Bishop Tuff, pyroxenes, magnetite, and biotite, all have rather similarly shaped light REE–enriched partition coefficient patterns with typical values of 5 to 20 for cerium and with Ce/Yb ratios commonly of 3 to 5. Bulk distribution coefficients for the high-temperature, allanite-free sample are about 0.9 for cerium and 0.1 for the heavy REE (*6, 10*). Michael (*6*) and Mittlefehldt and Miller (*7*) have pointed out that the addition of only trace quantities of allanite to the mineral assemblage will result in bulk distribution coefficients greater than 1 for cerium and neodymium and consequently depletion of the light REE with crystal fractionation.

If one determines bulk distribution coefficients of pumice samples by the "groundmass-mode" method (*10*), one avoids uncertainties encountered by Michael (*6*), arising from estimating the amounts of accessory minerals, estimating mineral/melt partition coefficients, using average compositions, and assuming that whole-rock (nonpumice) compositions represent the compositions of liquids. Using "groundmass-mode" bulk distribution coefficients and the Rayleigh equation, I find that the REE pattern of the medium-temperature pumice can be modeled by subtraction of 23 percent crystals (that is, 0.77 weight-fraction liquid remaining) from the parent high-temperature pumice. The low-temperature pumice can be modeled by subtraction of 42 percent crystals (that is, 0.58 weight-fraction liquid remaining) from the medium-temperature pumice. Thus the REE calculations suggest about 55 percent fractionation (that is, 0.45 weight-fraction liquid remaining) is required to derive the low-temperature pumice from a magma similar in composition to the high-temperature sample. The strontium isotopic diagram for the Bishop Tuff presented by Hildreth (*3*) requires some assimilation to accompany fractional crystallization. The REE were probably less sensitive to assimilation than strontium because there was less of a concentration difference between the magma and the wall rock for the REE than for strontium.

The major conclusion from these analyses is that the Bishop Tuff "early/late" REE trend reported by Hildreth mimics the groundmass/whole-rock relations of allanite-bearing pumice; that is, more differentiated rocks differ from less differentiated rocks as the groundmass differs from the whole rock in a single sample. Thus the trend reported by Hildreth is precisely that expected to result from crystal fractionation, and there is no need to invoke liquid-state differentiation to explain the REE geochemistry of the Bishop Tuff.

Hildreth (*1*) emphasized that the chemical gradients in the Bishop Tuff magma chamber were established before crystallization of the phenocrysts found in the rocks. The results of this study indicate that the REE gradients in the magma chamber could be the result of fractionation of phases similar in mineralogy and in relative proportion to those found in the rocks. Hildreth has convincingly demonstrated that crystals neither settled nor floated in the magmas chamber. The mechanism of crystal fractionation remains speculative; it may, however, involve precipitation or accretion, or both, of crystals onto the chamber walls.

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References and Notes

1. W. Hildreth, *Geol. Soc. Am. Spec. Pap. 180* (1979), pp. 43–75.
2. _____, thesis, University of California, Berkeley (1977).
3. _____, *J. Geophys. Res.* **86**, 10153 (1981).
4. G. Mahood and W. Hildreth, *Geochim. Cosmochim. Acta* **47**, 11 (1983).
5. C. R. Bacon, R. A. Macdonald, R. L. Smith, P. A. Baedecker, *J. Geophys. Res.* **86**, 10223 (1981); H. R. Crecraft, W. P. Nash, S. H. Evans, *ibid.*, p. 10303; A. Ludington, *ibid.*, p. 10423.
6. P. J. Michael, *Geology* **11**, 31 (1983).
7. D. A. Mittlefehldt and C. F. Miller, *Geochim. Cosmochim. Acta* **47**, 109 (1983).
8. C. E. Lesher, D. Walker, P. Candela, J. F. Hays, *Geol. Soc. Am. Abstr. Programs* **14**, 545 (1982); C. E. Lesher and D. Walker, *Eos Trans. Am. Geophys. Union* **64**, 883 (1983).
9. The high-temperature sample (HB77) was collected from Hildreth's (*2*) locality B77. Likewise, the low-temperature (HB52) and medium-temperature (HB133) samples are from Hildreth's localities B52 and B133, respectively. The pumice blocks came from nonwelded or slightly welded deposits. Sample HB77 is from a single block 45 cm in diameter, but samples HB133 and HB52 are composites, each consisting of three to five identical appearing smaller pumice blocks collected from within a few meters of one another. Hematite-stained alteration rinds were cleaned from the specimens, and only the fresh white interiors were analyzed. After crushing, the samples were split. One aliquot was set aside for the whole-rock analysis, and the other was used for separation of groundmass glass. The glass was concentrated with the use of heavy liquids and a Franz isodynamic separator, and then it was hand-picked free of impurities under a microscope.
10. Bulk distribution coefficients can be calculated by two methods. In the "mineral-mode" method,

