Evidence from Cd/Ca ratios in foraminifera for greater upwelling off California 4,000 years ago

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UPWELLING of nutrient-rich Pacific deep water along the North American west coast is ultimately driven by the temperature difference between air masses over land and over the ocean. The intensity of upwelling, and biological production in the region, could therefore be affected by anthropogenic climate change. Examination of the geological record is one way to study the link between climate and upwelling. Because Pacific deep water is enriched in cadmium, dissolved cadmium concentrations in coastal water off central California reflect the intensity of upwelling. By demonstrating that the Cd/Ca ratio in the shell of a benthic foraminifer, *Elphidiella hannai*, is proportional to the Cd concentration in coastal water, we show here that foraminiferal Cd/Ca ratios can be used to detect past changes in mean upwelling intensity. Examination of a sediment core from the mouth of San Francisco Bay reveals that foraminiferal Cd/Ca decreased by about 30% from 4,000 years ago to the present, probably because of a reduction in coastal upwelling. This observation is consistent with predictions of atmospheric general circulation models that northwesterly winds, which drive upwelling, became weaker over this period as summer insolation of the Northern Hemisphere decreased.

Strong winds blow south along the north American west coast during spring and summer because air masses over land become warmer than over the ocean[1]. The associated advection of surface water offshore is compensated by upwelling of Pacific deep water along the coasts of California, Oregon and Mexico. The composition of coastal water was strongly affected by upwelling at Pillar Point and Moss Beach in 1990 and 1991 (Fig. 1). Salinity, phosphate and Cd concentrations rose rapidly as northwesterly winds became stronger in April (Fig. 2). Maxima in May correspond to enrichments of these constituents observed in Pacific deep water 50 km offshore at a depth of ~300 m (ref. 2). The parallel increase of all three tracers also indicates that input of Cd and phosphate by shelf sediment diagenesis was not significant off central California. Salinity, phosphate and Cd returned to their previous values in late summer as upwelling winds became weaker (Fig. 2). The correlation between monthly averaged dissolved Cd concentrations and an upwelling index at 36° N calculated from the monthly averaged atmospheric pressure field for this period (ref. 3 and D. M. Husby, personal communication) was highly significant: the relation $C_{Cd} = 0.25(\pm0.03) + 1.7(\pm0.2) \times 10^{-3} \times U$, where C_{Cd} is concentration in nmol kg^{-1} and U is upwelling in $m^3 s^{-1}$ per 100 m coastline, gives $R^2 = 0.84$, $n = 12$. The mean dissolved Cd concentration during 1990–1991 was 0.42 nmol kg^{-1}, and the mean upwelling index for this period was very close to the long-term average value since compilation started in 1946 (ref. 3).

A relation between Cd/Ca ratios in biogenic calcium carbonate and dissolved Cd concentrations in sea water has been shown previously for deep-ocean benthic foraminifera[4,5] and scleractinian coral from the Galapagos Islands[6]. *Elphidiella hannai* is a benthic foraminifer that lives in coastal water shallower than 50 m along the north American west coast[7-9]. The composition of its calcitic shell also reflects Cd concentrations in ambient sea water (Fig. 3). We show this with samples collected from surface sediments at three locations. The first site is Pillar Point (Fig. 1) where the average Cd/Ca ratio of shells collected in rocky pools at low tide is 228 ± 13 nmol per mol ($n = 25$). The distribution coefficient for *E. hannai* is: $K_d = (Cd/Ca)_{shell}/(Cd/Ca)_{sea\ water} = 5.3 \pm 0.3$ (average Cd/Ca of sea water at Pillar Point is 43 nmol per mol). The second site is Richardson Bay, a protected inlet near the mouth of San Francisco Bay (Fig. 1). Here, the mean Cd/Ca ratio for *E. hannai* in surface sediments (362 ± 41 nmol per mol, $n = 6$) reflects an anthropogenic Cd enrichment in the water column throughout the year of ~0.2 nmol kg^{-1} relative to coastal water, because of anthropogenic inputs within San Francisco Bay (ref. 10, and unpublished data). The third calibration point is less well constrained. A single Cd/Ca determination (132 nmol per mol) is available for *E. hannai* from surface sediment off the Washing-

