

F-PCB

thick, and oriented parallel to (010) was prepared from the olivine crystal (composition determined by microprobe analysis). Examination of the sample by optical microscopy before the experiment revealed no inclusions or heterogeneities other than subboundaries, in agreement with the observations of S. H. Kirby and M. W. Wegner [*Trans. Am. Geophys. Union* 54, 452 (1973)] and M. W. Wegner and J. M. Christie [*Contrib. Mineral. Petrol.* 43, 195 (1971)] on olivine from the same locality. The disk was encased in a stainless steel container which included "momentum trap" plates [D. G. Doran and R. K. Linde, *Solid State Phys.* 19, 262 (1966)], and the container was impacted with a 16-mm. tungsten flyer-plate launched from a high-performance propellant gun.

9. We calculated the peak pressure, using standard impedance match techniques for multiple shock reverberations [J. M. Walsh and R. H. Christian, *Phys. Rev.* 97, 1544 (1955); L. V. Al'tshuler, *Sov. Phys. Usp.* 8, 59 (1965); R. V. Gibbons and T. J. Ahrens, *J. Geophys. Res.* 76, 5489 (1971)] based on the Hugoniot equation-of-state data (11) for tungsten and stainless steel, and it is accurate to within about 5 percent. The time at peak pressure is based on a calculation of the type given by G. R. Fowles [*J. Appl. Phys.* 31, 655 (1960)] and by Al'tshuler (see above).
10. Carried out with the 1-Mev electron microscope at the U.S. Steel Research Laboratory, Monroeville, Pa., and at 200 kv at the U.S. Geological Survey, Reston, Va.
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12. We made the simplifying assumption that the temperature in the sample which has attained peak pressure by multiple reverberations is approximately the same as the temperature of the container achieved by a single shock to peak pressure.
13. T. J. Ahrens, F. D. Tsay, D. H. Live, *Geochim. Cosmochim. Acta* (Suppl. 7) (1976), p. 1143. This is a maximum estimate since it is for the attainment of peak pressure by a single shock [see L. V. Al'tshuler (9)].
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17. E. C. T. Chao, in *Researches in Geochemistry*, P. Abelson, Ed. (Wiley, New York, 1967), vol. 2, p. 204. Note that the terms "diaplectic" and "equivalent terms".
18. T. J. Ahrens, J. H. Lower, P. L. Lagus, *J. Geophys. Res.* 76, 518 (1971); T. J. Ahrens and C. F. Petersen, in *The Application of Modern Physics to the Earth and Planetary Interiors*, S. K. Runcorn, Ed. (Wiley-Interscience, New York, 1969), p. 449. The Hugoniot data are consistent with results from static, high-pressure experiments [L. Liu, *Nature (London)* 262, 770 (1976); *Geophys. Res. Lett.* 2, 417 (1975); *Nature (London)* 258, 510 (1975)] which indicate major, reconstructive transformations at these pressures in magnesium olivine, for example, to (Mg,Fe)SiO₃ perovskite + (Mg,Fe)O rock salt phases [see R. Jeanloz and T. J. Ahrens, in *High Pressure Research: Applications to Geophysics*, M. Manghnani and S. Akimoto, Eds. (Academic Press, New York, 1977), p. 439]. Direct evidence for similar major, reconstructive transformations and reactions in nesosilicates under shock can be found in L. Liu [*Earth Planet. Sci. Lett.* 26, 425 (1975)], T. J. Ahrens and E. K. Graham [*ibid.* 14, 87 (1972)], and H. Schneider and U. Hornemann [*Naturwissenschaften* 62, 296 (1975)].
19. See B. J. Skinner and J. J. Fahey, *J. Geophys. Res.* 68, 5595 (1963), and references therein.
20. L. Liu and A. E. Ringwood, *Earth Planet. Sci. Lett.* 28, 209 (1975); A. E. Ringwood and A. Major, *ibid.* 12, 411 (1971). In these experiments, CaSiO₃ perovskite formed (and identified) at high pressure could only be quenched to a glass.
21. The free energy of a crystal is increased by an amount of the order of $1/2 \mu b^2$ per atomic length of dislocation (where μ is the shear modulus and b is the average length of the Burgers vectors of the dislocations). Taking the dislocation density to be about 10^{11} cm^{-2} or more in the tangles, $b \sim 5 \text{ \AA}$, $\mu = 80 \times 10^9 \text{ dynes/cm}^2$, and assuming that a typical difference in free energy between silicate crystals and their glasses is about 5 kilojoules per mole, it is possible for the glass to have a lower free energy than the dislocated crystal. See also R. M. J. Cotterill, E. J. Jensen,