$$D_a = X_1 * K_1 + X_2 * K_2 + \ldots$$

where D_a is the bulk distribution coefficient of element a, X_1 is the weight fraction of phase 1 in the mineral assemblage, and K_1 is the crystal/melt partition coefficient of element a for phase 1. Alternately, D_a can be calculated by the "groundmass-mode" method where

$$D_a = \frac{C_i}{C_l(1 - F')} - \frac{F'}{(1 - F')}$$

and F' is the weight fraction of liquid remaining (that is, weight-fraction groundmass in the mode), C_i is the concentration of element a in the original melt (in the whole rock), and C_l is the concentration of element a in the fractionated liquid (in the groundmass). Because there is considerable uncertainty in estimates of the modal amounts of accessory minerals, bulk distribution coefficients are calculated with the greatest confidence by the "groundmass-mode" method. The high- and low-temperature samples contain about 0.79 and 0.83 weight-fraction groundmass glass, respectively. These data, when combined with those from Table 1, yield $D_{Ce} = 0.88$, $D_{Nd} = 0.78$, $D_{Sm} = 0.52$, $D_{Eu} = 3.0$, $D_{Gd} = 0.31$, $D_{Dy} = 0.10$, $D_{Er} = 0.19$, and $D_{Yb} = 0.12$ for the high-temperature sample and $D_{Ce} = 1.86$, $D_{Nd} = 1.39$, $D_{Sm} = 0.71$, $D_{Eu} = 3.4$, $D_{Gd} = 0.31$, $D_{Dy} = 0.11$, $D_{Er} = 0.07$, and $D_{Yb} = 0.12$ for the low-temperature sample.
11. I thank G. Hanson for providing access to the isotope laboratory at the State University of New York, Stony Brook; J. Whitlock who prepared the glass separates; and J. B. Gill, M. G. Sawlan, and D. E. Sampson who made suggestions for manuscript improvement. A grant from the Faculty Committee on Research, University of California at Santa Cruz, supported the REE analyses. Field collecting expenses were defrayed by a grant from Institute of Geophysics and Planetary Physics, University of California, Los Angeles; Los Alamos National Laboratory; and the University of California.

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The Association of Iron and Manganese with Bacteria on Marine Macroparticulate Material

Abstract. *Evidence of in situ metal (iron and manganese) deposition onto bacteria associated with rapidly sinking particles in the open ocean is reported. Below 100 meters, bacteria are found with extracellular capsules containing metal precipitates; the frequency of these capsules increases with depth. The capsular metal deposits appear to contribute a major portion of the weakly bound fraction of the particulate iron flux.*

Microbes have frequently been implicated in the phase changes (for example, from dissolved to solid) and redox transformations of metals such as iron and manganese in soils (*1*), springs, streams, and lakes (*1–5*). Although bacteria capable of oxidizing manganese in culture have been reported from seawater (*2, 6*), evidence of their in situ activity in marine environments has thus far been found only in sediments and certain stratified areas such as Saanich Inlet (a British Columbian fjord with seasonally anaerobic conditions in its deep waters) (*2, 7*), in hydrothermal vent systems (*8*), and possibly in ferromanganese nodules (*2, 9*), but not in pelagic environments. We report here the discovery of iron and manganese deposits associated with bacteria commonly found with macroparticulate material in the oceanic water column. Our distributional data and a

vertical profile of the relative abundance of iron-depositing bacteria suggest that these biologically induced iron deposits may contribute significantly to the iron content of the mid-depth particle flux and consequently to the scavenging and vertical removal of this element from the water column.

