

- moderate-temperature palm worms, and vestimentiferan tube worms are abundant (12, 14). The terms "tube" and "tube structure" refer to a structure's shape and do not necessarily indicate that it results from a vestimentiferan tube worm. Because all of the described structures are relict and several types of worms are currently abundant at Endeavour, we are unable to define which worms are associated with the described structures. However, the worms' association with barite, a low-temperature phase (3, 10), suggests that low- to intermediate-temperature worms formed these structures.
14. M. Hannington and K. Juniper, *Ridge Res. Rep.* **3**, 38 (1992); V. Tunnicliffe and S. K. Juniper, *Prog. Oceanogr.* **24**, 1 (1990).
 15. D. S. Stakes and W. S. Moore, *J. Geophys. Res.* **96**, 21739 (1991).
 16. V. Tunnicliffe, S. K. Juniper, M. E. de Burgh, *Biol. Soc. Wash. Bull.* **6**, 453 (1985).
 17. S. K. Juniper, V. Tunnicliffe, A. R. Fontaine, *NOAA Natl. Undersea Res. Prog. Res. Rep.* 88-4 (1988), p. 99.
 18. S. K. Juniper, J. A. J. Thompson, S. E. Calvert, *Deep-Sea Res.* **33**, 339 (1986).
 19. D. R. Janecky and W. E. Seyfried Jr., *Geochim. Cosmochim. Acta* **48**, 2723 (1984).
 20. M. K. Tivey and R. E. McDuff, *J. Geophys. Res.* **95**, 12617 (1990).
 21. U. M. Graham, G. J. Bluth, H. Ohmoto, *Can. Mineral.* **26**, 487 (1988).
 22. T. L. Cook, thesis, University of California, Santa Cruz (1994).
 23. R. A. Berner, in *Princeton Series in Geochemistry*, H. D. Holland, Ed. (Princeton Univ. Press, Princeton, NJ, 1980), pp. 90–126.
 24. G. R. Taylor, *Mineral. Deposita* **18**, 129 (1983).
 25. R. A. Berner, *Econ. Geol.* **64**, 383 (1969); R. E. Sweeney and I. R. Kaplan, *ibid.* **68**, 618 (1973); U. M. Graham and H. Ohmoto, *Geochim. Cosmochim. Acta* **58**, 2187 (1994).
 26. J. N. Valette-Silver, A. Bates, D. Anderson, J. Deming, W. H. Zoller, *Eos* **66**, 97 (1985).
 27. J. B. Murowchick and H. L. Barnes, *Geochim. Cosmochim. Acta* **50**, 2615 (1986).
 28. R. M. Haymon, *Nature* **301**, 695 (1983).
 29. Evidence for chalcopryite replacement of wurtzite [atoll textures and disseminated chalcopryite inclusions or "chalcopryite disease" (2)] was observed in some of the structures.
 30. We thank the Alvin and Atlantis II crew for assistance in obtaining these samples. Z. Palacz assisted with isotopic analyses, J. Delaney supplied unpublished location maps of the Endeavour structures, A. Gough assisted with figures, and J. Deming, J. Gill, M. K. Tivey, L. D. Abbott, and two anonymous reviewers provided helpful reviews. Support for this project was provided by the Monterey Bay Aquarium Research Institute with funds from the David and Lucille Packard Foundation. The cruise to obtain these samples was funded by the National Science Foundation.

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Atmospheric Methyl Bromide (CH₃Br) from Agricultural Soil Fumigations

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The treatment of agricultural soils with CH₃Br (MeBr) has been suggested to be a significant source of atmospheric MeBr which is involved in stratospheric ozone loss. A field fumigation experiment showed that, after 7 days, 34 percent of the applied MeBr had escaped into the atmosphere. The remaining 66 percent should have caused an increase in bromide in the soil; soil bromide increased by an amount equal to 70 percent of the applied MeBr, consistent with the flux measurements to within 4 percent. Comparison with an earlier experiment in which the escape of MeBr to the atmosphere was greater showed that higher soil pH, organic content and soil moisture, and deeper, more uniform injection of MeBr may in combination reduce the escape of MeBr.

