ments and innovations of ancient Mesopotamians. Material compositionally identical to synthetic basalt, but without the vesicles, was a by-product of the ceramic and metallurgical industries before the second millennium B.C. The deliberate production of synthetic basalt suggests that the potentialities of those by-products as a substitute for imported grinding stones was perceived and that the pyrotechnologies developed by potters and smiths were pooled in an experimental process that eventually yielded a consistent product.

For synthetic basalt to be produced required (i) that the possibility of melting soil had to have been conceived, (ii) that the typically small metal-smelting furnaces be increased in size without decreasing the maximum temperatures attained, and (iii) that the resulting product be cooled relatively slowly to ensure adequate crystal growth. This technology can only have come about through experimentation and as part of the wider process of innovation.

REFERENCES AND NOTES

1. E. Stone, *J. Field Archaeol.* **17**, 141 (1990); E. C. Stone and P. Zimansky, *ibid.* **21**, 437 (1994); *Sci. Am.* **272**, 118 (April 1995).
2. Mashkan-shapir's occupation was early second millennium B.C. in date, but also experienced limited occupations during the fourth millennium B.C. and the early first millennium A.D., making the date of samples derived from the surface unknown.
3. Because the closest basalt sources are more than 500 km from Mashkan-shapir, it seemed best to eliminate the complete range of known basalts as the possible sources for our material.
4. The Gulf War and its aftermath severely limited the samples available for study. No samples have been collected since the 1990 season. Samples derived from surface collections include a fragment of a large slab, one somewhat atypical handstone, and two surface collections of "slag." Excavated samples, which can be dated to the early second millennium B.C., include tiny chips of slag that were recovered from wet sieving for the recovery of plant remains—most of which were too small for thin sectioning—and a handful of larger samples. Of the excavated samples, one showed all the characteristics of synthetic basalt and had probably broken off of one of the in situ grinders, confirming the early second millennium B.C. date of the synthetic basalt industry.
5. We determined the liquidus temperatures in graphite capsules suspended in a vertical quench furnace. We controlled the oxygen fugacity (FO_2) at about 10^{-14} atm (10^{-9} Pa) (within the fayalite stability field at these temperatures) with a CO/CO_2 gas mixture. These conditions lie above the graphite saturation surface, so the graphite capsules slowly burned, limiting the duration of these experiments to a few hours. We therefore used sealed platinum capsules to perform cooling-rate experiments. The portion of each capsule in contact with the sample had previously been alloyed with Fe foil, determined by trial and error, such that the samples neither gained nor lost Fe. Although we did not directly control FO_2 in those sealed-tube experiments, similar liquidus temperatures and product phases convince us that the redox conditions differed little from those of the gas-mixing experiments. We photographed the thin sections of the cooling-rate experiments, and three of us (E.C.S., M.T.F., and D.H.L.) made blind comparisons of their textures with microphotographs of thin sections of a slab (MS3652) and a handstone (MS4353) to find the closest match. Samples that were completely melted formed no phenocrysts and yielded groundmass much coarser than that of the synthetic basalt, evidently a nucleation phenomenon. Samples that were not completely melted before cooling formed phenocrysts, and the groundmass size depended on cooling rate, a result similar to that found by G. E. Lofgren [*J. Petrol.* **24**, 229 (1983)] for olivine and plagioclase. Cooling rates of 5°C per minute produced groundmass much more fine-grained than that of the archaeological samples. Rates of 1°C per minute produced grain sizes only slightly smaller than that of the groundmass of the slabs. Thus, we infer that the actual cooling rates may have been slightly slower than 1°C per minute, perhaps on the order of 0.5°C per minute.
6. E. Carter, *Sumer* **46**, 60 (1993). E. Carter generously allowed us access to samples that she had collected and exported as part of her 1% surface survey from al-Hiba, the remains of the largely third millennium B.C. city of Lagash.
7. Several lines of evidence suggest that the synthetic basalt formed under relatively reducing conditions, which implies the use of charcoal as a fuel: (i) Magnetite is absent in the synthetic basalt, although its absence could also reflect the relatively low total Fe content and the incorporation of Fe into cpx. (ii) The most Fe-rich pyroxenes in the basalt would have oxidized to magnetite (or another ferric Fe-bearing phase) at FO_2's approximately five to six orders of magnitude below that of pure air [D. H. Lindsley and B. R. Frost, *Am. Mineral.* **77**, 987 (1992)]; because no ferric-rich phase is present, the true FO_2 must have been lower. (iii) Experiments in reducing CO/CO_2 mixtures yielded products similar in color to most of the samples; (iv) Mössbauer spectrography measurements on a sample of gray-black synthetic basalt show that the $Fe^{2+}:Fe^{3+}$ is approximately 3. Measurements were made by M. Darby Dyar on sample TAD3653. Virtually all the Fe in the spectrum is in cpx; 25.1% is ferric and 74.9% is ferrous. This result is qualitatively supported by mineral formulas calculated from electron microprobe analyses of cpx. In addition, cpx from the rare green samples tends to have somewhat higher contents of $NaFe^{3+}Si_2O_6$ and $CaFe^{3+}{}_2SiO_6$ compared to gray-black samples. This is consistent with green samples—and perhaps the greenish rind on gray-black slabs—forming at slightly higher FO_2. The need to have hot furnace gasses penetrate the silt may have led the smiths to choose soil lumps that were partially cemented with caliche; this could explain the high calcium content of the synthetic basalt. Furthermore, decarbonation during melting may have contributed to the vesicular texture of the slabs.
8. At the cooling rates (~0.5°C per minute) suggested by our experiments, the microporphyritic texture of the "basalts" would have been produced during the first 100° to 150°C of cooling (~3 to 5 hours), and it is possible that the furnace was then opened to speed cooling. The relatively slow rates are a strong indication that the slabs of synthetic basalt cooled and crystallized within the furnace.
9. Basaltic Volcanism Study Project, *Basaltic Volcanism on the Terrestrial Planets* (Pergamon, New York, 1981).