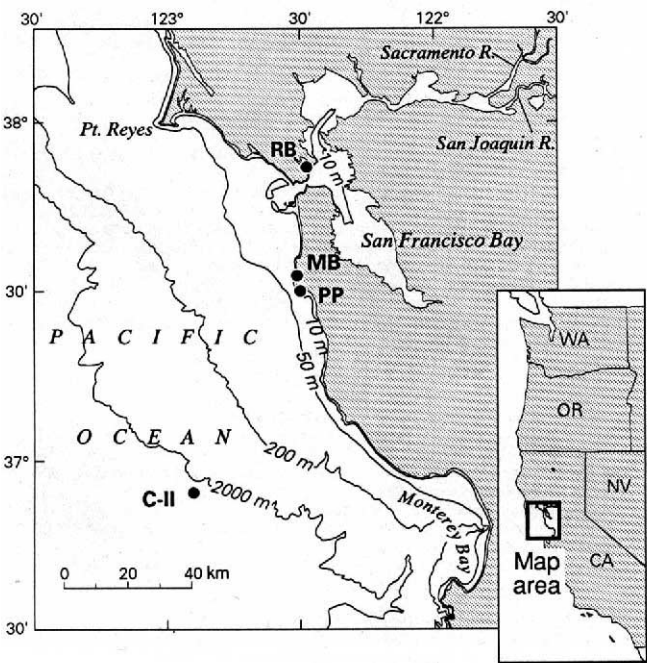

FIG. 1 Location of the sediment section in Richardson Bay (RB) and the near-shore water sampling sites at Moss Beach (MB) and Pillar Point (PP). A vertical profile collected by K. W. Bruland in July 1978 (ref. 2; location C-II in the map) shows that concentrations of upwelling tracers increase roughly linearly from the surface to a depth of 0.5 km within the California Current: 33.3 to 34.2‰ for salinity, 0.6 to 3 μmol kg^{-1} for phosphate and 0.2 to 1.0 nmol kg^{-1} for dissolved Cd. The composition of near-shore water sampled at the surface in May–June 1990 at PP and MB suggests that it originated from ~300 m depth at C-II.

ton coast where, according to wind patterns, upwelling is considerably weaker than off central California[1,3].

Our reconstruction of past upwelling off central California is based on a composite sediment section from Richardson Bay. We collected a 2.5-m-long gravity core in 6 m water depth and retrieved nine 0.5-m core sections nearby by drilling up to 11 m into the sediment (Fig. 4). Radiocarbon ages of five mollusc shell fragments measured by accelerator mass spectrometry (AMS)[11,12] indicate that the sedimentation rate was 0.26 ± 0.01 cm yr^{-1} over the length of the record ($R^2 = 0.989$). High Cd/Ca ratios in foraminifera from the top 0.6 m of the gravity core coincide with the penetration into the sediment of ^{137}Cs produced by atmospheric bomb testing. These elevated values probably reflect an anthropogenic Cd/Ca signal related to discharges into San Francisco Bay over the past century.

The Cd/Ca ratio decreases from 374 ± 16 ($n = 5$) nmol per mol at 11 m depth in the sediment core to a mean pre-industrialization foraminiferal ratio of 278 ± 22 nmol per mol ($n = 75$) between 1 and 2.5 m depth (Fig. 4). We believe that this reflects a change in the composition of coastal water outside San Francisco Bay. It seems that Richardson Bay was not strongly affected by local Cd inputs before it was disturbed by man. Conservative mixing of river water (Cd, 0.1×10^{-9} mol kg^{-1}; Ca, 4×10^{-4} mol kg^{-1}) with coastal water under present upwelling conditions (Cd, 0.42×10^{-9} mol kg^{-1}; Ca, 9.8×10^{-3} mol kg^{-1}) would predict a foraminiferal Cd/Ca ratio of ~240 nmol kg^{-1} for Richardson Bay before anthropogenic disturbance. This value is within the range observed in the gravity core between 1 and 2.5 m depth (Fig. 4). The comparison also shows that differences between the estuarine and the coastal environment (for example, salinity or sediment type) have little effect on the relation between dissolved and foraminiferal Cd/Ca.