There is great interest (1) in quantifying how much of the stratospheric ozone loss observed to date is due to catalytic destruction by gaseous Br and BrO, and in predicting how future ozone amounts will respond to a decreased usage of anthropogenic organic bromine compounds (denoted by R-Br). Br atoms are carried into the stratosphere in relatively stable R-Br molecules such as the halons (principally CBrF₃ and CBrClF₂) and CH₃Br (MeBr). The fluxes of halons are known reasonably well as they are totally synthetic (2), whereas the rates of emission of MeBr into the atmosphere are poorly quantified. Even the atmospheric

amounts of MeBr have been known only to within a factor of 2 until recently (3).

Two potentially significant sources of atmospheric MeBr have been recognized recently: emissions from large-scale biomass burning (4) and emissions from automobiles that burn leaded gasoline (5). Oceanic emissions have been considered a large natural source of MeBr, but recent data indicate that the oceans may be a net sink, not a source (6). Losses to the atmosphere during MeBr soil fumigations were recognized earlier but have not been well quantified. Model calculations show that MeBr escape from fumigated soils may be variable, depending on several factors (7). Whatever the putative sources, their total size, S , is constrained by $S = B/\tau$, where B is the atmospheric burden and τ is the atmospheric residence time, in an assumed steady state. Estimates of τ have changed recently

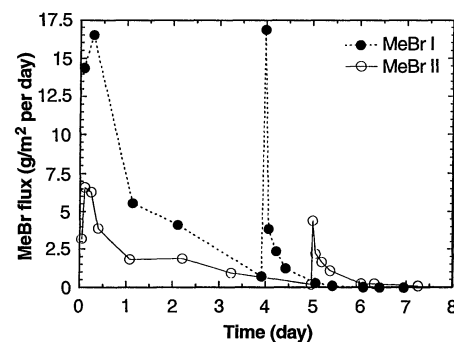


Fig. 1. Escape fluxes of MeBr measured with chambers placed over fumigated fields in two experiments near Irvine, California: MeBr I, 10 to 17 September 1992 and MeBr II, 8 to 15 October 1993. Data points are averages over all flux chambers ($n = 5$ in MeBr II and $n = 4$ in MeBr I). Polyethylene sheets covered the fields for 4 days in MeBr I and for 5 days in MeBr II. Standard deviations of the points for MeBr II varied between 8 and 27% of the means; the full range of variation for MeBr I was shown in (9).

from 2.0 to 1.3 years (8), and it is not clear that the sources identified to date can sum to $S = 1.4 \times 10^8$ kg/year (1.8×10^8 kg per 1.3 years). Constructing a budget of atmospheric MeBr requires more precise data.

Worldwide usage of synthetic MeBr increased from 4.2×10^7 to 6.3×10^7 kg/year between 1984 and 1990; about 80% of this amount was applied to agricultural soils before planting (7). MeBr may be removed from soils by hydrolysis, by adsorption to soil particles, by biological and chemical processes, and by transport. The rates and effectiveness of these varied processes have been shown, through modeling, to control the fraction of applied MeBr that escapes during soil fumigations (7). It is important to determine this escape fraction in actual fumigations and to identify the factors that control this escape so that they might be manipulated to minimize emissions.

We conducted a field fumigation experiment in which we measured the flux of MeBr into the atmosphere, the bromide contents of the soil before and after the experiment, and the gaseous MeBr in the soil versus depth. Measurement methods and other experimental details were those of Yagi *et al.* (9) except for the following modifications. The MeBr-chloropicrin mixture (75/25 by weight) was injected more uniformly than in (9) by a computer-controlled system, at a rate of 323 kg/ha (10). Plastic tarping was placed over the field immediately after the MeBr injection as described in (9), but it was left in place for 120 hours instead of 96 hours (11). We measured the fluxes by observing increases of MeBr gaseous concentrations in five flux chambers that were placed on top of the tarp, and after the tarp was removed, directly on the soil as described in (9). Soil gas concentrations of

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MeBr were sampled through steel tubes (12), and bromide ion amounts were measured by ion-specific electrodes (13).