Most samples in this study were collected with sediment traps on the VERTEX I and II expeditions; additional materials were obtained from the manned submersible R.V. *Alvin* (*10*) and the unmanned submersible sled *Deep Tow*, which was equipped with an opening-closing net (*11*). The locations of sampling stations and details of the collection devices and depths sampled are given in Table 1. Standard techniques for sample preparation, examination, and counting by transmission electron microscopy (TEM) were used (*12*). The metal-depositing bacteria were easily recognized by their characteristic extracellular capsules, which consisted of fibrillar-like matrices enclosing the cell (Fig. 1, a and b) (*13, 14*). Samples with capsules were further examined and elemental microanalyses performed by energy-dispersive x-ray spectrometry (EDS) in conjunction with either a Hitachi scanning transmission electron microscope (STEM) or energy-dispersive x-ray analysis instrument (Fig. 1d). We chose TEM because it revealed the bacterial source of the polymer-like matrices. In contrast, scanning electron microscopy (SEM) would not allow us to differentiate "capsules" from other amorphous microparticles such as flocculated fine clays (*15*). We emphasize that our methods cannot elucidate the mechanism of metal deposition, nor do they indicate whether the bacteria are actively mediating the deposition. Rather, we use the general term "metal-depositing bacteria" to indicate a simple form of indirect, or "induced" (*16*), biomineralization whereby the bacteria have at least incidentally provided the substrate (the capsule material) on which the metal deposits.

The metal-depositing bacteria were usually associated with flocculant amorphous aggregates [marine snow (*10*)], although they were occasionally also found to be abundant in some fecal pellets. The bacterial cells are small, Gram-negative cocci (a few rod-shaped cells were found), 0.3 to 0.5 μm in diameter. The overall diameter of the cell plus the capsule is usually 1 to 2 μm (Fig. 1, a and b). These capsules are very similar to those of iron- and manganese-dispositing bacteria reported from soils (*1*) and streams (*4*) and to those found in Saanich Inlet (*6*). The results of EDS analyses on the capsular material (Fig. 1, a and b) are shown in Fig. 1d (curves i and ii, respectively).

Strong iron peaks were always associated with capsules, whereas manganese was detected only in capsules from the deeper samples. Bacterial capsules are ubiquitous in most environments but are generally not visible under TEM without the application of polyanion stains (largely ruthenium red) (*13*). It has been noted that metal deposits may have contributed to the electron denseness of some capsule matrices from marine sediments that were not subjected to such stains (*14*). In our study capsules were visible (TEM) without ruthenium red, although its use significantly strengthened the image.

The metal deposits are apparently structurally amorphous or microcrystalline since electron diffraction analysis revealed no diffraction patterns. Significant iron or manganese peaks were also associated with occasional lithogenic, iron-rich aluminum silicates in the samples, but these were easily distinguishable both morphologically (Fig. 1c) and by their EDS spectra (Fig. 1d, curve iii). The occurrence of metal-depositing bacteria among the samples surveyed is presented in Table 1. Iron-depositing bacteria were found in all sediment-trap samples below 120 m, all *Alvin* samples, and the nepheloid layer sampled by the *Deep Tow* at about 2800 m. Generally, surface-collected particles do not host metal-depositing bacteria (*17*). However, bacteria isolated from these surface waters were able to oxidize manganese and iron in culture (*9*). Bacterial-mediated metal oxidation often results in the extracellular deposition of the metal on polymer matrices similar to those described here (*2, 18*).