A drop in San Francisco Bay salinity linked to higher discharge from the Sacramento and the San Joaquin rivers (Fig. 1) could not explain the elevated Cd/Ca ratio of 4,000-year-old shells. Ratios of $^{87}Sr/^{86}Sr$ measured in mollusc shells from our core constrain past salinities in Richardson Bay to a range of 20–30‰ over the past 4,000 years (ref. 13 and B. L. Ingram, personal communication). To increase dissolved Cd/Ca enough to cause the observed change in foraminiferal Cd/Ca at 11 m depth, river water would have to dilute the coastal water to a salinity of 7‰, well below the salinity range tolerated by *E. hannai*. Moreover, pollen data suggest that the effective moisture level in western north America at the time was comparable to or lower than today[14–16].

The elevated foraminiferal Cd/Ca ratios in Richardson Bay 4,000 years ago suggest that dissolved Cd concentrations in adjacent coastal water averaged 0.57 nmol kg^{-1}. Recorded fluctuations in yearly averaged upwelling show that this is a physically reasonable value. Coastal upwelling was particularly weak in 1950 and strong in 1955 (ref. 3). From the relation between monthly averaged upwelling and dissolved Cd defined earlier, we would predict mean Cd concentrations of 0.37 and 0.52 nmol kg^{-1}, respectively, for these years. It therefore seems

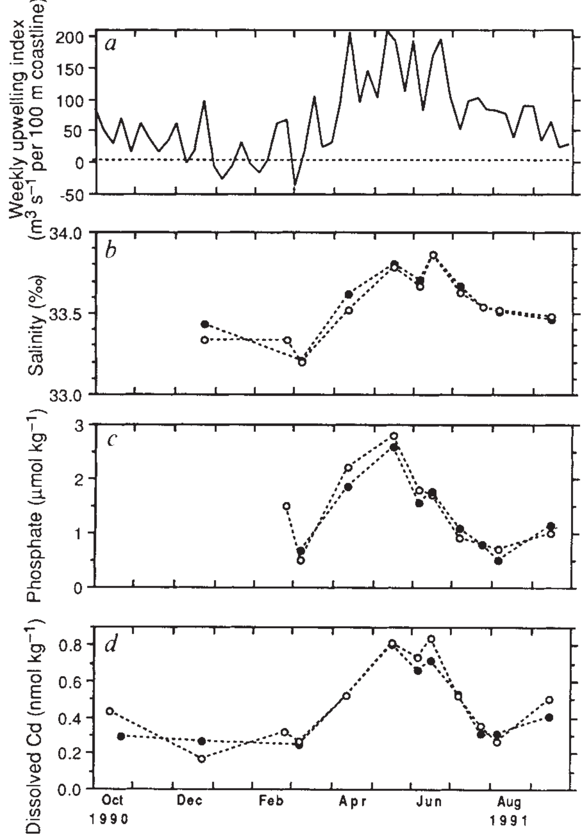

FIG. 2 Time series for weekly upwelling index, salinity, phosphate and dissolved Cd concentrations in near-shore sea water collected between October 1990 and September 1991. Open symbols, Moss Beach; filled symbols, Pillar Point. The upwelling index was calculated at NOAA/Pacific Environmental Fisheries Group (Monterey, California) from the weekly averaged atmospheric pressure distribution at 36° N (ref. 27, and D. M. Husby, personal communication). Note that this measure of upwelling is different from the index discussed in the text, which was based on the monthly averaged atmospheric pressure field[3]. Coastal water samples were collected from shore and analysed following procedures described in refs 28 and 29. Dissolved Cd, Cu, Ni and Zn concentrations measured at Pillar Point and Moss Beach show that there is little interaction between the water column and shelf sediments for these elements. Mixing with San Francisco Bay water has a negligible effect on phosphate and Cd at Pillar Point and Moss Beach[29].