As shown in Fig. 1, the fluxes into the atmosphere we measured in this experiment (referred to as MeBr II) were significantly different from those measured in our previous experiment (MeBr I) (9). In MeBr II, the fluxes were through the tarp for the first 5 days, and a secondary peak was then observed on removal of the tarp as upward transport was facilitated. In MeBr II, about 34% of the applied MeBr escaped into the atmosphere, whereas in MeBr I 87% escaped (14) and cumulative emissions were lower at all times (Fig. 2). By 7 days, the amount of gaseous MeBr left in the soil at all depths from the surface to 90 cm was negligible in both MeBr I and MeBr II (15). If we assume that the remainder of the applied MeBr was dissociated by hydrolysis according to $\text{CH}_3\text{Br} + \text{H}_2\text{O} \rightarrow \text{Br}^- + \text{H}^+ + \text{CH}_3\text{OH}$, or by substitution reactions with soil organic matter which would also produce Br^- , then there should have been

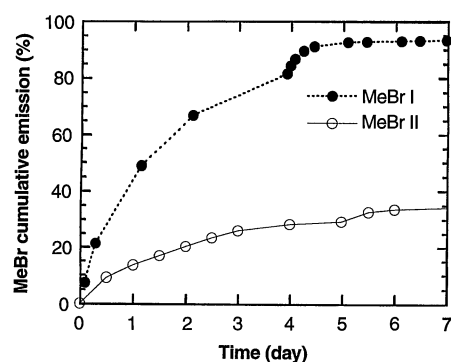


Fig. 2. Cumulative emissions of MeBr measured by chambers versus time for two experiments. Points are averages as in Fig. 1. For the final cumulative emission, the standard error of the mean was 24% for MeBr I and 6% for MeBr II. The total cumulative emission, as a fraction of the amount applied, was 87 and 34% for the two experiments, respectively. These emissions, when added to the growth in soil bromide for each respective experiment, yielded about 106% and 104% of the total applied, for MeBr I and MeBr II respectively, so reasonable mass balance was achieved experimentally.

Table 1. Some physical and chemical properties of the soil at the study site of MeBr II near Irvine, California. The soil was a San Emigdio loam. The fumigated field was about 1 ha. Flux and soil measurements were made in a subarea of about 100 m² near the center of the field.

Depth (cm)	Bulk density (g cm ⁻³)	Total porosity (cm ³ cm ⁻³)	Volumetric water content (cm ³ cm ⁻³)	Total C (%)	Total N (%)	C/N	pH (1:1 water)
3	1.12	0.579	0.089	0.75	0.074	10.2	6.9
10	1.19	0.553	0.141	0.72	0.070	10.2	6.9
20	1.12	0.579	0.134	0.73	0.068	10.7	6.9
30	1.53	0.423	0.190	0.56	0.054	10.4	7.0
60	1.66	0.375	0.171	0.33	0.037	8.9	7.2
90	1.58	0.404	0.135	0.22	0.029	7.7	7.3

an increase in soil bromide inventories of 66% in MeBr II and 13% in MeBr I, as respective fractions of the amounts applied.

The total vertical column of bromide measured (to 90 cm) at the end of MeBr II exceeded the initial column by 14.2 g/m², or 69.5% of the amount applied (Fig. 3). Because the observed escape flux of gaseous MeBr and the residual Br^- amounts sum to 104% (34% + 70%), a mass balance was achieved in the experiment (to within 4%), and the escape fluxes observed by the chamber method appear to be confirmed. Indeed, in early greenhouse experiments by Hamaker *et al.* (16), the escape flux of MeBr was estimated solely by measuring the difference between initial and final bromide contents of soils. If we assume that the initial Br^- amounts in MeBr I were as graphed in Fig. 3, then the difference between the final and initial bromide contents was 19% (13). The observed escape fraction of 87%, plus the soil bromide increase of 19%, equals 106% of the amount applied initially, a reasonable mass balance. In MeBr I, the actual escape fraction may have been only 80%; one chamber showed consistently higher fluxes during the period of tarp cover, and the tarp beneath it was found to be very thin (9).

