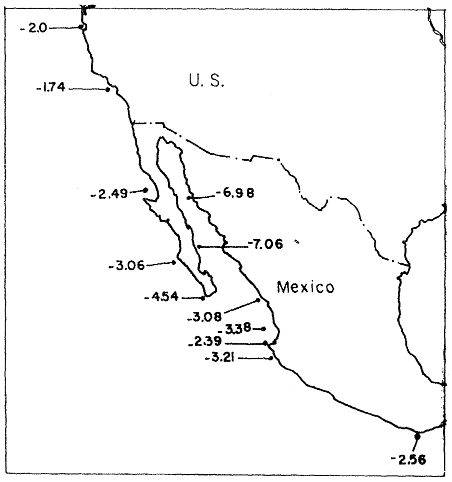

Fig. 1. Collection sites of shells used in this study.

UCLA-914 and UCLA-917 have a considerably higher apparent age than those from open ocean coasts. As has been pointed out by Hubbs and Roden (*10*), there occurs localized upwelling in this gulf along the eastern coast in the winter and along the western coast in the summer. Besides this mechanism for the introduction of C^{14}-poor water into the surface of the gulf, strong tidal currents cause extensive mixing of surface with subsurface waters. Since the upwelling in the gulf is thought to be less pronounced than on the Pacific Ocean coast of Baja California, the dominant mixing mechanism in the gulf must be due to the action of tidal currents, if the C^{14} content of water from similar depths in the open ocean and the Gulf is the same.

In the shallow northern portion of the Gulf of California, upwelling and tidal current effects apparently cannot draw on sea water of lower C^{14} content. This would explain the relatively low C^{14} depletion of −2.6 percent measured by the LaJolla Radiocarbon Laboratory for shells and sea water near San Felipe (LJ-648, LJ-701) (*11*). But at the mouth of the Gulf, near Cabo de San Lucas, strong currents result in the mixing of ocean water, as seen by UCLA-916, resulting in a depletion of −4.5 percent.

As a result of this study, several conclusions can be drawn of importance to the collectors of shells for archeological investigations, if no wood, charcoal, and so forth is available for C^{14} dating. First, it is necessary to establish the previous use of the shells in question. Those that had earlier been gathered primarily for their food content most likely had been gathered from places near the sites where the archeologists find them. But heirlooms may have already possessed an unknown age at the time of their last use, or may even have been obtained over great distances from a completely different oceanic environment. An example of the problem encountered with heirlooms has recently been discussed by Furst (*12*) and by Long and Taylor (*13*).

Once the origin of the shells has been established, the respective oceanographic conditions have to be ascertained. An area of restricted circulation with the open ocean and heavy admixture of river water, such as Galveston Bay or Lake Pontchartrain, will yield shells of very low C^{14} content. Similarly, shell beds exposed to upwelling and strong currents will also produce shells of high apparent age. Only areas of open interaction with the ocean, free from special mixing phenomena with deeper water layers, will produce shells with the least likelihood of possessing an unexpectedly low C^{14} content. Such shells cause only minimum errors that are due to an unknown high apparent age difference between marine and land-based samples of the same true calendar age.

Future study should determine to what extent it may be possible to follow local processes of upwelling in order to find the depth of origin of the rising water masses. This might be accomplished by measuring shells originating at different depths. As Sverdrup and Fleming estimate, the upwelling water rises only from depths of less than 200 m (*14*). But the vertical profiles of the ΔC^{14} content at stations in the Pacific Ocean indicate a relatively rapid rise in apparent age with increasing depth for the first 1000 m (*8*). As the average life-span of marine shells lasts from a few years to some 25 years (*15*), shells will acquire a radiocarbon content determined by the magnitude of seasonal changes in upwelling which carries ocean water of changing C^{14} content over the shell bed.

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Magnesium in Sea Water: An Electrode Measurement

Abstract. *Magnesium ion in standard I.A.P.O. sea water was measured with a magnesium-sensitive electrode. The results, presented either as magnesium-ion activity (0.017) or as the amount of ionized magnesium (0.048*M *or about 90 percent of the total magnesium), agree well with the data from the chemical model for sea water proposed by Garrels and Thompson.*

A recently developed (*1*) cation-sensitive electrode has considerable sensitivity to magnesium ion. It is approximately equally sensitive to divalent cations and responds to calcium or magnesium about ten times as strongly as to sodium ion; it is indifferent to *p*H between 5 and 10. One can use this many-functioned electrode to measure

Table 1. Molar concentrations of cations in calibrating solutions and in standard I.A.P.O. sea water of chlorinity 19.373 parts per thousand.

