our moon model and ordinary chondrites for most elements appears satisfactory. On the basis of this model, the thickness of the residual melt after crystallization of olivine and pyroxene minerals and settling is calculated at ~ 35 km. After anorthosite flotation, the thickness of the highland crust is calculated to be ~ 30 km, which compares favorably with a thickness of ~ 25 km proposed by Wood *et al.* (*1–3*) on the basis of isostatic calculations. The corresponding thickness of the basaltic basement is calculated to be ~ 5 km.

Implicit in these calculations is the assumption that the impacting planetesimals (*1–5*) punctured the anorthositic crust in areas that were small relative to the areas of the present lunar maria (~ 1/5 of the lunar surface) and that basaltic magma flowed over vast areas.

As noted by Urey and MacDonald (*43*), complete melting of the total moon may not seem possible; however, our material balance argument is valid in any fraction of the moon, on the assumption that complete melting of chondritic material and fractional crystallization into the four assumed rock phases occurred. For example, if we assume that the upper 200 km was completely melted, the thickness of the highland crust is calculated at ~ 10 km and that of the basaltic basement at ~ 2 km (see Table 3).

Urey and MacDonald (*40*) have recently reported some mass balance calculations of the major elements Si, Ti, Al, Fe, Mg, and Ca for differentiation of the average silicate phases of the ordinary chondritic meteorites into three principal components, namely, lunar anorthosites, titaniferous Apollo 11 and Apollo 12 rocks, and a dunitic phase. Although no specific thicknesses were calculated for the melting and differentiation of varying depths of the lunar exterior matter, the conclusions of Urey and MacDonald seem to be consistent with those of this work.

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Natural Oil Seepage at Coal Oil Point, Santa Barbara, California

Abstract. *Aerial, surface, and underwater investigations reveal that natural seeps off Coal Oil Point, California, introduce about 50 to 70 barrels (approximately 8,000 to 11,000 liters) of oil per day into the Santa Barbara Channel. The resulting slicks are several hundred meters wide and are of the order of 10^{-5} centimeters thick; tarry masses within these slicks frequently wash ashore.*

During the controversy surrounding federal oil leases in the Santa Barbara Channel, there has been periodic reference to the fact that these waters have long been polluted by natural submarine oil seeps. Although their existence is well known, the amount of pollutant oil that flows from these seeps has never been documented. Thus, meaningful evaluation of the sources and magnitude of oil pollution has been impossible. Our intent here is to clarify this situation by reporting, for the first time, realistic estimates of surface pollution resulting from submarine oil seeps at Coal Oil Point. This region, although only one of many, is generally believed to be the most prolific natural seep in the Santa Barbara Channel.

Despite its antiquity, natural seepage at Coal Oil Point has been more a subject of passing curiosity than an environmental problem deserving scientific study (*1*). It was not until the late 1950's that efforts were begun to investigate the pollution aspects of this phenomenon in a quantitative way. At that time, studies were initiated to determine the extent of oil contamination on beaches along the coast of southern California and to examine the chemical characteristics of the oily pollutants (*2*). One of the findings of these studies was that tar deposition on beaches in the Coal Oil Point area is at least 100 times greater than on any other beach from Point Conception to the Mexican border. A factor not determined, however, was the rate of submarine oil flow that produced this large amount of beach contamination.

Field studies were therefore conducted off Coal Oil Point in October 1969 to identify and examine the activity of several distinct regions of oil seepage (*3*). These highly active regions were surveyed by means of aerial, surface, and underwater techniques (see Fig. 1, regions "a" through "e".) Other significant regions of submarine oil seepage are known to exist a few miles seaward, but the major portion of oily beach deposits at Coal Oil Point probably originates from within these nearshore sources.

Mean water depths range from approximately 13 m in region "a" to more than 30 m at the seaward (or southernmost) portion of region "c." The bottom topography consists primarily of fractured shale which, in some areas, is exposed and, in other areas, is covered with a considerable overburden. Small rock outcroppings and reefs that are 1 to 2 m in height characterize the shallow areas; deeper regions have a gently sloping sandy bottom.