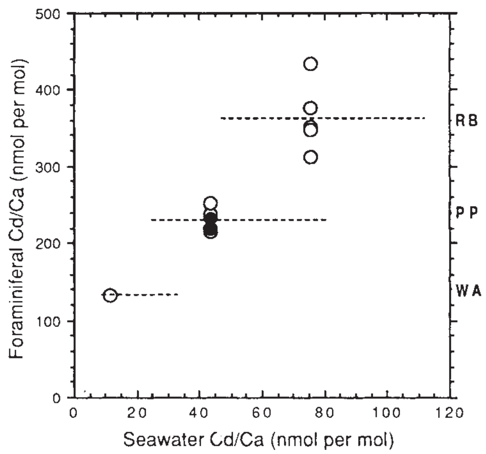

FIG. 3 Calibration of Cd/Ca response in *E. hannai* to ambient dissolved Cd concentrations. Open symbols show each foraminiferal measurement as a function of yearly mean dissolved Cd/Ca at Richardson Bay and Pillar Point. Filled symbols show the composition of Rose Bengal stained shells[30] collected in July 1991 and January 1992 at Pillar Point; during the preceding three-month periods the average dissolved Cd concentrations were 0.7 and 0.4 nmol kg^{-1}, respectively. Despite the considerable difference in coastal water composition, the Cd/Ca ratios of stained shells in July and in January are indistinguishable: 223 ± 8 ($n = 7$) and 222 ± 9 ($n = 4$). From this it seems that possible interactions between the life cycle of *E. hannai* and seasonal variations in dissolved Cd in coastal water do not bias the Cd/Ca ratio in the batches of 10–15 shells required for each determination. There was also no difference between the composition of unstained juvenile (<0.5 mm) and mature (>0.65 mm) foraminifera shells from Pillar Point. We cleaned and analysed shells following a slightly modified version of the procedure described in ref. 31. The seasonal range in measured dissolved Cd/Ca is shown by a horizontal dashed line at RB and PP. For the Washington coast sample, foraminiferal Cd/Ca is shown as a function of single available dissolved Cd measurement for the region[32]. A possible underestimate of mean dissolved Cd/Ca for this location is suggested by the estimated seasonal range obtained from the relation in the text and the mean monthly upwelling data for the Washington coast[3].

