also are unknown. Before the Sierra Madera event, Cretaceous strata lay nearly flat, but the sub-Cretaceous structure of Permian rocks of the area had a small northward regional dip and gentle undulations, with dips locally as high as 20 degrees.

Nevertheless, if the cones formed before the central uplift, their initial orientations can be approximated by assumption that the Permian beds were horizontal and that there were simple rotations. The facing direction of beds is known certainly for all but the three most central localities. For beds lying on recognizable folds (asterisks in Fig. 1b), the fold axes were first rotated to horizontal, then the beds unrolled to horizontal; for other localities, beds were rotated to horizontal simply about their strike lines.

The resultant pattern (Fig. 1b) clearly shows cones plotting inward and upward, as at other cryptoexplosion structures where shatter-cone orientations have been well studied (*3, 7*). When one considers the simplifying assumptions used for restoration of the beds to their initial positions, the in-and-up pattern is surprisingly good. One exception, the easternmost locality, lies in a chaotic sedimentary reef breccia having such high initial dips that the rotation assumption is not valid. A single location of outward point, in the southwest, is representative of the minority of cones that developed along the same axes but with points opposite those of the prevailing pattern (*8*). Apart from the easternmost locality, 13 percent of all striae used indicate cones pointing away from the center; 87 percent point toward the center.

Cone-axis plunges are steepest in the center and decrease outward. A very approximate central focus about 1 km above the lowest exposed Permian beds is suggested by restoration of the strata to a horizontal pile and by averaging of the upward projections of the cones. This focus lies approximately at the level of the youngest deformed rocks now exposed.

Our results generally confirm Manton's (*3*) at Vredefort. It is especially noteworthy that (i) variously oriented cone segments define an approximately common cone axis and a dominant direction of point in any structural block, (ii) cones predate the central uplift by whatever time elapsed (probably no more than seconds between explosion and the structural adjustment which followed), and (iii) cones restored to prefolding orientations point mainly inward and upward toward a crude central focus. The radial symmetry about this focus is consistent with suggestions (*3, 9*) that shatter cones are formed by an advancing shock wave emanating from a central source, and supports the hypothesis that shatter-coned cryptoexplosion structures are products of impact.

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6. For instance, eight whole cones measured directly in one locality show a spread of 30° in axial orientation, with a significant variation from bed to bed. Two comparisons were made between determinations from striae on single whole cones and on cone segments in the same outcrop. In one case, the discrepancies in axis and apical angle were less than 5°, approximately the limits of error of measurement. In the other, concordant results were obtained from two whole cones 20 feet apart, but cone segments in the same bed as one of the whole cones gave results that were different by 15° in axis and 19° in apical angle. Cone segments may, therefore, in some cases show even more dispersion than whole cones, and whole cones themselves are not perfectly circular (Fig. 4b). The localities in which we measured the most striae generally show the poorest fits of data to small circles on the stereonet. Axes differing by 17° and apical angles by 11° were determined on plots of cone segments from two commonly oriented beds 10 feet apart; plotting all the points together gave essentially the same orientation and angle as averaging the two, but with a poorer fit of data. Thus it appears that because of local variations in cones, measuring many striae from a large exposure will result in considerable data scatter, but a good average determination of cone axis and apical angle.
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Deep-Ocean Basalts: Inert Gas Content and Uncertainties in Age Dating

Abstract. *The radiogenic argon and helium contents of three basalts erupted into the deep ocean from an active volcano (Kilauea) have been measured. Ages calculated from these measurements increase with sample depth up to 22 million years for lavas deduced to be recent. Caution is urged in applying dates from deep-ocean basalts in studies on ocean-floor spreading.*

The radiogenic inert gas content of basalts from the deep ocean is used in the much favored potassium-argon method of dating these materials. Such dates are of great interest in correlating with other data to bolster the hypothesis of ocean-floor spreading (*1*). It has been suspected in certain cases that the ages obtained might be in error due to gas inherited from the magma from which the rocks were derived. Materials obtained from past and proposed (Mohole) deep-drilling programs also might suffer from this effect. We present data to show that in some instances volcanic rocks erupted into the deep ocean do in fact inherit radiogenic argon and helium, and when dated may yield unrealistic old ages.