The extent and activity of each seep region are variable. However, during the period of this study, we estimate that regions "a," "b," and "d" each covered approximately 1000 m^2 of the ocean floor. Within these regions, the oil exudes from discrete openings that are typically 0.5 cm in diameter; these openings are usually in areas covered by unconsolidated sediments. In some areas we could locate only an occasional point source, whereas in others we observed as many as 100 separate sources per square meter.

Table 1. Estimated width of oil slicks at Coal Oil Point. Seep regions are identified in Fig. 1.

Seep region	Slick width (m)
"a"	30 to 45
"b"	30 to 45
"c"	300 to 430
"d"	60 to 75

Seepage at region "e" was relatively small and intermittent; it could only be observed occasionally from the air—the actual source on the ocean floor was not located. Region "c," on the other hand, is an extensive area approximately 1000 m in length. Water visibility, depth, and available time prevented a thorough examination of the bottom in this region. However, the distribution of surfacing oil globules, combined with a knowledge of water depths and currents, suggested that the average flow rates per source were comparable to those of regions "a" and "b" but that the number of sources per unit area was significantly less.

Figure 2 shows an oil drop shortly after it has emerged from the ocean floor in seep region "a." Since the oil is less dense than seawater, it rises and forms a small globule or "head" with a connecting stringer that is attached to the source. Under the combined action of water currents and surge, the stringer eventually breaks, and the released oil globule rises to the surface. Several of these globules were collected and were found to contain between 1.7 and 3.9 g, with the average being 2.5 g. The density of this oil was very close to 1.0 g/cm^3.

The time between successive oil globule releases varies greatly among sources; it apparently depends on the strength of the current and surge, the nature of the oil, and the size of the hole through which the oil emerges. We observed some globules that appeared and broke away in as little as 15 seconds, but others remained relatively unchanged for as long as 5 minutes (the longest time any single point source was observed). The average, however, was in the range of 1 to 2 minutes.

When an oil globule reaches the surface, its behavior depends on the condition of the surface waters. If the wind or currents (or both) are strong, the area above a seepage zone is continually swept clear of oil that has previously surfaced. A new globule then quickly spreads into a thin iridescent slick,

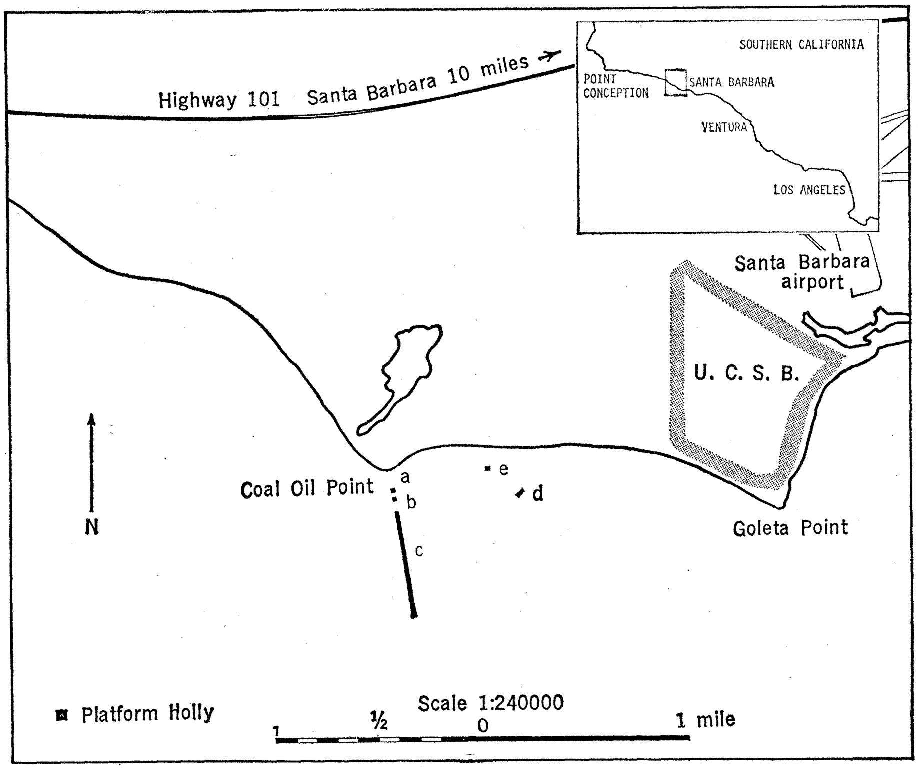
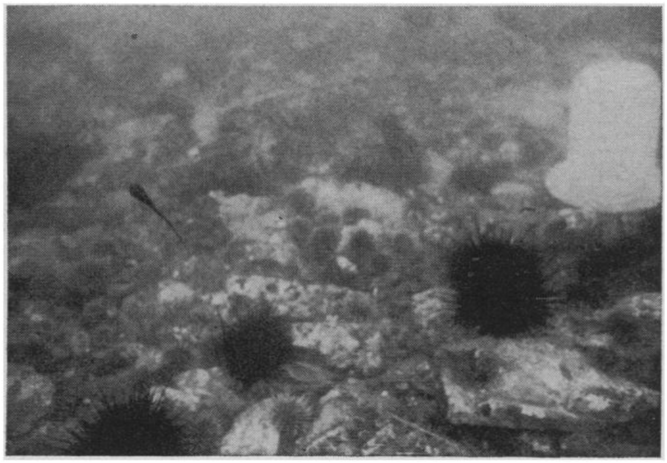