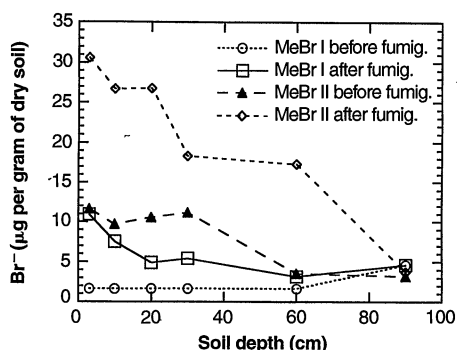


Fig. 3. Bromide concentrations measured (13) versus depth in the soil in two field fumigation experiments. The observed increases of Br^- after the fumigations (fumig.) are attributed to the decomposition of MeBr. Br^- was measured only at a depth of 3 cm before MeBr I; the dotted line is assumed (13).

The soil pH was about 0.7 units higher in MeBr II than in MeBr I. This difference may explain the lower proportional escape of MeBr in MeBr II; Gentile *et al.* (17) found that hydrolysis was enhanced at high pH. The soil in MeBr II was twice as moist at the surface and slightly moister down to 30 cm [see Table 1 and (9)] than in MeBr I, and the MeBr II soil contained more organic matter. Soil porosity was also higher in MeBr II. Soil gas measurements made minutes after the injection showed that MeBr amounts were greatest at 30 cm, the sampling depth nearest the depth of injection. With time, MeBr moved both upward and downward in the soil (15). After 3.3 days, amounts at depths from 10 to 90 cm were essentially equal.

There are several reasons for the major difference between our two sets of field results, that is, the lower emissions observed in MeBr II. (i) The soil pH and moisture were greater, which favored faster hydrolysis (17) in MeBr II. (ii) The soil organic content was larger, favoring MeBr degradation. (iii) The injection depth was greater and the injection method (10) was more efficient in MeBr II.

Our two field experiments demonstrate that although significant variability is to be expected, there is potential for limiting emissions. The data confirm several features of model predictions (7) including general features of the temporal patterns of soil concentrations of gaseous MeBr and that a secondary emission peak occurs just after the tarp is removed. However, our data show that concentrations of MeBr decay at a faster rate than is predicted by the model (7). Further, whereas some modeled emissions continue for 14 days (7), emissions from the fields we studied were insignificant after 7 days. To obtain a reliable average value for the global input to the atmosphere from field fumigations, more quantitative relations are needed between these factors and escape amounts, along with data on field conditions worldwide.

REFERENCES AND NOTES

1. J. G. Anderson, D. W. Toohey, W. H. Brune, *Science* **251**, 39 (1991); L. M. Avallone *et al.*, *Geophys. Res. Lett.* **20**, 1795 (1993); R. R. Garcia and S. Solomon, *J. Geophys. Res.* **99**, 12937 (1994).
2. A. McCulloch, *Atmos. Environ.* **26**, 1325 (1991).
3. Current background mixing ratios by volume in northern hemisphere air are about 11 parts per trillion, about 1.3 times as high as those in the southern hemisphere [B. R. Miller, R. F. Weiss, P. J. Fraser, R. G. Prinn, J. Huang, *Trans. Am. Geophys. Union* **75**, 141 (1994); M. A. K. Khalil, R. A. Rasmussen, R. Gunawardena, *J. Geophys. Res.* **98**, 2887 (1993)].
4. S. Manó and M. O. Andreae, *Science* **263**, 1255 (1994).
5. S. A. Penkett *et al.*, in *Scientific Assessment of Ozone Depletion: 1994* (World Meteorological Organization, Rep. No. 37, Geneva, 1995), chap. 10.
6. J. M. Lobert *et al.*, *Science* **267**, 1002 (1995).