Three samples of glassy, tholeiitic basalt dredged from the ocean bottom off the island of Hawaii on the submarine extension of the east rift zone of Kilauea volcano were examined (*2*). There is an evident lack of degassing of these samples, which thus can be used in magmatic gas studies. From the rate at which the subaerial extension of this rift zone has been covered by lavas in historical times, it is possible to deduce that these lavas are very young, probably less than 200 years old (*3*). The samples may, in fact, be very recent, as judged by their fresh appearance and the extreme thinness of the palagonite and manganese oxide layers on the surfaces. This relation of degree of palagonitization and manganese re-

Table 1. Radiogenic helium and argon contents and ages of deep-ocean tholeiitic basalts.

Sample	Depth (m)	Potassium* (%)	Helium-4		Argon-40		K-Ar age ($\times 10^6$ yr)
			Blank (%)	Radiogenic ($\times 10^{-7}$ cm^3/g)†	Air contamination (%)	Radiogenic ($\times 10^{-7}$ cm^3/g)†	
A-1	1400	0.39	20	6.6 ± 0.7	100		0
A-2	1400	.39	10	3.1 ± 0.3	100		0
B-1	3420	.33	100		70	1.6 ± 0.3	<12 ± 2>
B-2	3420	.33	100		65	1.3 ± 0.2	
C-1	4680	.37			49	4.7 ± 0.2	<21 ± 8>
C-2	4680	.37	82	0.7 ± 0.5	74	1.8 ± 0.2	
C-3	4680	.37	35	.8 ± 0.3	70	2.8 ± 0.3	
C-4 (− 400 mesh)	4680		82	.2 ± 0.1	92	2.0 ± 0.8	
C-5 (olivine)	4680		46	1.4 ± 0.2	72	1.4 ± 0.4	

* Data from reference (*2*). † At 0°C and 1 atmosphere.

placement to submarine lava age also has been investigated (*3*).

The lava samples we examined had been collected at depths of 1400, 3420, and 4680 m, respectively (Table 1). They are portions of glassy, tholeiitic, pillow basalt samples [Table 2 in (*2*)]. Their physical and petrologic character, chemical analyses, and norms have also been described (*2*).

The standard techniques for dating young rock materials by the potassium-argon method were used (*4*). In addition, the helium-4 content was measured. Except for sample C-4 ground to −400 mesh (Table 1), the inert gases were extracted by fusion of whole rock in an ultrahigh-vacuum system by the use of pieces as large as could be handled conveniently (up to 5 mm in diameter). The innermost less glassy sections of the samples were used. The gases were purified by absorption and gettering. Isotopic measurements were made in the static mode with a Reynolds-type mass spectrometer. An argon-38 spike technique was used for argon, and the analysis for helium was made by calibration of the mass spectrometer with a zircon sample previously analyzed for helium in other laboratories (*5*).

The results are listed in Table 1, with the probable errors of the gas measurements also indicated. An estimate of the individual errors in each measured quantity was included in calculating the errors, but they are controlled chiefly by the corrections for air contamination in the case of argon, and by the blank resulting from helium diffusion from air through the glass portions of the system. The uncertainty in the ages given is the standard deviation showing the imprecision based on repeated runs.