Fig. 1. Regions of natural seepage near Coal Oil Point (1 mile = 1.6 km).



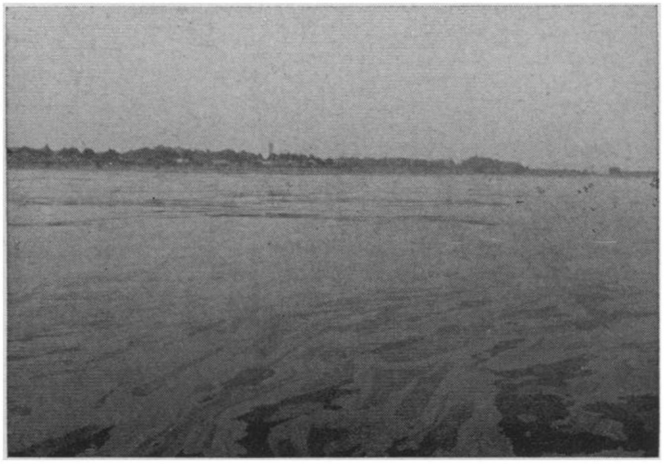


Fig. 2 (left). A representative oil globule as it leaves the ocean floor. A plastic collection jug can be observed in the background. Fig. 3 (right). Oil slicks resulting from natural underwater seeps at Coal Oil Point.

which is readily susceptible to assimilation by the environment. When conditions are stagnant, however, the globule will surface in an area that is already contaminated. In this case, the interfacial forces prevent the new globule from spreading, and the existing iridescent slick becomes streaked with dark portions of thicker oil (*4*). An example of this surface pollution phenomenon is shown in Fig. 3.

It is our belief that many of these heavy oil patches, which may persist for several days as a thick tarry material, eventually wash ashore and are responsible for the beach deposits so common in the area.

In our efforts to obtain a quantitative measure of submarine oil flow rates, the extensive area of seepage at Coal Oil Point presented a formidable problem. We therefore employed a number of independent methods to obtain both surface and ocean bottom measurements. The bottom measurements were conducted over a limited but well-defined portion of seep regions "a" and "b." The resulting data, when correlated with the nature and extent of surface slicks associated with these limited regions, could be extrapolated to a reasonable estimate of the total surface slick.

