from at least four locations and astrometric plates were obtained on the same night (6). Three groups reported an occultation [Calgary, Alberta, 6 seconds; Boulder, 38.3 seconds; and the High Altitude Observatory (HAO), uncertain, but consistent with Boulder], while a fourth group in Denver observed the appulse but recorded no occultation. The Boulder and HAO events correspond to occultation by an 800-km object, while the diameter of Pallas is accurately known to be no more than 560 km (7). The negative result at Denver was obtained at a distance of 47 km perpendicular to the Boulder path and is not reconcilable with either the Boulder or the HAO observation. The Calgary event is certainly not an observation of an occultation by the Boulder object, since the two stations are separated by 1400 km. The Boulder recording suggests a secondary component for the star, providing a possible explanation for the lengthy occultation. However, this interpretation actually increases the difficulties in reconciling the various observations, since the Boulder event suggests a brightness ratio of 2 to 1, while the Calgary observation requires a ratio of more than 5 to 1. An additional suggestion that the Boulder and HAO observations were spurious comes from the astrometric reduction of photographs taken from Las Cruces, New Mexico, which indicates that the main occultation event passed well to the north of the U.S.-Canadian border (8) (and presumably north of Calgary). The most satisfactory resolution of these contradictory results is the conclusion that the Boulder and HAO observations are not occultation events and that Calgary may have observed a short occultation. The observations are definitely not explained more satisfactorily by postulating a secondary body.

The case for minor planet multiplicity is being argued on the basis of the 532 Herculina event discussed above, a lightcurve behavior for several minor planets which is reminiscent of that of binary stars (9), and a number of single, unconfirmed reports of secondary occultations. So far, a majority of the unconfirmed observations appear to be spurious, and it is certainly premature to state that minor planet satellites are 'both numerous and commonplace'' (1).

It is not our contention that minor planet satellites do not exist but rather that the problem needs to be dealt with carefully and objectively. Certainly, many more reliable observations are needed before the frequency of such

multiplicity can be discussed. Because of the experimental problems associated with occultation observations, we urge the use of redundant photoelectric observations of the type reported here (10). It is perhaps from lightcurves or direct imaging that the most reliable data will be obtained.

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an approximately 80-arc second diaphragm (C. F Lillie, personal communication); they reported a 38.3-second event which had an abrupt begin-ning and end and showed a discrete change in brightness midway through. The HAO observa-tion was obtained by G. Emerson [IAU Circ. 2506 (1973)] through microphotometry of a pho-tograph made with a 15-cm f/4 lens and in-dicated a beginning time consistent with the Boulder observation and an approximately com-Boulder observation and an approximately com-parable duration. The Calgary event [T. A. Clark, E. F. Milone, D. J. I. Fry, *IAU Circ. 2506* (1973); T. A. Clark and E. F. Milone, *J. R. As-tron. Soc. Can.* **67**, 198 (1973)] was observed with a 40-cm telescope as a 6-second discrete feature (of 85 percent of the expected drop) su-perimposed on a modulation produced by telescope tracking error whose amplitude was great-er than the expected occultation depth. K. A. Janes and H. J. Reitsema [IAU Circ. 2094 (1973)] becaude from Deputy with a 51 or ror (1973)] observed from Denver with a 51-cm refractor and recorded no event. It is our opinion that the low-noise data of the Denver event have highest weight and may not be ignored in a resolution of the observations of this event . Photographic plates of the appulse were obtained at New Mexico State University, Las Cruces, by C. Knuckles with the f/40 61-cm telescope.

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- 11 The Lunar and Planetary Laboratory of the University of Arizona continues to develop its aster-oid occultation program with the support of NASA. We will be pleased to coordinate future observations with other investigators. 23 March 1979: revised 21 May 1979

## Stable Isotopes in a Mollusk Shell: Detection of Upwelling Events

Abstract. The California mussel Mytilus californianus records with high fidelity annual temperature variations of nearshore waters in the oxygen isotope composition of its shell. The onset and termination of upwelling events (and metabolic activity) are recorded in the associated carbon isotope signal, and the magnitude and timing of upwelling can be estimated. The method has implications for studying the history of upwelling and the life history of living and fossil mollusks and for analyzing shell midden deposits.

Coastal upwelling is of fundamental importance in the study of the physics, chemistry, and fertility of the ocean. Its intensity changes seasonally but there are also long-term changes on scales from decades to millennia as well as through geologic time (1). Mollusk shells are useful indicators of their environment of growth, through both morphology and chemical composition (2, 3). In particular, they record the range and successions of seasonal temperatures (4) and therefore provide time markers for the study of both physical and biological processes.

We show here how the <sup>13</sup>C/<sup>12</sup>C ratio in mollusk shells can be used to detect the onset and course of seasonal upwelling during the time of shell growth. The implication is that dated shells can provide a glimpse of seasonal variations in upwelling over a number of years, within a given period in the past.