10. We thank W. Vernon of MASCA whose initial petrographic study confirmed that the Mashkan-shapir samples are different from any naturally occurring material, E. Carter for samples from al-Hiba, S. Landsberger for copper analyses of the "basalt" samples, and M. Darby Dyar for providing the Mössbauer measurement. Experimental work was supported by NSF grant EAR9304699 to D.H.L. Work at Brookhaven National Laboratory by G.H. was carried out under contract DE-AC02-98CH10886. Archaeological research conducted at Mashkan-shapir by E.C.S. was supported by NSF grant BNS8905058, National Endowment for the Humanities grant RO21890-89, National Geographic grants 3920-88, 4022-88, 4055-89, and 4206-89, American Schools of Oriental Research Grant 3018891383, and private donors. We also thank D. Killick for extremely helpful comments on an earlier version of this paper, L. Wells and T. Wilkinson for their advice on the geomorphology of Southern Iraq and J. Blackman for discussions of ancient ceramic technology.

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$(Mg,Fe)SiO_3$-Perovskite Stability Under Lower Mantle Conditions

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In three different experiments up to 100 gigapascals and 3000 kelvin, $(Mg,Fe)SiO_3$-perovskite, the major component of the lower mantle, remained stable and did not decompose to its component oxides (Mg,Fe)O and SiO_2. Perovskite was formed from these oxides when heated in a diamond anvil cell at pressures up to 100 gigapascals. Both $MgSiO_3$ crystals and glasses heated to 3000 kelvin at 75 gigapascals also formed perovskite as a single phase, as evident from Raman spectra. Moreover, fluorescence measurements on chromium-doped samples synthesized at these conditions gave no indication of the presence of MgO.