In one underwater technique, oil was collected in gallon-size plastic jugs (1 gallon = 3.785 liters) that were screwed into annular lead weights and placed in an inverted position over the seeps to be measured (see Fig. 2). The translucent jugs would gradually fill from the top down (with the oil displacing the water therein), thus providing the data necessary to estimate the average daily flow rate. These estimates were corroborated at several seeps by timing and collecting individual globules in separate jars over a period of several minutes. By determining the average oil content per globule, we were able to estimate the daily flow rate on the basis of bottom globule counts for a given seep as well as from counts of globules surfacing within a given area.

In region "b," where the depth was approximately 20 m, another approach was used. A large vertical frame, which contained a translucent screen (½ by 1 m), underwater lights, and camera, was lowered to the bottom and positioned over an active area of seepage. The screen had a grid taped to it, which, when illuminated from behind, provided an excellent background for time-lapse photographs of globules rising directly in front of the screen. Although time did not permit the development of this technique to its full potential, it did provide data that compared well with the other methods employed.

To obtain an independent check on the estimated flow rates obtained from bottom surveys, a number of surface studies were also conducted. One such study was predicated on observing an oil slick of uniform configuration; it required the simultaneous measurement of film thickness, slick width, and rate of drift from its submarine source. This technique was found to be effective, except when hampered by the combined presence of westerly near-shore currents, easterly littoral drift, and shifting wind conditions.

The width and drift rate of the oil slicks were determined by aerial photography. Linear dimensions were scaled from floating reference markers spaced at known lengths, and drift rates were calculated by means of time-lapse photography with dye patches deployed at known time intervals. The results obtained from a number of separate measurements during the 1 month of fieldwork are summarized in Table 1. In all instances, the surface drift rate was observed to be westerly at approximately 0.3 m per second.

The oil film thickness was determined by means of a specially constructed sampling device and subsequent laboratory analysis. The procedure consisted of isolating a 1.0 ft^2 ($\simeq 0.1$ m^2) area of the slick and collecting the oil film onto an adsorbent material (cheesecloth was found to be effective). The oil was then extracted from the adsorbent material by a suitable solvent, and the resulting solution was analyzed by colorimetric techniques (*5*). By comparing the sample's absorbance with the absorbance of known standard solutions, the amount of oil in the 1.0-ft^2 film was readily determined. The results of these measurements gave an estimated oil film thickness that ranged from approximately 10^{-4} to 10^{-5} cm.

Measurements of the quantity of oil released from natural seeps off Coal Oil Point were subject to frequent variations in seepage activity and uncertainties associated with the sampling and analysis techniques. In addition, changing environmental conditions would tend to alter the characteristics of the oil and impose limitations on the success with which certain data could be collected. However, we conclude from these surface investigations that no less than 10 barrels of oil per day were released during this study and that, during the most active periods, seepage could be well in excess of 100 barrels per day.

These estimates, which reflect the bounding assumptions for surface slick conditions, are consistent with the results obtained from oil collection techniques on the ocean floor. For example, a flow of 5 to 8 barrels per day from seep region "a" alone was determined by capturing oil from several major portions of that region. This level of activity was typical of a majority of our observations.

After considering all the factors pertaining to our collected data, we arrive at a total estimated flow rate of the order of 50 to 70 barrels (approximately 8,000 to 11,000 liters) per day. We point out, however, that this estimate is an average and it applies only to the period of our study. The natural seeps off Coal Oil Point have been observed to vary considerably in activity over a period of a few days (possibly by as much as 100 barrels per day).

In assessing the resultant level of shoreline oil pollution, several factors must be considered. From a scientific point of view, very little is known about the mechanism by which an oil globule released from the ocean floor is transformed into a tarry beach deposit. The degree of beach contamination is undoubtedly related to the submarine oil flow rate, but our study indicates that this relationship is far from simple or direct. In addition, the location of Coal Oil Point and the predominant offshore currents in that area generally prevent oil from fouling waters and beaches that are frequently used. The extent of natural seepage therefore goes unnoticed by a majority of people along the coast of Santa Barbara County.

