ical reactions of the martian soil. To minimize contamination by atmospheric components, the KO_2 or ZnO_2 (0.1 g) was placed in a glass tube and evacuated to 10^{-1} torr. Then, 0.2 ml of 50 percent $H_2{}^{18}O$ was introduced into the tube. The use of ^{18}O-labeled water would also enable us to find the sources of O_2 generated by the interaction. Peaks at *m/e* 32 ($^{16}O_2$), 34 ($^{16}O^{18}O$), and 36 ($^{18}O_2$) were investigated by mass spectrometry. Relative peak intensities are listed in Table 3, with the background reading given before the reading for O_2 generated. The striking increase in the peak intensity at *m/e* 32 indicates that KO_2 and ZnO_2 easily release O_2 upon reaction with water. In the case of the interaction of KO_2 with water, the increase in the peak intensity at *m/e* 34 indicates that O_2 is also generated from the water. The formation of $^{16}O^{18}O$ may be explained as follows:

$$2K^{16}O_2 + H_2{}^{18}O \rightarrow 2K^{16}OH + 2\,^{16}O + {}^{18}O$$

$$^{16}O + {}^{18}O \rightarrow {}^{16}O^{18}O$$

These observations, although preliminary, strongly suggest that the results of the Viking GEX experiments may have been due to surface chemical reactions on Mars (*8*).

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References and Notes

1. H. P. Klein *et al.*, *Science* **194**, 99 (1976).
2. G. V. Kevin and P. A. Straat, *ibid.*, p. 1322.
3. K. Biemann *et al.*, *ibid.*, p. 72.
4. K. Biemann, personal communication.
5. In a blank experiment to check the background concentration of $^{13}CO_2$ produced by mixing the formate with the HCl solution, no $^{13}CO_2$ release was observed.
6. G. V. Levin and P. A. Straat, *Origins Life*, in press. This ^{14}C-labeled mixture was provided by Dr. H. P. Klein, director of Life Science, NASA Ames Research Center, Moffett Field, Calif.
7. T. A. Mutch *et al.*, *Science* **193**, 791 (1976); P. Toulmin III, B. C. Clark, A. K. Baird, K. Keil, H. J. Rose, Jr., *ibid.* **194**, 81 (1976); A. K. Baird, P. Toulmin III, B. C. Clark, H. J. Rose, Jr., K. Keil, R. P. Christian, J. L. Gooding, *ibid.*, p. 1288.
8. We are at present investigating the mechanisms and kinetics of the Viking LR experiment (C. Ponnamperuma, A. Shimoyama, M. Yamada, T. Hobo, R. Pal, paper presented at the 5th International Conference on the Origins of Life, Kyoto, Japan, 5–9 April 1977).
9. We thank Dr. H. Okabe of the National Bureau of Standards and Dr. L. Stief of the Goddard Space Flight Center for assistance with the UV radiation; we thank Dr. H. P. Klein, leader of the Viking Biology Team, and Professor J. McNesby of the Department of Chemistry, University of Maryland, for extensive discussions. This work was supported by NASA grant NGR 21-002-317 from the Office of Planetary Biology.

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Shock-Produced Olivine Glass: First Observation

Abstract. *Transmission electron microscope (TEM) observations of an experimentally shock-deformed single crystal of natural peridot, $(Mg_{0.88}Fe_{0.12})_2SiO_4$, recovered from peak pressures of about 56 × 10^9 pascals revealed the presence of amorphous zones located within crystalline regions with a high density of tangled dislocations. This is the first reported observation of olivine glass. The shocked sample exhibits a wide variation in the degree of shock deformation on a small scale, and the glass appears to be intimately associated with the highest density of dislocations. This study suggests that olivine glass may be formed as a result of shock at pressures above about 50 to 55 × 10^9 pascals and that further TEM observations of naturally shocked olivines may demonstrate the presence of glass.*

We know of no case in which olivine liquid (Mg_2SiO_4 to Fe_2SiO_4 in composition) has been quenched to a glass. Numerous studies of the liquidus of olivine (*1–3*) and corresponding compositions in analogs of the system $(Mg,Fe)O$-SiO_2 [for example, LiF-BeF_2 (*4*)] have never resulted in the unequivocal quench of such a glass. Furthermore, attempts to produce olivine glass by means of rapid fusion and quench techniques have also been unsuccessful (*5*). Similarly, the presence of olivine glass has never been unambiguously demonstrated in the extensive studies of naturally and (a few) experimentally shocked olivines (*6, 7*), although it is known that most silicates that have been studied become amorphous when subjected to shock of high enough intensity (*7*).