The signals recorded in epifaunal mollusk shells exposed to the open ocean are

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temperature (as oxygen isotope variation) and upwelling (as carbon isotope variation). Our sample is a modern shell of the California mussel Mytilus californianus from the shores of La Jolla, California. The seasonal variations of the temperature of growth of the mussel are known (Fig. 1A). Temperatures corresponding to the oxygen isotopic variations can be calculated from a paleotemperature equation (5) for comparison with the actual temperature measurements (Fig. 1B).

The seasonal course of upwelling in the region is reflected in the Bakun upwelling indices (6) (Fig. 1C). These indices are based on the sea-surface stress fields estimated from atmospheric pressure fields. Wind stress transports surface water offshore and causes this water to be replaced by the upwelling of deeper water. The stress field determines an Ekman transport field, the offshore-directed component of which is considered an indication of the amount of upwelling required to replace water carried offshore in the wind-transported surface layer. We chose upwelling indices that have been computed for 33°N, 119°W as the closest to the area of study.

Comparison of the temperature curve and the upwelling curve (Fig. 1, A and C) shows that upwelling sets in with the onset of warming in March and peaks May to June, roughly coincident with the maximum rate of change of temperature. It subsides in July and August, when seasurface temperatures reach their maximum.

No measurements are available for the seasonal fluctuations of  $\delta^{13}$ C of the coastal waters. However, the effect can be estimated from other observations.

Measurements of the  $\delta^{13}$ C (7) in the dissolved inorganic carbon (mostly bicarbonate ion) in the Pacific show a gradation from about 2 per mil with respect to Pee Dee belemnite (PDB) at the surface to a minimum value of about 0 per mil at a depth of a few hundred meters (8). The depletion of <sup>12</sup>C in surface waters is due to its preferential removal by planktonic algae during photosynthesis. Conversely, the combustion of organic material, which causes the oxygen depletion in subsurface waters, increases <sup>12</sup>C relative to 13C. The amount of combustion which has taken place can be estimated from the apparent oxygen utilization (AOU) (9, 10)-that is, the difference between saturation oxygen values and the actual oxygen content. The necessary data on temperature, salinity, and oxygen content are available (11). We took the monthly averages over the period 1950 to 1965 for California Cooperative Oceanic Fisheries Investigations (CalCOFI) station 90028, which is approximately 60 km north, along the coast, from our area.

The amplitude of the change in  $\delta^{13}$ C is best estimated for a depth below waveaction effects; we show estimates for depths of 20 and 30 m (Fig. 1D), since the near-surface mixing processes introduce new oxygen. We emphasize that our intention is to show the expected seasonal range of  $\delta^{13}$ C values as a function of upwelling rather than the absolute  $\delta^{13}$ C composition.

Comparison of the Bakun upwelling indices and the (generalized)  $\delta^{13}$ C estimates indicates good agreement in the timing. There does appear to be a slight phase difference of about 1 month, with the AOU-derived signal leading the one derived from wind stress.

Our hypothesis is that mollusk shells record the temperature and upwelling signals rather faithfully, under favorable 13 JULY 1979 Fig. 1. (A) Monthly averages of sea-surface temperatures at the SIO Pier, 1974 through 1977 (solid line) and averages 1920 from through 1973 (dashed line). (B) Variations in <sup>8</sup>O in modern mussel shell calcite, with the corresponding paleotemperature calculated scale. The recorded pier temperature (dashed line) is replotted against the paleotemperature scale (23). (C) Monthly Bakun upwelling indices. Units are cubic meters per second per 100-m length of coast. (D) AOU-derived <sup>13</sup>C changes reconstructed from CalCOFI data averages for the period 1950 through 1966. Curve 1, 30 m; curve 2, 20 m. (E) Variations in <sup>13</sup>C in the modern mussel shell calcite (solid line); Bakun upwelling index (dotted line); 20-m AOU upwelling index (dashed line).

circumstances. We selected *Mytilus californianus* for study because of its abundance and its exposed-shore habitat. It occurs along the western coast of North America from Alaska to southern Baja California. It is abundant in masses in the upper intertidal zone on surf-exposed rocks (12).

The modern specimen was collected live in August 1977 from an exposed rock (Dyke Rock) in the intertidal zone approximately 800 m north of the Scripps Institution of Oceanography (SIO) Pier.

The shell valves were scraped to remove any obvious foreign material and then washed with deionized water and dried at 80°C. The periostracum of the modern shell was peeled off to expose the outer prismatic layer, which is composed of calcite (2). Each valve was soaked in 2 percent Clorox solution for 3 hours to help destroy organic matter and then washed in deionized water and dried at 80°C.

The subsamples used for isotopic analysis were removed with a dental drill (0.5 mm in diameter) along the growth direction of the prismatic layer. Each subsample weighed about 0.5 mg. Standard analytical procedures were used (I3). The analytical precision was 0.07 per mil.

The  $\delta^{18}$ O results (given as per mil PDB) track the temperature fluctuations, as expected (Fig. 1B). Although the correspondence is excellent, it is not exact. Comparison of the temperature curve in Fig. 1A (shown as the dashed line in Fig. 1B) and the  $\delta^{18}$ O curve suggests that, as it ages, the mussel grows slightly faster



during cold and cool periods and adds relatively less shell material during summer.