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4. Our observations indicate that oil film thicknesses of the order of 10^{-5} cm can significantly retard the spread of a surfacing oil globule.
5. Although a number of solvents could be used, commercial paint thinner was found to be adequate. The instrument used in these tests was a Bausch & Lomb "Spectronic 20" colorimeter, and the wavelength was set at 625 nm.

27 August 1970 ■

Alkalinity and Formation of Zeolites in Saline Alkaline Lakes

Abstract. *The solubility of rhyolitic glass increases with increasing alkalinity, whereas the ratio of silicon to aluminum decreases with increasing alkalinity. The strong correlation observed between alkalinity and zeolite mineralogy in saline, alkaline lakes is thought to be a function of this relationship between pH and the Si/Al ratio. It is suggested that this function is a result of the reaction between silicic glass and alkaline solution whereby (i) a gel forms, whose Si/Al ratio is controlled by the Si/Al ratio of the solution, and (ii) a zeolite forms from the gel, whose Si/Al ratio is, in turn, controlled by the composition of the gel.*

In modern environments, where authigenic silicates are forming, a relationship has been noted between the Si/Al ratio of the low-temperature zeolitic alteration products of silicic glass and the alkalinity of the lake waters responsible for that alteration (*1, 2*). Specifically, more siliceous zeolites such as clinoptilolite and mordenite are the most common alteration products of silicic glass in marine and freshwater environments, whereas less siliceous phillipsite and erionite are the dominant alteration products in saline, alkaline lakes (Table 1) (*3*).

In addition, Senderov (*4*) pointed out that an increase in the concentration of hydroxide in the initial synthesis mixture results in the production of a zeolite phase with a lower Si/Al ratio. For example, mordenite is replaced by analcime in experiments characterized by high *p*H. Thus, experimental work on the low-temperature synthesis of zeolites also has shown that a relationship exists between the Si/Al ratio of the zeolite and the alkalinity of the mixture from which it formed (*5*).

In recent years it has been realized that zeolites are among the most common authigenic silicate minerals in sedimentary rocks (*3*). Thus it is important to understand the relationship between the Si/Al ratio of a zeolite and the alkalinity of its environment of formation; this knowledge will result in a significant insight into the chemical mechanisms characterizing sedimentary environments. The purpose of this report is to suggest the following model to explain this relationship: as a consequence of the reaction between silicic glass and alkaline solutions (i) a gel forms, whose Si/Al ratio is controlled by the Si/Al ratio of the solution, and (ii) a zeolite forms from the gel, whose Si/Al ratio is, in turn, controlled by the composition of the gel.

Much of the discussion of authigenic silicate formation has been predicated on the familiar curves of Correns and others, in which the solubility of amorphous silica is plotted as a function of *p*H (*6*). These curves suggest a precipitous rise in the solubility of silica at high alkalinities ($pH > 9$). More recently, Lagerstrom has shown that with an increase in alkalinity there is a more gradual rise in silica solubility (*7*). This fact has been documented in recent studies of natural environments (*8*). Jones *et al.* have shown that in the alkaline environments they have investigated, such as Lake Magadi, Kenya, the concentration of silica in solution is over 1000 parts per million (ppm). In saline, alkaline lakes of central Wyoming silica also has been found in excess of 1000 ppm (*9*). The fact that these natural alkaline environments are saturated with respect to silica suggests that saturation with respect to amorphous SiO_2 can be achieved. However, the source for the silica in these environments is not volcanic glass, but instead probably the weathering of feldspar [that is, $NaAlSi_3O_8 + 6\frac{1}{2}\ H_2O + CO_2 = Na^+ + HCO_3^- + 3\ Si(OH)_4 + \frac{1}{2}\ Al_2O_3$ (in clay)] (*8*).

On the basis of a consideration of the solution chemistry of silica alone, the erroneous conclusion can be drawn that in alkaline environments the activity of silica would be high and the more siliceous zeolites would form. An explanation for the lack of correlation