tilus californianus shells from the Nestor Terrace [a Pleistocene terrace remnant about 5 km north of the SIO Pier (*18*)] shows δ^{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 δ^{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 sea-level variations.

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7. δ^{13}C (per mil) =
$$[(^{13}C/^{12}C)_{\text{sample}}/(^{13}C/^{12}C)_{\text{standard}} - 1] \times 1000$$
is the delta value for carbon. For oxygen, δ^{18}O is defined in an identical manner except that ^{18}O/^{16}O ratios are used.
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15. The amount of ^{13}C incorporated into precipitated calcium carbonate shows a small temperature dependence and is positively correlated (*21*). After correction is made for this small temperature effect, the average extent of δ^{13}C changes during 1975, 1976, and 1977 in the shell calcite is 0.7 per mil. This is comparable with the 0.5 per mil change indicated by the δ^{13}C reconstructions above. [The actual values of δ^{13}C in the mussel shells demonstrate that the calcite precipitates out of thermodynamic equilibrium with respect to carbon. According to Emrich *et al.* (*21*), for example, at 20°C the value of δ^{13}C for calcium carbonate precipitated from water with dissolved inorganic carbon of 0.0 per mil should be 1.85 ± 0.23 per mil. Obviously, the δ^{13}C values in the shell calcite are all much lighter than expected for equilibrium values. The deviation from equilibrium is presumed not constant and is probably amplified by increased metabolic activity which may be associated with the upwelling period.]
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23. From records of surface salinity over the same time period, we estimated the ^{18}O composition of seawater (*22*) used in the paleotemperature equation. It was necessary to correct for the nonlinear relationship between shell length and shell age; therefore, we determined the shell dimension scale by reference to a growth curve obtained by plotting maxima and minima ^{18}O values against corresponding seasonal temperature.
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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 superconducting 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 ~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 ~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 ^{231}Pa, the isotope used.

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

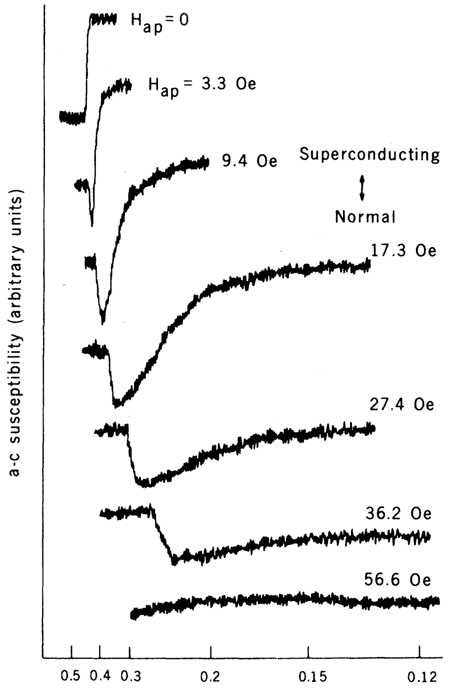

Fig. 1. Superconducting transitions of protactinium in various applied fields. These recorder traces of the a-c susceptibility have been slightly broadened by the 1.25-Oe (root-mean-square), 34-Hz modulation field.

two resistivity samples used by R. Bett for low-temperature measurements. This cut sample had a tetragonal form 0.32 mm high and 0.58 mm wide on the sides. It had a mass just under 2 mg. This shape was dictated both by the need to cool the sample through large flat faces and the desire that we would be able to calculate the internal field for critical field measurements.

The cryostats have been described previously (*10*). The first was a conventional ^{3}He a-c susceptibility cryostat in which the bare sample was simply submerged in liquid ^{3}He. The second cryostat was a ^{3}He-^{4}He dilution refrigerator in which the sample was cooled via contact with copper and vacuum grease. For the critical field measurements, a small superconducting magnet that applied a field perpendicular to the large square faces of the sample was added in the dilution refrigerator. Also, a set of Helmholtz coils was employed outside the Dewar to apply small fields in other directions (after removal of the magnetic shielding).