Solution (No.)	Ion concentration (M)			
	Na	K	Ca	Mg
1	0.469	0.0097	0.0088	0.0248
2	.469	.0097	.0088	.0496
3	.469	.0097	.0088	.0465
Sea water	.469	.0097	.0102	.0534

magnesium ion in sea water by calibrating it in solutions that have the competing cations already present, varying only the concentration of magnesium ion. In sea water some of the magnesium is complexed by bicarbonate, carbonate, and sulfate ions, but as far as is known there is no complexing of magnesium, calcium, or sodium ion by chloride ion (*2*). The calibrating solutions were made up from the chloride salts of the several cations; their compositions, and the composition of standard sea water from data of Sverdrup *et al.* (*3*), appear in Table 1. Calcium concentration in the calibrating solutions is 86 percent of that in the sea water—about as much as is considered to be ionized in sea water (*2*). The sea water used was standard I.A.P.O. (International Association of Physical Oceanography) sea water; chlorinity, 19.373 parts per thousand.

The electrode-potential measurements were made against a saturated KCl-calomel reference electrode with an expanded-scale voltmeter (10 mv, full scale) and a strip-chart recorder. The solutions were stirred magnetically, and temperature was controlled at 25° ± 0.1°C. The potential measurements were repeated several times; reproducibility was about ± 0.1 mv.

The best values for the four solutions were, in millivolts: solution 1, − 56.2; solution 2, − 50.6; solution 3, − 51.2; and sea water, − 50.9. The potential for sea water lies halfway between the potentials for solutions 2 and 3, which have, respectively, 0.0496 and 0.0465M magnesium; ionized magnesium in sea water may be taken as the average of these two concentrations, 0.048M. The total magnesium present in the sea water being 0.0534M (Table 1), it is apparent that only about 90 percent of the magnesium in sea water is ionized; this finding is in fair agreement with the data of Garrels and Thompson who calculated that about 87 percent is ionized (*2*).

To convert the electrode-potential measurements to activities of magnesium ion one must use an individual ion activity coefficient. The ionic strengths of the calibrating solutions are nearly the same as that of the sea water, so I shall use the activity coefficient for magnesium ion used by Garrels and Thompson in their model. (I realize that I have combined a molal-activity coefficient with a molar concentration, but the differences between molal and molar magnesium in these solutions are less than 1 percent.)

With the use of this activity coefficient, 0.36, the calculated activities for magnesium ion in the calibrating solutions are: solution 1, 0.0089; solution 2, 0.0179; and solution 3, 0.0167. Because the potential in standard sea water lies midway between the potentials for solutions 2 and 3, the activity of magnesium ion in sea water may be taken as their average—0.0173, which also is in fair agreement with the value calculated by Garrels and Thompson, 0.0169.

Recently another value for the activity of magnesium ion in sea water was reported by Pytkowicz *et al.* (*4*); they measured the *p*H of sea water that was presumably saturated with brucite, $Mg(OH)_2$, obtaining 0.0084 for the activity of magnesium, a value about half as great as the one I report. It is difficult to reconcile their measurement with the assumptions used in constructing the chemical model of Garrels and Thompson. If, as Pytkowicz *et al.* suggest, 39 to 53 percent of the magnesium in sea water forms $MgSO_4^0$-ion pairs, virtually all the sulfate present in sea water must be combined with magnesium, because sulfate is less than 53 percent as abundant as magnesium.

But the dissociation constants compiled by Garrels and Thompson indicate that about as much $NaSO_4^-$-ion pair is formed as is $MgSO_4^0$. Possibly the different result may be explained by assumption that the solubility of brucite is not known closely enough, or that in their experiment equilibrium was really attained with a hydroxy carbonate of magnesium, such as hydromagnesite $[Mg_4(CO_3)_3(OH)_2]$.

On the other hand, the good agreement between the values obtained by this electrode measurement and the calculations of Garrels and Thompson tends to support the assumptions on which construction of their model for sea water was based: that estimated values for individual ion activity coefficients, used in conjunction with thermodynamic dissociation constants involving the eight major species in sea water, yield at least a first approximation of the extent of interaction among those species. If the activity coefficients used in the model were not reasonably correct, the calculated amount of ionized magnesium would probably not agree so well with the measured value.

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Rare Earths in Hawaiian Basalts

Abstract. *Rare-earth elements have been determined by neutron activation analysis in 20 basalts from the Hawaiian Islands. The abundance patterns of these elements form groups coinciding closely with groupings based on other evidence, and a fractional crystallization mechanism for change in rare earth abundance is implied.*

Volcanic rocks of the Hawaiian Islands have been under intensive study, from the standpoint of petrology and major-element chemical composition, by a number of investigators (*1–5*) who seek answers to the questions of the origin of these rocks and differentiation of the earth. We have analyzed some of these rocks for rare-earth elements by means of a neutron activation procedure used in previous work (*6*). In this preliminary report we present some of the relations revealed by abundance patterns of the rare earths.

In Table 1 we describe the samples analyzed and group them according to the similarity of rare earth abundance patterns given below. Following the practice of this laboratory (*7*), we compared the rare earth abundance pattern of each rock, element by element, with a common reference, for example, the average of ordinary chondritic meteorites (*8*). The relative abundance of each rare earth (that is, enrichment factor relative to the reference) is plotted logarithmically versus a linear scale of the atomic numbers of the rare earths. These elements decrease in size with increasing atomic number, and an ap-