We report the first observation of olivine glass and its synthesis by means of shock. A disk, cut from a crystal of San Carlos, Arizona, peridot, $(Mg_{0.88}Fe_{0.12})_2$-SiO_4, was shocked along [010] (propagation direction of the shock wave) (*8*). A peak pressure of 56 × 10^9 pascals (560 kbar) was achieved by the "multiple-reverberation" technique for a period of approximately 0.5 μsec (*9*).

Transmission electron microscope (TEM) observations (*10*) on ion-thinned slices of the shocked olivine revealed patchy, nondiffracting zones of no contrast within crystalline and diffracting sample material (Fig. 1, a and c). The lack of diffraction contrast implies that the zones consist of material lacking crystalline order down to a scale of several nanometers. These zones grade into the surrounding crystalline olivine, and diffracting fragments within the amorphous material indicate remnants of crystalline material. There is no evidence for phase separation or other heterogeneities within the glass. Marked, spotty asterism in the diffraction pattern indicates misorientation of fragments and bending of the olivine (Fig. 1d). Although the amorphous zones attain maximum dimensions of 10 μm and more (representing approximately 1 to 2 percent of the sample by volume), they were not evident during optical microscopic examination carried out on the shocked olivine prior to the TEM analysis.

Regions of low dislocation density (Fig. 1b), as well as the high-density tangles (Fig. 1, a and c), can be found in the shocked sample, an indication of wide variations in shock-induced deformation on an extremely small scale. Significantly, the glassy zones are located within the regions of highest dislocation density. This result may indicate that a threshold stress for the production of diaplectic glass exists, which was only achieved locally in the present experiments.

Estimates of the average temperature of the sample at peak pressure are between 740 and 1000 K, based on the equation-of-state properties of the sample container (*11, 12*) and a model presented in (*13*). The temperature attained immediately upon the release of pressure is poorly constrained as a result of its strong dependence on the details of the irreversible thermodynamic path followed by the sample on compression and decompression (*14, 15*). Nevertheless, a temperature well below the melting point of olivine [above 2000 K at 1 atm and presumably much higher at 56 × 10^9 pascals (*1, 3, 16*)] is indicated at peak pressure and probably on pressure release (*13, 14*).

These results suggest that the shocked olivine contains diaplectic glass [glass apparently formed in the solid state by shock (*7, 17*)]. The fact that the glassy zones are associated with the regions of the sample showing the highest amount of crystalline deformation suggests that they possibly represent portions of the sample quenched from material which at one point was in a high-pressure phase or phases. Although no microtextural evidence for the formation of any high-pressure phases was seen in the TEM studies, Hugoniot equation-of-state data for olivine indicate partial transformation to one or more high-density phases at 56 × 10^9 pascals [transformation is apparently initiated at pressures in excess of about 26 × 10^9 pascals (*13, 18*)]. Intense strain would be expected in areas surrounding zones of high-pressure phases as a result of the volume changes associated with transformation. The observed glass might then represent the olivine which has retransformed from the high-pressure phase or phases upon (or during) release, forming a metastable glass rather than crystalline olivine. Such a process has been documented for SiO_2 (*19*) and has even been found in static, high-pressure experiments (*20*). It is also possible that the phases formed in the olivine under shock compression lack long-range order and that the diaplectic glass may effectively have formed at high pressure, modified only by release to ambient conditions. In this regard, it is possible that olivine glass may be more stable than a highly dislocated crystal. For dislocation densities like those in the tangles (Fig. 1, a and c) the crystalline material might have a higher free energy than the glass, thus favoring spontaneous conversion to glass (*21*).