Signatures of the Martian Atmosphere in Glass of the Zagami Meteorite

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Isotopic signatures of nitrogen, argon, and xenon have been determined in separated millimeter-sized pockets of shock-melted glass in a recently identified lithology of the meteorite Zagami, a shergottite. The ratio of nitrogen-15 to nitrogen-14, which is at least 282 per mil larger than the terrestrial value, the ratio of xenon-129 to xenon-132 = 2.40, and the argon isotopic abundances match the signatures previously observed in the glassy lithology of the Antarctic shergottite EETA 79001. These results show that the signatures in EETA 79001 are not unique but characterize the trapped gas component in shock-melted glass of shergottites. The isotopic and elemental ratios of nitrogen, argon, and xenon closely resemble the Viking spacecraft data for the martian atmosphere and provide compelling evidence for a martian origin of the two shergottites and, by extension, of the meteorites in the shergottites-nakhlites-chassignites (SNC) group.

The SNC group of igneous meteorites is derived from a parent body with an oxygen isotopic signature that is distinct from that of other solar system objects (1). The crystallization ages of these meteorites, although the subject of some debate, are clearly less than 1.3×10^9 years, possibly as low as 180×10^6 years (2), and must have formed on a geologically complex parent body (3). Bogard and Johnson (4) and Becker and Pepin (5) discovered that trapped noble gases and nitrogen in lithology C of the Antarctic shergottite EETA 79001 had elemental and isotopic ratios similar to those measured by the Viking lander (6) in the martian atmosphere, lending support to the suggestion that these meteorites may have come from Mars. The shergottite EETA 79001 remains the only shergottite that shows clear signatures of entrapped martian atmospheric gases (7). Recently, Watson *et al.* (8) studied the hydrogen isotopic signatures in Zagami and other SNC meteorites and found high deuterium/hydrogen (D/H) ratios, which are similar to that measured in the martian atmosphere by Earth-based telescopes (9).

In this work, we present the results of the first petrographic and isotopic studies on the shock-melted glasses in Zagami.

Zagami was selected for study because it probably crystallized near the surface of Mars (10) and thus is in close proximity to the source of the implanted atmospheric gases. Zagami is also a recent fall (1962), and the degree of terrestrial contamination was expected to be less severe than in the Antarctic shergottite EETA 79001. Multi-millimeter-sized pockets of shock-melt suitable for separation and isotopic analyses are not evenly distributed in Zagami. Most of Zagami (~80%) has a basaltic lithology (10, 11), termed "normal Zagami," in which shock-melting is evident only because of the presence of ~100- μ m-wide shock-melt veins of roughly whole-rock composition that cross-cut the sample (10). These veins are too small for separation and isotopic analyses. A second, recently recognized lithology occupies ~20% of Zagami and is termed the "dark, mottled lithology" (12). It is enriched in late-stage crystallization product and represents a later stage in the crystallization of Zagami. It is within this lithology that we find the multimillimeter-sized shock-melt pockets separated for isotopic analyses.

Two shock-melt pockets were selected for study: one for petrographic examination from samples provided by R. Haag (Fig. 1) and one for isotopic analyses from U.S. National Museum sample 6545. Both pockets were ~3 mm in diameter, much smaller than the centimeter-sized pockets studied from EETA 79001. Like those in EETA 79001, the bulk composition of the petrographically examined shock-melt pockets in Zagami is similar in composition to the bulk lithology in which it occurs. The Zagami pockets differ from the EETA 79001 pockets (13) in being enriched in some incompatible elements (for example, Fe, P), reflecting the enrichment of these elements in the "dark mottled lithology" of Zagami. Both pockets have irregular outlines, including embayments into the host, but