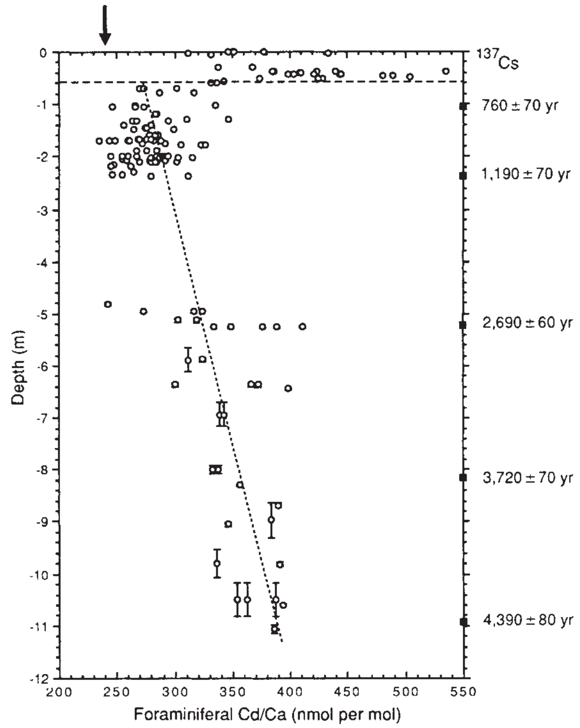

FIG. 4 Composite record of Cd/Ca in *E. hannai* for San Francisco Bay extending to 4,000 years before present. The predicted composition of pre-anthropogenic shells from Richardson Bay is indicated by the vertical arrow. This calculation assumed modern upwelling intensity, conservative mixing and a salinity of 27‰ before river flow control and diversion for agriculture[33] (~6.5‰ lower than the mean salinity of the coastal water endmember). Symbols above the horizontal dashed line are within the zone of penetration of bomb-produced ^{137}Cs and reflect anthropogenic discharges into San Francisco Bay over the past century. The depth interval covered by shells for each Cd/Ca determination is smaller than symbol size unless indicated by vertical error bar. The dotted line shows a linear regression of Cd/Ca as a function of depth in the 1 to 11 m interval: Cd/Ca = 256(±13) + 12.3(±0.9) × *d*, where Cd/Ca is in nmol per mol, and *d* is depth in metres, $R^2 = 0.64$, $n = 110$. The provenance and age of mollusc shells, dated by radiocarbon accelerator mass spectrometry, is also indicated. Extrapolation of radiocarbon years to the surface yields an age of 400(±140) years, slightly lower than the apparent pre-bomb age of northeast Pacific surface waters[34]. Radiocarbon ages of 800 ± 90 and 1,070 ± 70 years for two mollusc shell fragments from the top interval of the drilled core (4.1 to 4.6 m depth) indicate that sediment from a shallower depth was not effectively blown out of the hole casing before the first drilled core section was taken. For this reason, we have omitted this section from the discussion and the Cd/Ca data (299 ± 16 nmol per mol, $n = 8$) from the figure.

that yearly averaged coastal upwelling 4,000 years ago was consistently as high as the maximum value recorded over the past four decades and has been decreasing since then. Temperature anomalies in coastal water are synchronous along the north American west coast, indicating that such variations in upwelling are not just a local feature[17]. Positive temperature anomalies, in particular, are associated with El Niño years[18]. We cannot exclude the possibility that a deepening of the Cd gradient offshore[2] unrelated to coastal upwelling might have contributed to decreasing Cd concentrations in coastal water over the past 4,000 years, but this is not a requirement because salinity (and by inference Cd) profiles 95 km offshore from San Francisco Bay were virtually identical below 300 m depth in 1950 and 1955 (refs 19, 20).

Summer insolation of the Northern Hemisphere has decreased gradually by ~8% from a maximum 9,000 years ago, because of variations in the Earth's orbit around the Sun. Calculations from general circulation models indicate that temperatures over north America decreased by 2-4 °C, and that the atmospheric pressure gradient between land and sea, which causes upwelling winds during summer, was reduced[14]. A similar mechanism has been invoked to explain decreasing upwelling in the western Arabian Sea over the past 9,000 years as recorded by the faunal distribution of planktonic foraminifera[21]. Our data suggest that upwelling off western north America also responded to the modest decrease in summer insolation of 3% over the past 4,000 years. A resulting reduction in the biological productivity of surface water and, consequently, a decrease in oxygen consumption by decaying organic matter at depth, may explain why deposition of laminated sediment along the central California continental slope ended ~5,000 years ago[22]. In the Gulf of California, variations in the oxygen isotopic composition of diatoms[23] and the sediment radiocarbon record[24] were also attributed to a reduction in upwelling. Greenhouse warming predicted for the next century, comparable in magnitude to summer warming 9,000 years ago[14], would result in a greater land-to-sea atmospheric pressure gradient off California because the heat capacity of land is lower than that of the ocean[25]. Although the forcing of greenhouse warming would be year-round, rather than seasonal as was the case 9,000 years ago, the sensitivity of upwelling to changes in insolation in the past suggests that the intensity of coastal upwelling may increase in the future[26]. □

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