Although some past studies indicate that silicate perovskite is a dominant component of the lower mantle (*1*, *2*), recent experiments with CO_2 and yttrium-aluminum-garnet (YAG) laser heating in the diamond anvil cell (DAC) have suggested that $(Mg,Fe)SiO_3$-perovskite decomposes to (Mg,Fe)O and SiO_2 above 65 GPa (*3*, *4*). In one experiment where the temperature was not measured, (Mg,Fe)O and SiO_2 formed from $Mg_{0.87}Fe_{0.13}SiO_3$-perovskite at 70 GPa, with a CO_2 laser and a NaCl pressure medium (*3*). In another study, with a YAG laser but no pressure medium (*4*), $MgSiO_3$ broke down to MgO and SiO_2 above 65 GPa. The reason for this decomposition is most likely disequilibrium associated with large temperature gradients caused by the poor thermal insulating properties of the NaCl pressure medium, the lack of laser stabilization (*3*, *5*, *6*), or the

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YAG laser-heating technique used in the second experiment (*4*, *7*). Large temperature gradients are known to drive cation diffusion, resulting in the production of nonequilibrium multiphase assemblages (*8*, *9*). This effect has been demonstrated at pressures as low as 26 GPa with pyroxene ($Mg_{0.9}Fe_{0.1}SiO_3$) as a starting material (*10*).

We heated samples that were thermally insulated from the highly conductive diamonds with the defocused beam of a stabilized CO_2 laser (*11*, *12*). The pressure medium was either argon or CsCl, both providing quasi-hydrostatic pressure conditions around the heated samples. The combination of high optical absorption of the samples at the laser wavelength of 10.6 μm, the small thickness of the samples (on the order of 10 μm), and the effective thermal insulation by the argon or CsCl allowed essentially uniform heating of the sample with temperature gradients on the order of 10°/μm (*13*). We measured the temperature from the center of the hot spot with an uncertainty of ±100 K using the Planck radiation function (Fig. 1) (*14*). Heating durations ranged from 5 to 30 min. The temperature was quenched to ambient conditions within milliseconds by switching off the laser. Pressures were measured from micrometer-sized ruby chips placed at 2- to 3-μm distances from the sample. Pressure differences between ruby chips in the heated area did not exceed 1 GPa.

Four different starting materials were used: (i) fine-grained powder pellets (*15*) of stoichiometric mixtures of MgO and SiO_2, (ii) $Mg_{85}Fe_{15}O$, SiO_2, and synthetic ($MgSiO_3$), (iii) crystals (enstatite) (*16*), and (iv) glasses (*17*). For the stoichiometric mixtures of MgO and SiO_2 as well as $Mg_{0.85}Fe_{0.15}O$ and SiO_2, we used CsCl as a pressure medium because the pressed powder samples often disperse in an argon pressure medium. The powder mixtures were heated to 2800 K at 100 GPa, 2600 K at 78 GPa, and 2600 K at 74 GPa for 15, 15, and 5 min, respectively. We used Raman spectroscopy for phase identification because it is effective in detecting subtle structural changes in silicate perovskite to high pressures (*18*) and in identifying high-pressure polymorphs of SiO_2 (*19*). Raman spectra obtained from several spots of the heated area after temperature quenching (Fig. 2, A to C) showed all major lines of perovskite (*18*), but no lines for SiO_2 were detected (*19*).

In a second set of experiments, we heated synthetic enstatite to 2750 K at 75 GPa for 15 min. Again, the spectra (Fig. 3) only show features associated with perovskite. The perovskite Raman frequencies shown in Figs. 2 and 3 agree with those extrapolated from 65 GPa (*18*, *20*). We did not detect any modes associated with SiO_2 polymorphs (*19*, *21*).

In a third experiment, we used a method (*22*) for the detection of small amounts of MgO, which is Raman inactive and therefore could not have been detected in the above experiments, by doping samples with Cr^{3+}. MgO containing traces of Cr^{3+} exhibits a sharp fluorescence line at 699.2 nm at room pressure (*23*, *24*). As a test, we heated Cr-doped Mg_2SiO_4 (forsterite) at high pressure, producing MgO and $MgSiO_3$-perovskite. This test resulted in the perovskite Raman spectrum and the MgO:

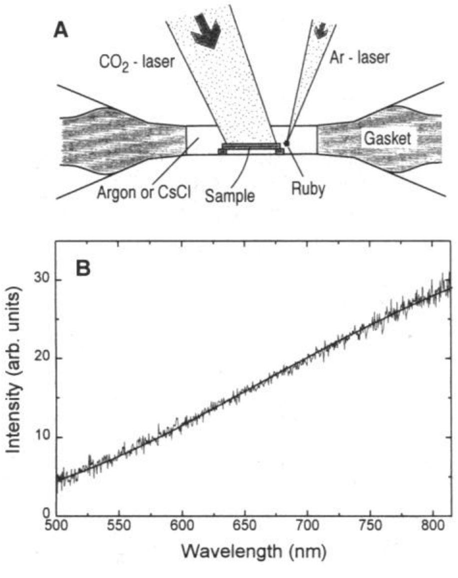


Fig. 1. (**A**) Schematic of the laser-heated DAC used in this study. The dried samples (dimensions 10 μm × 40 μm × 40 μm) were thermally insulated from the diamonds and heated with a defocused stabilized CO_2 laser (*11*, *12*). (**B**) Emission spectrum and the fitted Planck function of the heated sample at 78.0 GPa and 2578 ± 100 K; arb. units, arbitrary units.

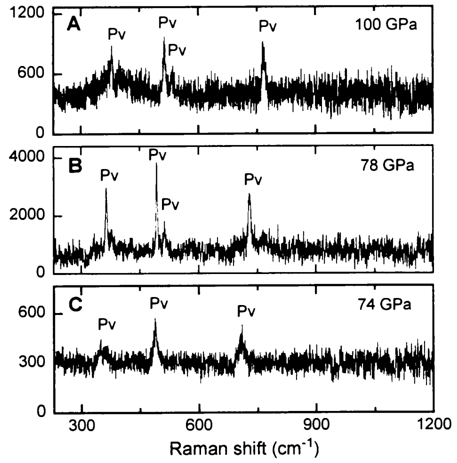


Fig. 2. Raman spectra taken at room temperature after heating stoichiometric powder mixtures of MgO and SiO_2 to (**A**) 2800 K at 100 GPa and (**B**) 2600 K at 78 GPa. (**C**) Raman spectrum of $Mg_{0.85}Fe_{0.15}O$ and SiO_2 heated to 2600 K at 74 GPa. All spectra exhibit only perovskite (Pv) bands (*18*).

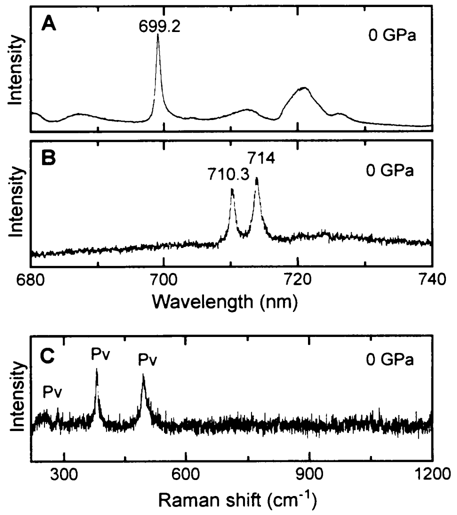
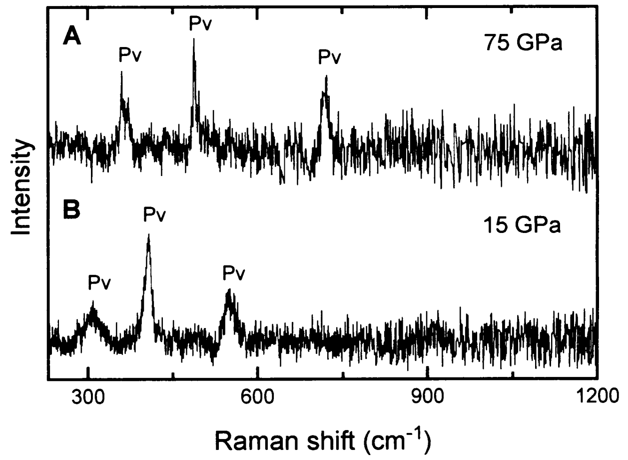


Fig. 4. Fluorescence spectra at ambient conditions of (**A**) MgO doped with 0.1 atomic % Cr^{3+} and (**B**) the recovered $MgSiO_3$ perovskite sample synthesized from Cr^{3+}-doped $MgSiO_3$ glass at 3000 K and 73 GPa. (**C**) Raman spectrum of the recovered sample in (B).