A depth profile of capsuled bacteria as a percentage of total bacteria from the VERTEX II station sediment trap samples (Fig. 2) indicates an absence of capsuled bacteria in the near-surface samples. There is a subsurface (100 to 200 m) increase to 5 percent, and at mid-depths (400 to 1450 m) over 30 percent of

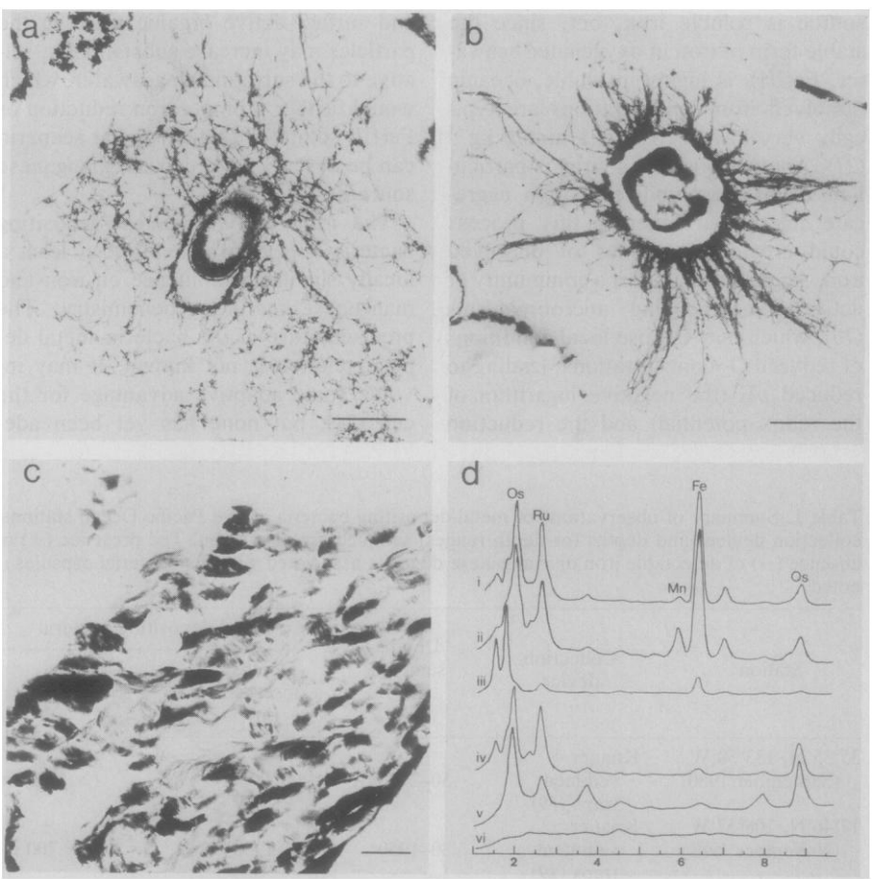

Fig. 1. (a and b) TEM micrographs of metal-depositing bacteria; (c) TEM micrograph of an aluminum silicate mineral (scale bars, 0.5 μm); (d) EDS spectra for selected microparticles from sediment trap material: curves i and ii, extracellular capsule material from (a) and (b), respectively; curve iii, the mineral in (c); curve iv, a fecal pellet; curve v, a bacterium with no visible (TEM) capsule material; and curve vi, background resin near a capsule. The horizontal scale is in kiloelectron volts; the vertical scale for curves i through iii is five times the scale for curves iv through vi.

the total bacteria are in the aggregate material.

The complexity arising from the mixture of living and nonliving organic materials and inorganic biogenic and lithogenic detritus in the samples, plus the variability of the capsule polymer densities, preclude straightforward quantification of the contribution of the capsule iron or manganese deposits to the total flux. Nevertheless, we made tentative estimates of the contribution of iron-depositing bacteria to the particulate iron flux by making some conservative extrapolations of the iron content of the capsules and using other VERTEX II data on bacterial abundance and total particle flux (*19*). Comparing the metal deposits associated with the capsuled bacteria with the weakly bound (weak acid–soluble) iron flux data derived from replicate sediment traps of the same deployment (*20*), we found that the estimated bacterial capsule contribution was 0 percent in the surface, 26 to 100 percent at mid-depths (120 to 800 m), and 9 to 70 percent for deep waters (1450 to 1950 m).