Examination of Table 1 indicates the following. (i) The average radiogenic argon content of the basalts and their ages increase with the depths at which the samples were taken. The appearance of the samples and the slight extent of palagonitization (*3*) belie any such real age differences, so one is led to conclude that the differences are due to increased retention of magmatic gas with a high content of radiogenic argon. It would seem that lavas erupted at depths greater than 1400 m may retain a portion of inert gas from the parent magma. (ii) That fine grinding (Table 1, C-4, −400 mesh) did not decrease the content of argon beyond the experimental error suggests that the argon is a lattice component or is held in very small imperfections not opened by this treatment. This is contrary to the general situation in crystalline lava inclusions which seem to have the main portion of inherited gas contained in segregated sites (*6*). This was further substantiated by converse experiments in which sample C was ground in high vacuum, and the released gas was analyzed. Gas removed in this manner comes largely from lattice imperfections and inclusions (*6*). Although highly contaminated by air (90 percent average), with a high probable error for the measurement (50 percent), the radiogenic argon found averaged only 17 percent of the amount released by fusion, again indicating that this gas was not contained in relatively large segregated sites in the rock. (iii) A high content of helium was found for the lava extruded into the shallowest depth. Moore (*2*) noted an increase of olivine in these samples with the depth from which they were dredged and suggested that the lava erupted at each level taps a corresponding level in the subvolcanic magma chamber, with the olivine content reflecting differentiation in the magma. This also has been observed in subaerial lava flows. Helium is notably fugitive in silicates, and the high content in the shallowest sample may represent the effects of an upward segregation of this gas, producing a high helium partial pressure in the upper sections of the lava chamber. (iv) The olivine separated from the deepest sample (Table 1, C-5) had a relatively high content of both helium and argon. This is not sufficient, however, to account for the total inert gas content of the entire sample, because the olivine is only a fraction (about 14 percent) of the rock (*2*).

The helium-to-argon ratio in earth gases is low for gases from igneous sources, and has been found to have a very low value (averaging about 0.4) for gases released from certain crystalline inclusions frequently found in lava and presumably carried up from great depths (*6*). With the data for sample C from the deepest source (Table 1) an average ratio of 0.24 is computed, which indicates that this gas also may come from great depth and probably is representative of magmatic gas.

The main significance of the results is that they point to a need for caution in accepting the "ages" obtained by inert gas methods (potassium-argon or uranium-helium) when used on basaltic samples taken from deep-ocean sites. Therefore the ages measured on samples taken from depths greater than about 1400 m must be applied with some circumspection when being correlated with other phenomena. The other evidence of some differential segregation of helium, and of the location of gas in lattice sites other than in fluid inclusions (*6*), may have relevance to the role of gases in the mechanics of lava eruption in volcanology.

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Solid Ion-Exchange Electrode Selective for Calcium Ion

Abstract. *A calcium-selective electrode with solid ion exchanger was prepared from a solution of the calcium salt of a dialkylphosphoric acid in collodion. The electrode responds rapidly and reproducibly to activity of calcium ion and demonstrates a selective response for calcium ion in the presence of alkaline earth and alkali metal cations.*

Measurement of calcium ion activity is of great practical importance in many areas of biology and geology. In an attempt to develop an electrode responsive to calcium and other divalent ions, a variety of materials have been investigated. Among the solid materials that have been shown to have a response to calcium ion are glasses (*1*), clays (*2*), ion-exchange resins supported in an inert matrix (*3*), and stearate multilayers (*4*). These substances, however, have little practical application because of poor selectivity or slow dynamic response, or both. A calcium-selective electrode that makes use of a liquid ion exchanger has recently been reported (*5*).

We report here a solid ion-exchanger electrode of simple construction which responds rapidly and selectively to calcium ion. This electrode has as its ion-sensitive element a solid solution of the calcium salt of a disubstituted organophosphoric acid in collodion. The characteristic behavior of this electrode is analogous to that of *p*H and cation-sensitive glass electrodes. The organophosphate salt provides exchangeable sites with a favorable selectivity for calcium ion while still allowing an appreciable calcium ion mobility within the solid phase.

The phosphoric acid employed should have carbon chains of sufficient length to render the compound essentially water-insoluble. Typically, dioctylphosphoric and didecylphosphoric acids are used. The calcium salt was prepared by neutralizing the acid with calcium carbonate and heating to 100°C to drive off the water and carbon dioxide that formed. The salt was then dissolved in three to five parts by weight of an alcohol-ether solution of collodion (*6*); a film or plug of the collodion solution was formed over the end of a 6-mm glass tube and dried for several hours at 50° to 60°C. After the exchanger had hardened, the tube was filled with 0.01M calcium chloride and fitted with a silver–silver chloride half-cell. Resistance of the electrode ranges from 1 to 10 megohms.