Alternatively, in the above calculations it is assumed that the thermal energy is uniformly distributed throughout the sample on compression and decompression (accounting for phase transformation). However, it has been argued (*22*) that yielding under shock is inherently inhomogeneous, leading to zones of high strain surrounding relatively unstrained material. As a result, thermal energy would be localized along "adiabatic shear bands" and the final shock deformation should be highly heterogeneous, as observed in the shocked olivine sample. Such heterogeneous deformation could originate from the interaction of the shock and release waves with heterogeneities (such as subboundaries) in the original sample. If shear bands exist as postulated (*22*), they could generate high temperatures locally, allowing rapid solid-state phase transformations or melting (*22*). In either case (transformation to either a solid or liquid), it is easy to understand how glass could be formed in conjunction with heterogeneous yielding under shock.

Finally, the results presented here suggest that further TEM observations should yield some olivine glass in naturally shocked samples if peak pressures were sufficiently elevated and postshock recovery sufficiently minor. On the basis of the present study, it appears that glass forms incipiently in olivine shocked to about 50 to 55 × 10^9 pascals.

Note added in proof: Recent TEM observations have revealed traces of glass in a sample cut from the same olivine crystal and shocked to 54 × 10^9 pascals in a separate experiment. We also wish to note Cotterill's suggestion that there may be a "natural" upper limit to dislocation densities (*23*). Applying his calculations to olivine yields an estimate (probably a lower bound) on the order of 10^{13} cm^{-2} for the limiting, dynamic dislocation density.

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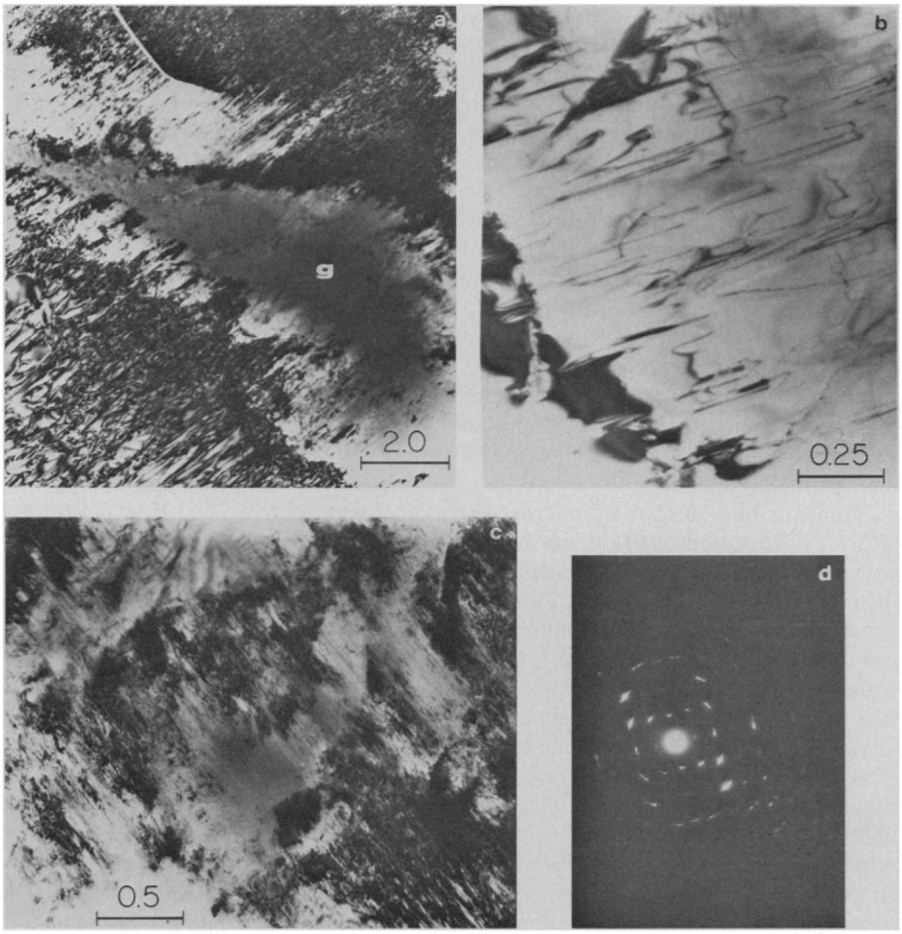