There are two potential sources for the iron deposited on the capsules. The first source is soluble iron, but, since the stable form of iron in oxygenated seawater, Fe(III), is highly insoluble, oceanic dissolved iron concentrations are typically very low, ~ 0.5 to 1 nmole kg^{-1} (*21*). Another possible source is particulate Fe(III) resolubilized within aggregate microenvironments; this process could create microzones of dissolved iron. Aggregates support a community of actively metabolizing microorganisms (*10*), which may impose local conditions of reduced O_2 concentrations, leading to reduced *p*E (the negative logarithm of the redox potential) and the reduction and resolubilization of particulate $Fe(OH)_3$ or FeOOH to Fe(II), a more soluble form of iron than Fe(III). In addition, the concentration of dissolved and surface-active organic acids in the particles may increase substantially, relative to the surrounding seawater, which would further promote iron reduction or Fe(III) solubility (*22*). A similar scenario can be described for capsule manganese sources.

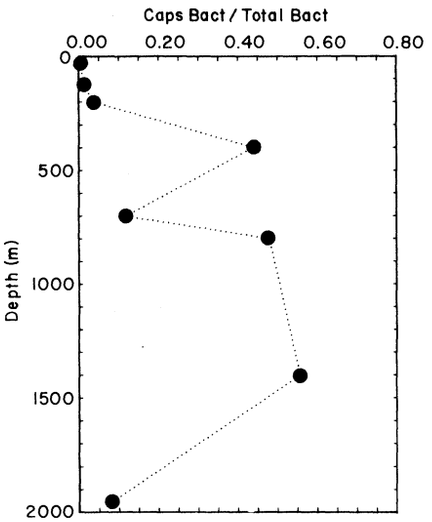

Fig. 2. Depth profile of metal-depositing bacteria. The ratio of metal-depositing bacteria (*Caps Bact*) to total bacteria (*Total Bact*) is plotted against depth for the VERTEX II station in the eastern subtropical North Pacific. Samples were collected by sediment traps.

The iron- and manganese-depositing bacteria appear to constitute at least a locally significant influence on iron and manganese marine geochemistry. The precise nature of the bacteria–metal deposit relation is not known. It may involve some adaptive advantage for the cell (*23*), but none has yet been adequately demonstrated. In any event, the distribution of the associated iron and manganese deposits would still be influenced by the water column geochemistry in concert with the microbes' microenvironment.

Table 1. Summary of observations of metal-depositing bacteria at five Pacific Ocean stations; collection devices and depths (or depth ranges) sampled are also given. The presence (+) or absence (−) of detectable iron or manganese deposits associated with the bacterial capsules is noted.

Station	Collection device	Depths sampled (m)	Metal-depositing bacteria		
			Depths observed (m)	Deposits	
				Fe	Mn
35°35′N, 133°50′W (September 1980)	Knauer sediment traps (*19*)	50–2000*	200–2000*	+	+ (> 1450 m)
17°46′N, 108°57′W (November 1981)	Knauer sediment traps (*19*)	30–1950*	30–1950*	+	+ (≥ 700 m)
32°31′N, 118°03′W (August 1979)	*Alvin* (*10*)	1650	1650	+	+
21°46′N, 104°50′W (December 1982)	*Alvin* (*10*)	2500	2500	+	−
0°33′S, 85°33′W (April 1978)	*Deep Tow* (*11*)	Nepheloid layer†	Nepheloid layer	+	+

*Inclusive range of sample depths. †Located 10 to 100 m above the sea floor at depths of 2700 to 2900 m.