Potentiometric measurements were made with a Beckman research *p*H meter employing the cell

$$\mathrm{Ag}\,\Big|\,\mathrm{AgCl}\,\Big|\,\mathrm{CaCl_2}\,\Big|\,\begin{array}{c}\text{Ion-exchange}\\ \text{membrane}\end{array}\,\Big|$$
$$\text{Test solution}\,\Big\|\,\mathrm{KCl\ (sat.)}\,\Big|\,\mathrm{Hg_2Cl_2}\,\Big|\,\mathrm{Hg} \quad (1)$$

Individual ion activities were calculated from the extended Debye-Hückel equation, with the use of the correction given by Meites (*7*) at higher ionic strengths. Soaking the electrode in dilute calcium ion solution for several hours before initial use makes the response more stable and repeatable.

Figure 1 shows the response of the solid ion-exchanger electrode in solutions of calcium chloride, magnesium chloride, and calcium chloride plus 0.01M magnesium chloride. In solutions containing only a single salt, the observed potential (E) is given by a form of the Nernst equation

$$E = \text{constant} + \frac{2.303\ RT}{2F} \log a_{M^{2+}} \quad (2)$$

where M is a divalent cation [in this case, calcium or magnesium (*1*)]; R, the gas constant; T, absolute temperature; F, the faraday; and a, activity. The constant includes terms relating to the choice of reference electrode, the reference electrode junction potential, and the calcium ion activity in the internal solution. The electrode behavior is Nernstian with respect to calcium ion over a concentration range of 10^{-1} to $10^{-4}M$ and to magnesium ion over a range of 10^{-1} to $10^{-3}M$. Plots of potential against the negative logarithm of metal ion activity are linear and yield a slope of 30 ± 1 mv per decade. Response to calcium and magnesium ion extends as low as 10^{-5} and $10^{-4}M$, respectively, but sensitivity in this range is diminished. At these levels the solubility of the calcium organophosphate possibly becomes a limiting factor.

Foreign cations moderate the electrode response to calcium ion by varying degrees. The upper curve in Fig. 1 describes the change in potential with calcium ion activity in the presence of 0.01M magnesium ion. From data of this type selectivity coefficients may be calculated which indicate the extent of the interference by other cations. The selectivity coefficient $K_{\mathrm{Ca}M}$ in Eq. 3,

$$E = \text{constant} + \frac{2.303\ RT}{2F} \times \log\left[\ a_{\mathrm{Ca}^{2+}} + K_{\mathrm{Ca}M}(a_{M^{z+}})^{2/z}\ \right] \quad (3)$$

is defined in such a way that a value of $K_{\mathrm{Ca}M} < 1$ indicates a selectivity for Ca^{2+} relative to the ion M^{z+}, where z is charge. Table 1 lists values of $K_{\mathrm{Ca}M}$

Table 1. Selectivity coefficients of calcium dioctylphosphate–collodion electrode calculated from response in solutions of mixed ions.

Interfering ion	$K_{\mathrm{Ca}M}$
Mg^{2+}	0.34
Ba^{2+}	.90
Na^{+}	.029
K^{+}	.034
H^{+}	1.5×10^{4}

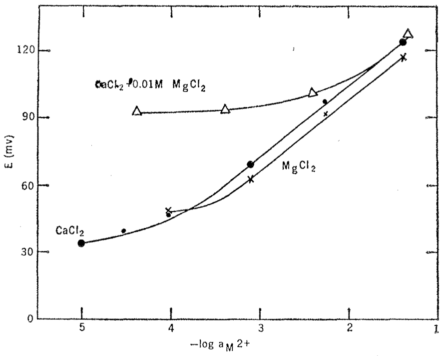

Fig. 1. Electrode potential at *p*H 8 plotted versus $-\log a_{\mathrm{Ca}^{2+}}$ for solutions of calcium chloride and calcium chloride in 0.01M magnesium chloride, and versus $-\log a_{\mathrm{Mg}^{2+}}$ for solutions of magnesium chloride. Electrode consists of 25 percent, by weight, calcium dioctylphosphate in collodion.