The single crystal was first tested in the ^{3}He cryostat. No superconductivity was seen down to a bath temperature of 0.38 K. It was clear from the following measurement that this was due to a small temperature rise of the sample above the bath probably caused by both Kapitza resistance and the poor thermal conductivity of the liquid ^{3}He. [Interestingly, this is the same cryostat used by Fowler *et al.* (*1*, *3*) after removal of the adiabatic demagnetization stage that they had added late in their measurements.] Next, the single crystal was tested in the dilution refrigerator, where a superconducting transition, centered at 0.42 ± 0.02 K, shown in Fig. 1, was detected. Its width for the central 80 percent of the transition was 0.005 K (5 mK). This is an extremely narrow transition for a moderately radioactive material. In work with americium (*10*) and with neptunium alloys (*11*), superconducting transition widths of the order of 1/3 T_c or greater were routine. In this earlier work, the broad transitions were attributed to strains and self-heating. In the present work the samples are effectively annealed by their deposition at high temperature. Hence, by eliminating strains, we find that we can observe a narrow transition in the presence of the self-heating. So it seems that strains disturb the uniform transfer of heat within the sample by their effect on thermal conductivity, as well as causing a genuine variation of T_c throughout the sample.

The 5-mK width of the transition does not mean that there is a 5-mK maximum temperature variation within the sample volume. The thermal conductivity of the protactinium cannot be that high. Rather, since the a-c susceptibility technique sees surface superconductivity as though the entire sample were superconducting, the 5-mK width indicates simply that all points on the surface are at temperatures within 5 mK of one another. It is this condition that can be disturbed by strains. This form of surface superconductivity, which is innate to radioactive materials, can of course penetrate far deeper than the coherence length or the traditional penetration depth. We have thus observed an extremely sharp superconducting transition at 0.42 K in protactinium in the presence of rather high self-heating.

The application of a magnetic field yielded results that demonstrate bulk superconductivity. Some cooling curves in a field are shown in Fig. 1. At fields $\geqslant 0.8$ Oe a differential paramagnetic effect (DPE) is exhibited (*12*). That is, the diamagnetic superconducting transition is preceded by a differential paramagnetism as the sample is cooled in a magnetic field. Our DPE showed no thermal hysteresis. Hein and Falge (*12*) have discussed this phenomenon. For the conditions under which it is observed here, they point out that the Meissner effect must dominate the effects of infinite conductivity. Furthermore, the DPE is then indicative of a bulk transition, as opposed, for example, to a filamentary superconducting network. The appearance of the DPE in protactinium is especially significant in light of all the previous uncertainty. We may ask how a seemingly bulk superconducting sample could yet be normal in the center (from the effects of heating). To restate the argument in the preceding paragraph, the surface is superconducting to a sufficient depth that no suggestion of the normal metal at the center can be detected by the experimental probe.

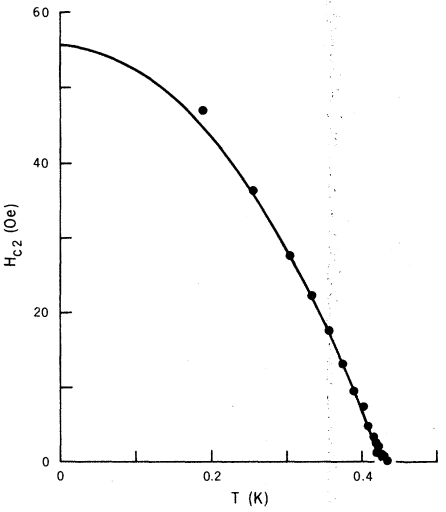

Fig. 2. Variation of H_{c2} as a function of temperature for a single crystal sample of protactinium.

Figure 1 shows that as the applied field is further increased, the height of the superconducting transition, or the "throw," decreases, and indeed the diamagnetic part of it disappears at a lower field than does the differentially paramagnetic portion; this is an extended mixed state. The curves in Fig. 1 at the higher fields do resemble a magnetic transition more than a superconducting transition, but this is a result of the measuring technique. Similar behavior was seen in americium, where the higher heating (6.2 mW/g) and the lack of a DPE led to a simpler qualitative picture (*13*). Basically, the applied field can drive more of the sample normal than is held normal by the self-heating. Then, since the magnetically normal regions have a higher thermal conductivity than when they are superconducting, the temperature distribution must shift. A truly complex interplay can occur between these two methods of driving portions of the sample normal. This situation is then aggravated by the limits of the a-c susceptibility technique, in which the normal regions can be partially shielded from detection by the superconducting regions. The result of all this is that no useful information can be gathered from the experimental curves once the throw is reduced from the low-field value. For the case of americium it was possible to detect the beginning of flux penetration into the sample (H_{c1}), but it was not possible to measure H_{c2} (*13*). We were not able to detect H_{c1} for protactinium for technical reasons. We shall, however, show later that for protactinium we can measure H_{c2} adequately down to $\sim 1/2\ T_c$ before this distortion of the cooling curves becomes severe.