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References and Notes

1. R. Gebers and P. Hirsch, in *Environmental Biogeochemistry and Geochemistry*, W. E. Krumbein, Ed. (Ann Arbor Science, Ann Arbor, Mich., 1978), vol. 3, p. 911.
2. K. H. Nealson, in *Microbial Geochemistry: Studies in Microbiology*, W. E. Krumbein, Ed. (Blackwell, Oxford, 1983), pp. 191–221.
3. S. C. Chapnick, W. S. Moore, K. H. Nealson, *Limnol. Oceanogr.* **27**, 1004 (1982).
4. D. E. Caldwell and S. J. Caldwell, *Geomicrobiol. J.* **2**, 39 (1980).
5. I. C. Macrae and J. F. Edwards, *Appl. Microbiol.* **24**, 819 (1972).
6. J. P. Cowen, unpublished data.
7. S. Emerson, S. Kalhorn, L. Jacobs, B. Tebo, K. H. Nealson, R. Rosson, *Geochim. Cosmochim. Acta* **46**, 1073 (1982).
8. H. L. Ehrlich, in *Environ. Biogeochem. Ecol. Bull.* **35**, 357 (1983); H. W. Jannasch and C. O. Wirsen, *Appl. Environ. Microbiol.* **41**, 528 (1981).
9. P. A. La Rock and H. L. Ehrlich, *Microbiol. Ecol.* **2**, 84 (1975).
10. M. W. Silver and A. Alldredge, *J. Mar. Res.* **39**, 501 (1981).
11. K. F. Wishner, *Deep Sea Res.* **27**, 203 (1980).
12. M. W. Silver and K. W. Bruland, *Mar. Biol.* **62**, 263 (1981). Sections were placed on nylon grids for STEM-EDS analysis.
13. J. W. Costerton, R. T. Irwin, K.-J. Cheng, *Annu. Rev. Microbiol.* **35**, 299 (1981).
14. D. J. W. Moriarty and A. C. Hayward, *Microbiol. Ecol.* **8**, 1 (1982).
15. S. Honjo, *J. Mar. Res.* **38**, 53 (1980).
16. H. A. Lowenstam, *Science* **211**, 1126 (1981).
17. Surface samples included sediment-trap and many scuba-collected aggregates from most of the stations in Table 1; scuba collections from Monterey Bay, California; and a series of stations from 20°N to 20°S, 160°W. A single exception to this general rule was a capsule found in the 30-m sediment trap from the September 1980 deployment.
18. W. C. Ghiorse and P. Hirsch, *Arch. Microbiol.* **123**, 213 (1979).
19. The contribution of the iron-depositing bacteria to the vertical flux of iron was calculated as follows:

$$\text{iron flux}_{\text{cap bact}} = B_T f R_c V_c d_r C_{Fe}$$

where B_T is the total number of bacteria per milligram of dry weight of sediment-trap material [10^7 cells per milligram of dry weight (M. Gowing, personal communication)]; f is the total material flux caught by individual sediment traps (in milligrams of dry weight per square meter per day) (*16*); R_c is the ratio of the number of capsuled bacteria to the number of total bacteria; V_c is the volume occupied by the capsule of a single bacteria (in cubic micrometers); d_r is the specific density of sample embedded in resin (1.02 g cm^{-3}); and C_{Fe} is the estimated mass fraction of the EDS analysis volume by weight contributed by iron.
20. R. M. Gordon, J. H. Martin, G. A. Knauer, *Nature (London)* **299**, 611 (1982); G. A. Knauer and J. Martin, personal communication.
21. K. W. Bruland, in *Chemical Oceanography*, J. P. Riley and R. Chester, Eds. (Academic Press, London, 1983), pp. 158–220.
22. C. J. Miles and P. L. Breyonik, *Environ. Sci. Technol.* **15**, 1089 (1981).
23. B. D. Grosovsky, *J. Theor. Biol.* **97**, 83 (1982).
24. We thank K. Nealson and K. Bruland for their valuable help and advice. We also thank K. Bruland, K. Nealson, and G. Knauer for critically reviewing the manuscript. The work was supported by the VERTEX Program (grants NSF 80-003200, OCE 82-16672, and OCE 82-00379) and by the *Alvin* Program (grant OCE 80-19525).

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