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Polychlorinated Biphenyls: Penetration into the Deep Ocean by Zooplankton Fecal Pellet Transport

Abstract. *High concentrations of polychlorinated biphenyls (PCB's) were found in fecal pellets from natural populations of euphausiids collected in the Ligurian Sea. Since biogenic particulate products, especially fecal pellets, are known to sink rapidly and intact to the ocean bottom, the transport of PCB's by such sinking particles could be an important mechanism which contributes to the penetration of PCB's into the deep sea.*

The rate of vertical mixing in the ocean (1) is too slow to account for the quantities of polychlorinated biphenyls (PCB's) found in Atlantic and Mediterranean abyssal sediments (2) if one assumes that they penetrate into the deep ocean only in the dissolved state. An alternative explanation is that PCB's are carried to the sediments by rapidly sinking particles. Several investigators have hypothesized that sinking biogenic material such as zooplankton fecal pellets and molts may accelerate the downward vertical transport of certain metals and radionuclides (3). Analytical work has shown that both euphausiid fecal pellets and molts contain significant quantities of trace elements (4, 5) and radionuclides (6); therefore, the sinking of these particulate products, especially fecal pellets, is strongly implicated in the removal of many such elements from surface waters. Experimentally determined sinking rates of several hundred meters per day (7-9) for zooplankton fecal pellets and molts are compatible with the hypothesis that these products could act as effective conveyors of surface-introduced pollutants into the deep sea. Recent field studies (9, 10) have shown conclusively that zooplankton fecal pellets not only penetrate to great depth (2000 to 4000 m) intact but also in large numbers—650 pellets per square meter per day. We have found that freshly released euphausiid fecal pellets collected from natural populations contain relatively high concentrations of PCB's, and we propose that such biogenic particles make a significant contribution to the vertical transport of PCB's in the ocean.

The euphausiid *Meganyctiphanes norvegica* was examined since it is an abundant member of the zooplankton com-

munity in the western Mediterranean and North Atlantic and sufficient biological data on the production rate of particulate products have been compiled for this species (4, 11). During 1974-1975 *M. norvegica* and the microplankton which serve as its food were collected at a station 5 km off Villefranche-sur-Mer, France. We fished for euphausiids and microplankton at night with an Isaacs-Kidd mid-water trawl and a 1-m plankton net (76- μm mesh aperture), respectively, by making several short oblique tows between 100 m and the surface. All microplankton samples were carefully examined and found to be free from adhering tar, oil, and paint chips.

Glass and metal implements cleaned in advance were used to sort euphausiids from other species in order to avoid contaminating the samples. Euphausiid fecal pellets and molts were collected on board and later in the laboratory by methods described elsewhere (11, 12) with the exception that all containers were either glass or metal. Although extreme care was taken to avoid unnecessary contact between the samples and plastic materials, some contact inevitably occurred between the organisms and the nylon plankton nets. Cross-contamination of PCB's between plankton and nylon nets can occur (13); however, extraction of the nets used in our study indicated that PCB contamination from this material was negligible.

Samples were analyzed by standard procedures (14) with modifications to adapt to small sample quantities. All samples were frozen, lyophilized, and pulverized in preparation for extraction. The relatively abundant samples, such as microplankton (0.1 to 1.5 g dry) and euphausiids (1 to 8 g dry), were subjected

to extraction with hexane in a Soxhlet extractor (8 hours at four cycles per hour). We batch-extracted the less abundant samples, fecal pellets (15 to 90 mg dry) and molts (50 to 150 mg dry), by shaking with hexane in sealed, conical-bottomed, centrifuge tubes. We removed the extracts by first centrifuging to settle the sample residue and then transferring the supernatant solvent with the aid of a Pasteur pipette. Each sample was extracted ten times. Interfering substances were eliminated from the hexane extracts by chromatography on Florisil and by treatment with concentrated H_2SO_4 . It was not necessary to remove fatty substances by acetonitrile-hexane partitioning. Hexane extracts were then further concentrated to a convenient volume (usually 0.2 to 0.5 ml) in a Kuderna-Danish concentrator and analyzed by gas chromatography. Precautions were employed to ensure that contamination from chemicals, apparatus, and glassware was negligible (15). During the November 1974 collection, a surface water sample was also collected and analyzed for PCB's according to the method of Harvey and Steinhauer (16). The PCB concentration (DP-5) was 2.5 ng/liter, a value that is considered representative for these waters (17).