The  $\delta^{13}$ C results (also in per mil PDB) show fluctuations which tend to parallel the Bakun upwelling index and the AOU-derived  $\delta^{13}$ C estimate (Fig. 1E). Thus, the evidence suggests that the  $\delta^{13}$ C curve does indeed record effects of upwelling. However, the amplitude of variation is greater than that expected from the AOU index. It appears that the  $\delta^{13}$ C values of the mussel shell record metabolic effects, in addition to purely environmental ones. As with other organisms (10, 14), the periods of high metabolic activity are reflected as a decrease in  $\delta^{13}$ C, which is superimposed on the effect from the changing composition of the water (15).

There are changes in the pattern of upwelling from year to year, with the upwelling maximum sometimes several months offset from the average given by the AOU index. Tont has demonstrated (*16*) that there is a good correlation between primary production (related to upwelling) and negative temperature anomalies in this region.

From a comparison of the SIO Pier temperatures (1974 through 1977) with a 53-year average (Fig. 1A) it is clear that the negative temperature anomaly for 1975 indicates abnormally early upwelling which is reflected in the  $\delta^{13}$ C signal of the mussel shell. The primary production for 1975 was exceptionally strong and increased earlier than normal (*17*).

Some preliminary work on fossil My-

tilus californianus shells from the Nestor Terrace [a Pleistocene terrace remnant about 5 km north of the SIO Pier (18)] shows  $\delta^{18}$ O ranges similar to those of modern shells, in agreement with the results of Valentine and Meade (19), who estimated paleotemperatures of Californian Pleistocene mollusks.

Seasonal changes in the  $\delta^{13}C$  of the fossil mollusks are also closely correlated with the modern record and suggest that upwelling occurred along this coast during the 120,000-year interglacial in a manner similar to modern upwelling. However, the possibility of diagenetic alteration, which could affect the isotopic values, has not been ruled out. Clearly, an extensive isotopic survey of modern and fossil shells is necessary before positive statements can be made with regard to paleo-upwelling and the direction and duration of paleowinds.

We conclude that a definite record of upwelling can be obtained from stable isotope measurements on modern mollusk shells. Moreover, the isotopic curves may be used to fix the time of death of the animal. Such timing can be important in studying shell middens, in determining seasonal occupation (20), and in deciding whether shell heaps are in fact midden deposits, a question that arises sometimes in connection with sealevel variations.

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- We thank P. E. Smith and R. Eppley for advice, P. Remeika for assistance in sample collection, and H. R. Thierstein and E. Vincent for helpful 24 omments on the initial draft of this manuscript. This work was supported by NSF Oceanogra-phy Section grant OCE76-84029 A02.
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## **Superconducting Properties of Protactinium**

Abstract. The superconducting transition temperature and upper critical magnetic field of protactinium were measured by alternating-current susceptibility techniques. Since the superconducting behavior of protactinium is affected by its 5f electron character, it is clear now that protactinium is a true actinide element.

Protactinium metal was reported to be superconducting below 1.4 K by Fowler et al. (1) at Los Alamos in 1965. In 1972 Mortimer (2), at Harwell, reported no superconductivity in protactinium down to approximately 0.9 K. There was one more round of publications from the two laboratories that still did not settle the question of the superconductivity of protactinium (3, 4). This continued disagreement over experimental results was clearly due to problems with the crystal structure and the sample purity that arise when dealing with small amounts of radioactive material.

The theoretical situation was more certain. Both Hill (5) and Johansson (6) were convinced that protactinium was a superconductor. Its position in the early actinide elements, where there is a smooth variation of electronic properties, and specifically its position between two superconductors (thorium and uranium), led to confidence that protactinium must also be a superconductor.

It has now become possible to obtain very high purity protactinium by a Van Arkel procedure. This has been done at Karlsruhe (7) and Harwell (8). We report here on measurements of the super-

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conducting properties of the protactinium metal prepared at Karlsruhe. We have measured the superconducting transition temperature  $(T_c)$  and the upper critical field  $(H_{c2})$  as a function of temperature, using a-c susceptibility techniques. The very high purity samples permitted useful  $H_{c2}$  measurements down to  $\sim 1/2$  of  $T_c$ , a point where the effects from radioactive self-heating obscure  $H_{c2}$ .

The samples prepared at Karlsruhe were available as single crystals (9) or polycrystals in the body-centered tetragonal phase that is stable at room temperature. Chemical analyses were not performed on these samples, but typical total impurities (including gases) are in the range of 50 to 500 parts per million (ppm) (7). One sample of each type was measured at low temperatures. The single crystal we selected resembled a pyramid and had a mass of  $\sim 0.5$  mg. The particularly small mass was chosen for the initial search for the  $T_c$  to minimize the self-heating. We calculate a heating rate of 1.7 mW/g from the radioactivity of <sup>231</sup>Pa, the isotope used.

The second sample we chose was polycrystalline and was cut from one of