Fig. 3. Raman spectra at room temperature (**A**) after heating $MgSiO_3$ orthoenstatite to 2750 K at 75 GPa and (**B**) after decompression of the sample in (A) to 15 GPa with no further heating. All bands belong to the perovskite structure (*18*).



Cr fluorescence spectrum. Thus, we would expect that a breakdown of Cr-doped $MgSiO_3$ to its oxide components would also result in such a fluorescence spectrum (25). The lack of phase transitions in MgO additionally allowed measurements with higher sensitivity on the recovered samples outside the diamond cell. We found no MgO after heating $MgSiO_3$ glass, doped with 0.1 atomic % Cr^{3+}, in an argon medium at 3000 K and 73 GPa for 10 min (Fig. 4, A and B). Instead, the recovered perovskite crystal (Fig. 4C) exhibits two prominent fluorescence peaks at 710.2 and 714 nm (Fig. 4B).

We have shown that silicate perovskite heated with small temperature gradients in a quasi-hydrostatic pressure medium does not decompose to its component oxides and that instead these oxides react to form perovskite when heated to the highest pressures in our experiments (100 GPa). These results are important in view of new evidence for a dense high-pressure polymorph of SiO_2 (26), because they show that, at the present pressure and temperature conditions, $(Mg,Fe)SiO_3$-perovskite is more dense than a $(Mg,Fe)O$-SiO_2 assemblage.

REFERENCES AND NOTES

1. E. Knittle and R. Jeanloz, *Science* **235**, 668 (1987).
2. N. Funamori and T. Yagi, *Geophys. Res. Lett.* **20**, 387 (1993).
3. C. Meade, H. K. Mao, J. Hu, *Science* **268**, 1743 (1995).
4. S. K. Saxena *et al.*, *ibid.* **274**, 1357 (1996).
5. We laser-heated samples in a large variety of pressure media and found that the laser power required in a NaCl pressure medium is markedly higher than that for CsCl or KBr media. This result is consistent with a comparative study of several alkali halides, where the thermal conductivity of NaCl in the B2 structure was estimated to be at least three times that of CsCl [G. A. Slack and R. G. Ross, *J. Phys. C* **18**, 3957 (1985)].
6. We measured temperature fluctuations in silicate samples using unstabilized CO_2 laser techniques of order 1000 K.
7. YAG laser heating without thermally insulating media causes temperature gradients in silicates ranging from 100° to 1000° per micrometer depending on the peak temperature [D. L. Heinz and R. Jeanloz, *J. Geophys. Res.* **92**, 11437 (1987)].
8. A. J. Campbell and D. Heinz, *Geophys. Res. Lett.* **19**, 1061 (1992).
9. H.-k. Mao, G. Shen, R. J. Hemley, *Science* **278**, 2098 (1997).
10. Y. Fei, Y. Wang, L. W. Finger, *J. Geophys. Res.* **101**, 11525 (1996).
11. R. Boehler and A. Chopelas, in *High Pressure Research: Applications to Earth and Planetary Sciences*, Y. Syono and M. H. Manghnani, Eds. (American Geophysical Union, Washington, DC, 1992), pp. 55–60.
12. A. Chopelas and R. Boehler, in *High Pressure Research: Applications to Earth and Planetary Sciences*, Y. Syono and M. H. Manghnani, Eds. (American Geophysical Union, Washington, DC, 1992), pp. 101–108.
13. R. Boehler and A. Zerr, *Science* **264**, 280 (1994).
14. The emitted light from the sample was measured from areas of 2 to 3 μm in diameter in the center of the hot spot with a charge-coupled device (CCD) detector in the wavelength range of 500 to 815 nm. Emissivity was taken to be independent of the wavelength.
15. We used MgO and SiO_2 with 99.999% purity. $Mg_{0.85}Fe_{0.15}O$ was provided by S. Kesson (Australian National University). Powder mixtures with 1- to 2-μm grain size were compressed at about 5 GPa with a DAC to form pellets with about 10-μm thickness.
16. The orthoenstatite sample was from the Smithsonian Institute (#137311).
17. Cr-doped $MgSiO_3$ glass samples were provided by S. Kesson and were also synthesized from stoichiometric amounts of MgO and SiO_2 quartz powders of 99.999% purity and Cr_2O_3 of 99.5% purity by melting with a CO_2 laser and rapid quenching between two platinum-plated copper blocks.
18. A. Chopelas, *Phys. Earth Planet. Inter.* **98**, 3 (1996).
19. J. K. Kingma, R. E. Cohen, R. J. Hemley, H. K. Mao, *Nature* **374**, 243 (1995).
20. The linear extrapolation of the Raman frequencies from 65 GPa (*18*) agrees with those found here to 100 GPa, except for the highest wavenumber mode, which at the highest pressure is 13 cm^{-1} lower. Upon pressure release, the position of the Raman modes matches those measured previously.
21. The strongest Raman mode in the post-stishovite phase (*19*) would appear at 950 cm^{-1} at 70 GPa. To check whether some other phase of SiO_2 had formed, we released the pressure in our experiments to within the stability field of stishovite, because the reported high-pressure polymorphs of SiO_2 were found to revert to the stishovite phase upon pressure release (*19*, *26*). We did not detect any Raman mode of stishovite, the strongest of which would appear, for example, at 801 cm^{-1} in the spectrum taken at 15 GPa (Fig. 3B).
22. G. Serghiou, A. Zerr, A. Chopelas, R. Boehler, *Phys. Chem. Miner.* **25**, 193 (1998).
23. A. Chopelas, in *Mineral Spectroscopy: A Tribute to Roger Burns*, M. D. Dyar, C. McCammon, M. W. Schaefer, Eds. (Special Publication 5, Geochemical Society, Columbus, OH, 1996), pp. 229–242.
24. Raman and fluorescence spectra from the samples were excited with the 457.9-nm line of a Spectra Physics 2025-5 argon ion laser. The laser light entered the diamond cell at an incident angle of 25° and was focused to a 15-μm spot on the sample with powers ranging from 5 to 100 mW depending on pressure. The signal was detected with a liquid nitrogen–cooled CCD detector or a photomultiplier. Spectra were taken at room temperature from the laser-heated spot.
25. Cr^{3+} on part per million levels in MgO crystals has been detected by this method [A. M. Glass, *J. Chem. Phys.* **46**, 2080 (1967)].
26. L. S. Dubrovinsky *et al.*, *Nature* **388**, 362 (1997).
27. We thank A. Chopelas, O. Tschauner, V. Hillgren, and L. Nigay for many helpful discussions.