Concentrations of PCB's in euphausiid bodies, molts (18), and fecal pellets as well as in the microplankton upon which they feed are given in Table 1. Fecal pellets contained the highest concentrations of PCB's in all samples examined. The PCB concentration in feces (wet weight) from the November 1974 collection was 1.5×10^6 greater than that present in the surrounding water. Furthermore, the PCB concentrations in feces (dry weight) ranged from 3.5 to 21 times higher than those in the food organisms which formed the feces. A similar concentrating process has been found to occur for several trace elements and radionuclides in the same species (4-6).

Recently, estimates have been made of PCB deposition rates into sediments in the northwestern Mediterranean region (19). These estimates are based on sediment concentrations in a series of cores taken at a depth of 400 m off the coast of Nice, France. Computed values range from approximately 80 to 125 μg of PCB (DP-5) per square meter per year over a period of 15 to 20 years.

It is conceivable that PCB's could be transported to sediments by way of fecal pellets, molts, eggs, and carcasses released from an overlying euphausiid population. Molting, egg laying, and death (carcass production) in euphausiids are

Table 1. Polychlorinated biphenyls (15) in euphausiids (*Meganyctiphanes norvegica*), their particulate products, and microplankton which serve as the euphausiids' food. Water sampled during the November 1974 collection contained 2.5 ng of PCB per liter.

Sample	Ratio of wet weight to dry weight	DP-5 [$\mu g/kg$ (dry weight)]
November 1974		
Whole animal	4.7	620
Molts	4.6	1,400
Fecal pellets	4.4	16,000
Microplankton*	10.7	4,500
January 1975		
Whole animal†		260, 290
Molts		170
Fecal pellets		4,800
March 1975		
Whole animal		38
Molts		Not detectable
Fecal pellets†		11,000; 38,000
Microplankton*		1,800

*Principally copepods, phytoplankton, and detritus. †Two separate samples.

discontinuous processes compared to defecation. Hence, the production rates for these products are much lower than that for fecal pellets (4, 8). This lower production rate and the fact that PCB concentrations in molts and whole euphausiids appear to be much lower than corresponding concentrations in feces indicate that defecation should be far more effective in removing PCB's from surface waters than the discontinuous processes. Accordingly, we have attempted to calculate roughly how much of the total vertical flux of PCB's into sediments in this area could be attributed to sinking fecal pellets from an overlying population of *M. norvegica*. Production rates of fecal pellets for this euphausiid have been found to range between approximately 1.8 and 5.1 percent of the organism's dry body weight per day, depending on the available food supply (4). From the data of Franqueville (20), we have computed that the annual average biomass of *M. norvegica* in the Ligurian Sea is approximately 0.17 mg (dry weight) per cubic meter. Coupling these data with the mean fecal pellet PCB concentration [$\approx 17,000 \mu g/kg$ (dry weight)] for the three sampling periods shown in Table 1 leads to values for fecal-released PCB's ranging from 5.2×10^{-5} to $15 \times 10^{-5} \mu g m^{-3} day^{-1}$. If these data are integrated over the photic zone (top 75 m) where the majority of the fecal pellets are released during the time the euphausiids are actively feeding, we obtain delivery rates of PCB's to sediments of 1.4 to 4.1 $\mu g m^{-2} year^{-1}$, which are between one and two orders of magnitude lower than estimates based on deposition by all

routes. However, measurements of zooplankton biomass (20, 21) made in the same region indicate that *M. norvegica* comprises only 1 to 5 percent of the total zooplankton biomass. If PCB concentrations in feces and fecal pellet production rates measured in *M. norvegica* are typical of those for other zooplankton species (notably copepods, which probably form the bulk of the zooplankton biomass), the delivery rates arising from zooplankton defecation will approach those based on PCB concentrations in the sediments. Our calculations are admittedly crude because of the limited data available and are subject to many assumptions that may not be entirely valid; nevertheless, the close similarity between PCB flux rates derived from fecal pellet data and those based on sediment values suggests that sinking zooplankton fecal pellets contribute significantly to the downward vertical transport of surface-introduced PCB compounds.

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