting solvent. This solvent separated the sample into six distinct bands (Fig. 1). Band G was of particular interest because its visible-light absorption spectrum was similar to that of pheophytin a (Fig. 2). Its green color and appearance under ultraviolet light were also very similar to those of pheophytin a. This led us to suspect (*2*) that the conjugated system might indeed be similar or identical to that of pheophytin a. A Molisch phase test (*3*) was performed on pigment G with positive results. This indicates that the cyclopentanone ring is probably intact and similar to that of chlorophyll a. An HCl number test (*4*) eliminated pheophytin a as a suspect for the identity of this pigment. The HCl number of pigment G was found to be 16, which is identical to that of methyl pheophorbide a. Methyl pheophorbide a was then synthesized (*5*) from fresh chlorophyll a with cold methanolic HCl. Its visible-light absorption spectrum was similar to that of pigment G (Fig. 3). Also its R_F value was identical, within experimental error, to that of pigment G. Paper chromatograms of mixtures of pigment G and methyl pheophorbide a were obtained with three different eluting solvents (*6*). No separation was observed under these conditions. Both pigment G and methyl pheophorbide a were saponified with methanolic KOH; and, with the same eluting solvents mentioned above (*6*), mixed chromatograms of the products again showed no separation. Both compounds were then treated with boron trifluoride in methanol, and mixture chromatograms showed no separation.

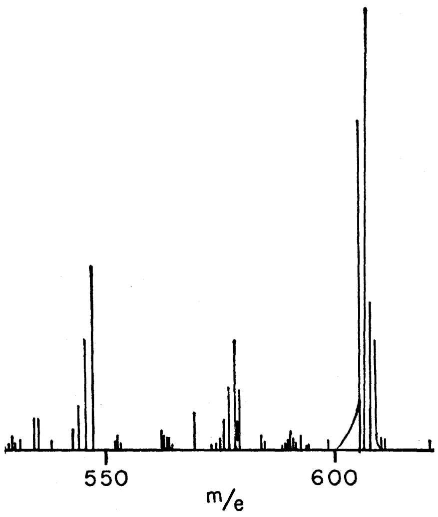
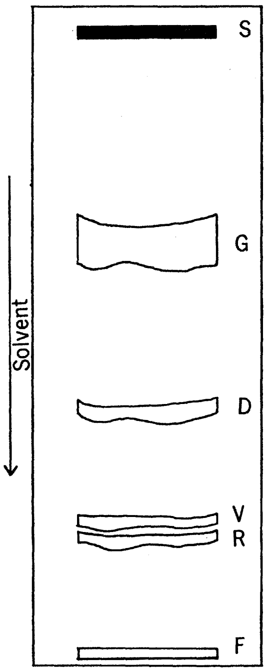
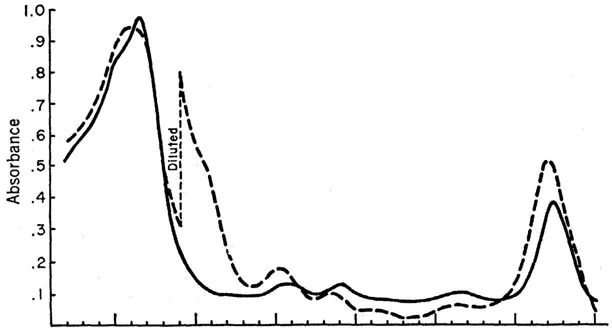


Fig. 4. Selected portion of the mass spectrum of pigment G. Run at 6 kv; ionizing voltage, 70 ev; source temperature, 250°C; filament current, 200 μa. Resolution is 1 part per 15,000.

As a final check on contamination, the extract of the surface was evaporated under a stream of nitrogen, and the concentrate was subjected to descending flow, paper chromatography. Appearance of the bands on the chromatogram and subsequent visible-light absorption spectra led to the conclusion that no noticeable differences existed between the surface extract and the subsequent extracts. In addition, the two extraction procedures showed very little difference in the results. However, a somewhat lower concentration of pigment G was observed in the Soxhlet extract, possibly indicating a small amount of thermal breakdown; but no major differences were observed. Infrared spectra of the sample were not entirely free of contamination in our opinion, but rather strong ester and carbonyl absorption peaks were observed. However, these peaks correspond closely to the peaks observed in the infrared spectra of modern methyl pheophorbide a.

Mass spectra on pigment G (Fig. 4) showed the following: the parent ion





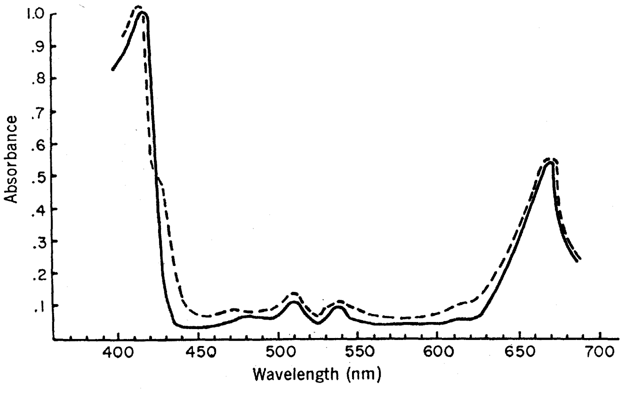


Fig. 1 (left). Chromatogram of the chloroform extract of the fossil green leaves and associated brown coal. Solvent, 30 percent $CHCl_3$ in C_7H_{16}; Whatman chromatographic paper No. 4 was used. Fig. 2 (top right). Solid line, visible-light absorption spectra of modern pheophytin a; broken line, green fossil pigment G in chloroform. Fig. 3 (bottom right). Solid line, visible-light absorption spectra of methyl pheophorbide a; broken line, pigment G in chloroform.