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Perennial Antarctic Lake Ice: An Oasis for Life in a Polar Desert

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The permanent ice covers of Antarctic lakes in the McMurdo Dry Valleys develop liquid water inclusions in response to solar heating of internal aeolian-derived sediments. The ice sediment particles serve as nutrient (inorganic and organic)–enriched microzones for the establishment of a physiologically and ecologically complex microbial consortium capable of contemporaneous photosynthesis, nitrogen fixation, and decomposition. The consortium is capable of physically and chemically establishing and modifying a relatively nutrient- and organic matter–enriched microbial "oasis" embedded in the lake ice cover.

The McMurdo Dry Valleys, Antarctica, is one of the coldest and driest deserts on Earth. Lakes in this region are permanently ice covered (*1*). The ice is typically 3 to 6 m thick and contains a layer of sand and organic matter of aeolian origin below the surface. This layer represents a dynamic equilibrium between downward movement of sediments as a result of melting during the summer and upward movement of ice from ablation at the surface and freezing at the bottom. Liquid water inclusions are present in this layer for about 150 days during the summer when solar radiation is continuous; up to 40% of the total ice cover volume during this period can be liquid water (*2*, *3*). We discovered that the ice meltwater supports a viable microbial assemblage associated with the sediment layer. Here, we describe the ecosystem.

We collected ice samples from six lakes (Bonney, Hoare, Fryxell, Miers, Vanda, and Vida) between August and October 1993 and 1995 using 10-cm-diameter coring devices. Cores were sectioned, melted, and analyzed for photoautotrophic and heterotrophic activity; biomass, sediment, and nitrous oxide content; and chemistry (*4*). Most of

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