The tetragonally shaped polycrystalline sample showed a superconducting transition at 0.45 ± 0.02 K, slightly higher than the first sample. While this slightly higher T_c is within experimental error of the first, there are two rather obvious possible causes for the difference. First, the early Los Alamos work (*1, 3*) showed that impurities can either raise or lower the T_c, since all of the transitions were measured for the body-centered tetragonal modification of protactinium. So perhaps our second sample is less pure. The second and more interesting cause may be that internal strains effectively pressurize the sample, thus raising T_c. A positive pressure effect was reported in (*3*), and this observation is probably correct because protactinium should somewhat resemble uranium, which has a dramatic pressure effect (*14*). We note that no matter how well annealed a sample may be, if it is noncubic and polycrystalline it will be significantly strained by thermal contraction after cooling to low temperatures. Thus, our measurements on the polycrystalline protactinium sample were obviously made on a strained sample.

The applied field curves for this second sample were similar to those in Fig. 1. However, the signal-to-noise ratio was improved since the sample was larger. Also, the DPE did not appear until the applied field was ~ 10 Oe because of defects from the strains that should inhibit the Meissner effect somewhat. As expected (*12*), no DPE was observed in the curves taken with the Helmholtz coils since the signal coils were then oriented perpendicular to the applied field.

Figure 2 shows the critical field points for the first sample where we have taken the T_c's as the onsets of the transitions in the applied fields. The polycrystalline sample had a slightly higher H_{c2} but the curves became difficult to interpret at a higher temperature than for the single crystal. That is, the data was more like that of americium (*13*). For the highest-temperature points in Fig. 2 there is a small departure from a proper critical field dependence. This feature is not uncommon and is usually considered to be due to compositional variations (*15*). We feel that, once again, the self-heating and strains can interact to simulate such compositional variations in protactinium. As done in (*15*), we will exclude such points from further consideration.

The curve in Fig. 2 is a least-squares fit of the data to

$$H_{c2}(T)/H_{c2}(0) = 1 - T^2/T_c^2 \qquad (1)$$

Because of the rather limited temperature range of useful data, there is little reason to consider a fit of the data to a more sophisticated function or to consider the deviations of the data from a Bardeen-Cooper-Schrieffer curve. Such considerations involve departures from Eq. 1 of a few percent—of the same magnitude as the possible errors due to sample heating. A few self-consistent parameters based on the fit are

$$T_c = 0.430\ \mathrm{K}$$

$$H_{c2}(0) = 56\ \mathrm{Oe}$$

$$(dH_{c2}/dT)_{T_c} = -260\ \mathrm{Oe/K}$$

We feel that until measurements such as resistivity and heat capacity are made on high-purity protactinium, further pursuit of superconducting parameters is too speculative. At best, we can say that the Ginsburg-Landau parameter κ is of the order of unity, and conclude that protactinium is type II.

We have found the superconducting properties of protactinium to be in the appropriate place between those of thorium [T_c = 1.4 K (*5*)] and those of uranium [T_c < 0.1 K (*5, 14*)]. There is no longer any doubt that a smooth variation of superconducting properties in the early actinides can be caused by the increasing *f* character in the energy bands as the early actinide elements slowly acquire their electrons (*16*). It then seems quite likely that many of the interesting properties of uranium (*14*) that are not seen in thorium may be observed to some extent in protactinium.

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A Nodule-Specific Plant Protein (Nodulin-35) from Soybean

Abstract. *Nodulin-35, a 35,000-molecular-weight protein, is present in soybean root nodules developed by different strains of* Rhizobium japonicum, *irrespective of their effectiveness in fixing atmospheric nitrogen. This protein is not detected in uninfected plants and bacteroids or in free-living* Rhizobium *and appears to be synthesized by the plant during the formation of root nodules.*

Development of root-nodule symbiosis between legumes and *Rhizobium* species, which results in effective fixation of atmospheric nitrogen, requires the specific expression of both host (*1*) and *Rhizobium* (*2*) genes. Through classical genetic experiments, several plant genes have been linked to effective nodulation, but, with the exception of leghemoglobin (*3*), no other plant gene product that is obligatory for the development of symbiosis has yet been identified. We report here the presence in soybean root nodules of a 35,000-mo-