Fig. 1. (a) Transmission electron microscope (TEM) image (200 kev, bright-field) of shocked olivine showing nondiffracting glassy zone (*g*) within diffracting and crystalline olivine (light areas) containing a high density of dislocations [presumably [001] screw dislocations (*6, 7*)]. (b) Bright-field TEM image (1 Mev) of shocked olivine exhibiting dislocation densities almost as low as that found in the starting material (typically 10^6 to 10^7 cm^{-2}); (c) A TEM image (1 Mev, bright-field) of shocked olivine with glassy patches (dark, no contrast) grading into crystalline material containing a high density of dislocations. Scales in (a to c) are in micrometers. (d) Electron diffraction pattern (1 Mev) of the area in (c).

References and Notes

1. B. T. C. Davis and J. L. England, *J. Geophys. Res.* **69**, 1113 (1964).
2. D. H. Lindsley, *Carnegie Inst. Washington Yearb.* **65**, 227 (1965).
3. S. Akimoto, E. Komada, I. Kushiro, *J. Geophys. Res.* **72**, 679 (1967).
4. For example, D. M. Roy, R. Roy, E. F. Osborn, *J. Am. Ceram. Soc.* **37**, 300 (1954).
5. This includes fusion with a CO_2 laser: K. Keil, personal communication [see M. Blander, H. N. Planner, K. Keil, L. S. Nelson, N. L. Richardson, *Geochim. Cosmochim. Acta* **40**, 889 (1976)].
6. J. M. Christie and A. J. Ardell, in *Electron Microscopy in Mineralogy*, H.-R. Wenk *et al.*, Eds. (Springer-Verlag, Berlin, 1976), p. 374; J. S. Lally, J. M. Christie, G. L. Nord, Jr., A. H. Heuer, *Geochim. Cosmochim. Acta* (Suppl. 7) (1976), p. 1845; N. L. Carter, C. B. Raleigh, P. S. DeCarli, *J. Geophys. Res.* **73**, 5439 (1968).
7. D. Stöffler, *Fortschr. Mineral.* **51**, 256 (1972).
8. A polished disk 4.67 mm in diameter, 295 μm

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.
11. R. G. McQueen, S. P. Marsh, J. W. Taylor, J. N. Fritz, W. J. Carter, in *High Velocity Impact Phenomena*, R. Kinslow, Ed. (Academic Press, New York, 1970), p. 294.
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*)].
14. T. J. Ahrens and J. D. O'Keefe, *Moon* **4**, 214 (1973).
15. D. R. Waldbaum, *Nature (London)* **232**, 545 (1971).
16. N. L. Bowen and J. F. Schairer, *Am. J. Sci.* **29**, 161 (1935).
17. E. C. T. Chao, in *Researches in Geochemistry*, P. Abelson, Ed. (Wiley, New York, 1967), vol. 2, p. 204. Note that thetomorphic and diaplectic are 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 magnesian olivine, for example, to $(Mg,Fe)SiO_3$ 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, $CaSiO_3$ 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 $1/2\ \mu b^3$ 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^{12} cm^{-2} or more in the tangles, $b \sim 5$ Å, $\mu = 80 \times 10^9$ pascals, 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, W. Damgaard Kristensen, and R. Paetsch [*J. Phys. (Paris)* **36**, C2 (1975)].
22. D. E. Grady, in *High-Pressure Research: Applications to Geophysics*, M. Manghnani and S. Akimoto, Eds. (Academic Press, New York, 1977), p. 389; ______, W. J. Murri, P. S. DeCarli, *J. Geophys. Res.* **80**, 4857 (1975); D. E. Grady and W. J. Murri, *Geophys. Res. Lett.* **3**, 472 (1976).
23. R. M. J. Cotterill, *Phys. Lett.* **60A**, 61 (1977).

24. We are grateful for discussions with I. Jackson and L. Liu, and for reviews from A. Albee and D. Grady, all of which were very helpful. This research was supported by NASA grant NGL 05-002-105 and contract NAS9-14749 (U.S. Steel Research Laboratory). Contribution No. 2889, Division of Geological and Planetary Sciences, California Institute of Technology.

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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 community 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