7. D. D. Reible, *J. Hazard Mater.* **37**, 431 (1994). About 20% of the MeBr produced worldwide is used to fumigate structures and shipments of fruits and vegetables.
8. J. H. Butler, *Geophys. Res. Lett.* **21**, 185 (1994); and see (5). A more accurate relation between sources, sinks, and lifetime of MeBr can be obtained from a model that treats northern and southern hemispheres separately; see, for example, Khalil *et al.* in (3) who also report a 3% per year increase of atmospheric MeBr between 1988–92.
9. K. Yagi, J. Williams, N.-Y. Wang, R. J. Cicerone, *Proc. Natl. Acad. Sci. U.S.A.* **90**, 8420 (1993).
10. Injection rates were metered continuously, and the total amount applied (323 kg/ha = 288 lbs/acre) was also determined to within 1% by weighing the fumigant supply tanks before and after fumigation. The fluid mixture was injected with a Noble-plow design injector to a depth of 35 cm. This injector is configured so that the lines of injection are not directly beneath the furrows caused by plow shanks. Standard plow shanks, in contrast, may facilitate escape of MeBr, as the lines of injected liquid are directly beneath the furrows.
11. The tarp material was high-density polyethylene, nominally 0.025 mm thick (0.001 inch). The actual thicknesses of the sections beneath our flux chambers were between 0.035 and 0.042 mm.
12. Soil sampling at 10, 20, 30, 60, and 90 cm was achieved as in (9) but also with a second set of new sampling tubes at each location. The new tubes were of low dead volume and were placed inside a stainless steel main tube with an outer diameter of 1.27 cm that had solid disks fused inside at each sampling depth. Each individual sampling tube connected to holes drilled into its disk, and the other tubes passed through the disk to greater depths. Flame ionization gas chromatography was used to measure MeBr as in (9).
13. The electrodes were manufactured by Orion Research, Boston. Air-dried soil samples (25 g, diameters <2 mm) were treated with 50 ml of 0.4 M NaNO₃ to extract bromide. Calibration was by NaBr solutions (0.1, 1, and 10 parts per million) prepared in 0.4 M NaNO₃. Samples from three locations about 1.5 m apart were combined for surface soil and for the depths of 10, 20, and 30 cm; samples from two such sites were used for the 60- and 90-cm depths. Bromide concentrations measured before and after MeBr II are shown in Fig. 3. Bromide amounts before MeBr I were measured to be 1.65 μ g/g at 3 cm and assumed to be the same down to 60 cm, and to increase linearly to 4.64 μ g/g at 90 cm (the same value that was observed at the end of MeBr I). Comparison with measurements after MeBr I implied that there was an increase of 4.09 g of Br⁻ per square meter during the 7-day experiment, or 19% of the applied bromine.
14. We observed smaller fluxes when we made additional flux measurements from those parallel strips where adjacent tarp sheets overlapped. We accounted for this effect by using area-weighted flux values for the part of the field (93%) that was covered by a single thickness of tarp and the 7% covered by double-thick tarp. We also found negligible fluxes from unfumigated areas horizontally adjacent to the fumigated field.
15. Vertical profiles of gaseous MeBr were reported in (9) for the duration of MeBr I. In the present experiment, MeBr II, we measured vertical profiles in even more detail but do not include the results here.
16. P. Hamaker, H. de Heer, A. M. M. van der Burg, *Acta Hort.* **152**, 127 (1983).
17. I. A. Gentile, L. Ferraris, S. Crespi, *Pestic. Sci.* **25**, 261 (1989). In our own laboratory experiments with several soils (to be reported elsewhere) we also found bromide production from MeBr to be about 35% faster with pH 6.9 than for pH 6.1.
18. Discussions with T. Duafala and D. Ito of TriCal and access to fields professionally fumigated by TriCal are appreciated. Supported by NSF grant ATM-9321867 and Department of Energy National Institute for Global Environmental Change award W-GEC91-089-UCI.

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