(ratio of mass to charge m/e was 606) was the largest peak; other prominent peaks nearby were $M-28$ and $M-59$, the first due to the loss of a two-carbon fragment and the latter probably due to a loss of -COOCH_3. Background noise became noticeable near m/e 300.

It is unusual to find methyl pheophorbide a in sediments as old as the middle Eocene because in almost all fossil sediments further reduction and decarboxylation have produced highly stable porphyrins, such as commonly occur in oil, coal, and fossil-rich shale. In the Eocene the Geisel valley was a poorly drained shallow basin (*7*), receiving organic sediments from plants and animals living along its swampy margins. In this swampy environment extensive deposits of peat accumulated and were subsequently slightly altered, producing brown coal. The amount of compression that occurred during the formation of the brown coal does not seem to have been excessive, and it is unlikely that the brown coal has ever been altered by high temperatures. The preservation of such fossils as frog epidermal cells containing nuclei and bacteria in the Geisel brown coal suggests an anaerobic environment with relatively rapid deposition, in which organic decay was slow and organic accumulation extensive. The rapid burial of plant material in an anaerobic environment and the fact that brown coal has a history of low temperatures may account for the preservation of this phorbin from the middle Eocene.

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Pollen Sequence from Late Quaternary Sediments in Yellowstone Park

Abstract. *A radiocarbon-dated pollen diagram from a depression near the end of the southeast arm of Yellowstone Lake, Wyoming, records the vegetation sequence from the retreat of Late Wisconsin (Pinedale) ice to the present time. The tundra* Picea-Abies-Pinus albicaulis *(spruce–fir–whitebark pine) parkland vegetation inferred during late glacial time changed rapidly to a* Pinus contorta *(lodgepole pine) forest shortly before 11,550 carbon-14 years ago, suggesting a warming trend at that time. The* Pinus contorta *forest persisted with minor modification throughout postglacial time.*

A series of depressions at the end of the southeast arm of Yellowstone Lake were cored for pollen and seed analysis. The most suitable core was from an abandoned lagoon 15 feet (1 foot = 0.3 m) above Yellowstone Lake level (elevation, 7750 feet). The present vegetation surrounding the site is *Pinus contorta* Dougl. (lodgepole pine) forest. A small forest opening characterized by *Artemisia tridentata* Nutt. (big sagebrush) occurs along the north edge of the fen. *Picea engelmannii* Parry (Engelmann spruce), *Abies lasiocarpa* (Hook.) Nutt. (subalpine fir), and *Pinus albicaulis* Engelm. (whitebark pine) are dominant on nearby slopes less than 100 feet above the coring site. The altitude of the present tree line averages about 9800 feet on adjacent plateaus.

The pollen and seed diagrams were divided into two pollen-assemblage zones. The late glacial *Picea–Juniperus–Pinus albicaulis* zone is overlain by the postglacial *Pinus contorta* zone. A radiocarbon date on sediment near the base of the upper zone is 11,550 ± 350 years B.P. (W-2285) (Fig. 1). The lower zone is characterized by maxima of *Pinus albicaulis*-type (*1*), *Picea, Abies, Juniperus, Salix* (willow), *Betula* (birch), *Populus* (poplar), Gramineae, *Artemisia,* and Compositae pollen percentages. Two other pollen diagrams from Yellowstone Park show a similar late glacial sequence (*2, 3*). The relatively low percentage of *Pinus* pollen (about 40 percent), the high percentages of *Artemisia* and Gramineae pollen, and the presence of rare grains of *Bistorta* (bistort), *Polemonium* (Jacob's ladder), Caryophyllaceae, Rosaceae, and *Selaginella densa* Rydg. (rock selaginella) are characteristic of late-glacial assemblages. This pollen assemblage is found only in those modern samples from alpine areas in Yellowstone Park and the Beartooth Plateau (*3*). Surface samples from tundras contain 45 to 65 percent tree pollen in this area, probably because tundra plants do not produce much pollen and high winds in alpine areas carry up pollen from lower tree-covered areas. Macrofossils of trees are rare at the bottom of the *Picea–Juniperus–Pinus albicaulis* zone, but they are more common in the upper half of this zone (Fig. 1). The pollen and macrofossils indicate that the first woody plants to be established in the area were *Pinus albicaulis* Engelm., *Picea engelmannii* Parry, *Abies lasiocarpa* (Hook.) Nutt., *Populus balsamifera* L. (balsam poplar), and *Juniperus communis* L. (prostrate juniper).

The vegetation was a subalpine parkland or alpine tundra near the tree line during late glacial time. Either interpretation allows for an estimated lowering of the tree line by about 2000 feet during the late phases of Pinedale glaciation. A cold, moist climate is implied by such vegetation. If a lapse rate of 3.5°F per 1000 feet is applied, the average annual temperature in the late glacial would have been about 7°F cooler than at present. The closest weather station on the north side of Yellowstone Lake has an average annual temperature of 32.8°F. A rough approximation of the late glacial mean annual temperature is thus about 26°F.

The *Pinus contorta* zone is characterized by pollen and needles of this species, and it was certainly a dominant tree during the postglacial. *Pseudotsuga* (Douglas fir) pollen occurs discontinuously at low percentages in the postglacial. But in surface samples, even where *Pseudotsuga* grows locally, its pollen is rare (*4*). Presence of its pollen in this zone probably means that *Pseudotsuga* was at least occasionally present in the area. The many taxa that show maxima in the late glacial all fall off to low percentages in the postglacial. Three subzones are defined within the