surface of elastomeric stamps or flexible photomasks. Subsequent processing steps transform patterns on these cylindrically symmetrical substrates into structures with different symmetries and more complex topologies. Microelectrochemistry provides an additive method that strengthens thin metal patterns produced by printing and etching and that welds proximal, nonconnected structures. Potential applications for these techniques may be in the fabrication of ultralight structures for micro air and space vehicles, components for microelectromechanical systems, 3D metallic membranes and electrodes, and, at smaller dimensions, dielectric structures for photonic band gap materials.

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From Shifting Silt to Solid Stone: The Manufacture of Synthetic Basalt in Ancient Mesopotamia

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Slabs and fragments of gray-black vesicular "rock," superficially resembling natural basalt but distinctive in chemistry and mineralogy, were excavated at the second-millennium B.C. Mesopotamian city of Mashkan-shapir, about 80 kilometers south of Baghdad, Iraq. Most of this material appears to have been deliberately manufactured by the melting and slow cooling of local alluvial silts. The high temperatures (about 1200°C) required and the large volume of material processed indicate an industry in which lithic materials were manufactured ("synthetic basalt") for grinding grain and construction.

Lacking basic raw materials such as stone, metal ores, or large timber, the ancient inhabitants of southern Mesopotamia used the one natural resource they possessed in abundance, alluvial silt, for pottery, architecture, writing materials, objects of art, and even tools such as sickles. The evidence presented here, however, demonstrates that they also converted silt into a material that in color, texture, and mechanical properties is similar to natural vesicular basalt—that is, a hard, durable, useful substitute for stone that could be used for such purposes as grinding grain.

A surface survey (*1*) conducted at the early second millennium (*2*) B.C. site of Mashkan-shapir suggested that some of the overfired material that litters Mesopotamian sites might not be kiln debris. Several large, rectangular (about 80 cm by 40 cm by 8 cm) slabs were found near the remains of the main temple in Mashkan-shapir (Fig. 1). One of the two large sides of each was flat, with the opposite face uneven. The material resembles basalt, but the uniform size, shape, and characteristic appearance of the slabs suggest that they are not naturally formed rock. They appear to be the result of deliberate manufacture and not an accidental by-product of some other manufacturing process.

At Mashkan-shapir, these slabs were only found in the southern, religious quarter, but their characteristic profile, with uneven top and flat bottom surfaces (Fig. 2), can be used to link them with several hundred fragments found across the site. The large slabs and fragments were around 8 cm thick, except where the latter had been worn down by grinding. Except where broken, the edges show evidence of deliberate trimming. Closest to the flat face, the vesicles are small (0.1 to 0.5 mm), and they increase in size as they approach the uneven face (2 to 3 mm). The pieces are black to dark gray in color except for the uneven surface, which usually exhibits a greenish tinge. Compositionally, this material falls outside the range of known basalts (*3*), particularly in the high CaO and K_2O concentrations and low amounts of Al_2O_3 and total Fe, but is similar to the composition of a sample of alluvial silt from the area (Table

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Table 1. Comparison of synthetic basalts with natural basalts. All analyses normalized to 100% by weight to facilitate comparison; errors are ±1% of the amount present. In the sample column, MS indicates a sample from Mashkan-shapir, and AH indicates al-Hiba.

Sample	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
Range of natural basalts (9)	47.6–55.9	1.0–3.3	12.5–18.1	8.7–14.4	0.19–0.27	2.7–10.5	6.9–11.9	1.89–3.27	0.1–0.7	0.07–0.4
Gray-black slab (MS 3652)*	52.93	0.79	12.52	6.56	0.13	6.44	16.94	1.89	1.62	0.18
Green handstone (MS 4353)*	53.33	0.77	11.78	6.22	0.13	6.97	16.93	1.76	1.90	0.21
"Slag" (MS-H6A), green inclusions*	53.28	0.67	11.14	5.35	0.13	8.11	16.29	2.31	2.13	0.58
"Slag" (MS-H6A), gray-black matrix*	53.51	0.71	11.21	6.06	0.12	7.33	16.18	2.06	2.16	0.67
Gray-black slag (AH-5)*	51.06	0.70	12.19	6.49	0.13	7.3	16.7	2.06	2.4	0.98
Silt from auger sample from MS†	51.70	0.64	11.77	6.67	0.14	6.85	18.09	2.08	1.60	0.45

*Analysis conducted by x-ray fluorescence by XRAL Industries. †Silt from Mashkan-shapir at the 45- to 70-cm level—chosen because it probably represents the surface alluvium at the time the site was occupied—was taken from the one drill-core sample exported to the United States. Analysis of this sample was by electron microprobe on glass made by fusing the soil at 1200°C.

1). The samples contain less than 10 ppm Cu, indicating that they were not formed as a by-product of Cu smelting. Thus, this material may be anthropogenic in origin.

Small pieces of synthetic basalt were found throughout the site, on the surface and in excavation (4). In a 1000-m^2 excavation area, 17 pieces were encountered, all lying in situ, the flat side up and used for grinding grain. One still had the handstone, also of synthetic basalt, lying on top. In addition, some fragments on the surface were used for construction, either built into baked brick walls or fashioned into door sockets. The consistency in size, shape, color, and texture of the synthetic basalts as well as their ubiquity—we estimate more than 100 m^3 of the material in the site as a whole—indicate that this was not simply reuse of material that had been accidentally overfired. Thus, synthetic basalt appears to have been manufactured in some quantity as a substitute for the natural basalt that had been used for grinding grain in all parts of the ancient Near East since the beginnings of agriculture.

In petrographic thin section, synthetic basalts were characterized by matted clinopyroxene (cpx) crystals of the diopside-hedenbergite series embedded in a glassy matrix. Plagioclase was rare to absent; most samples contained sparse, isolated quartz and chromite grains, each usually surrounded by a reaction zone. Typically, the synthetic basalt was microporphyritic, with blocky cpx phenocrysts (typically 80 μm by 100 μm) set in a matrix of felted acicular cpx (2 to 10 μm by 80 μm) and orange-brown glass (Fig. 3). By contrast, the overfired debris found at Mashkan-shapir lacked microphenocrysts, had only the felted acicular cpx, was generally very small in size, and the glass was usually clear.

The microporphyritic texture of the synthetic basalts suggests that a pyroxene-normative material was brought almost to its liquidus, thus allowing the cpx phenocrysts to crystallize, and was then cooled slowly enough for finer, groundmass cpx to form. Our experiments (5) show that the liquidus (complete melting) temperatures for both the synthetic basalt and the local alluvial silts are close to 1200°C. We were able to approximate the microporphyritic texture by heating either material to 1180° or 1190°C (just below the liquidus) and then cooling it at a rate of 1.0°C per minute. Our ability to recreate the texture of the Mashkan-shapir slabs starting with silt provides strong support for the assumption that silt was the raw material for making the synthetic basalt.

The use of local silts for the production of synthetic basalt at Mashkan-shapir would seem to link this technology to the ceramic industry, but it was the metal-workers who had perfected high-temperature melting and the clean separation of the final product. It is commonly held that all Mesopotamian copper and bronze was originally imported in ingot form and that the Mesopotamian smiths did no more than refine and cast the final products. However, the discovery of cuprous slags and copper ores from Mashkan-shapir and al Hiba (6)—the two southern Mesopotamian sites that have been the most intensely surveyed—provides evidence for copper smelting, albeit on a small scale, taking place within the southern floodplain. By contrast, the large size of the synthetic basalt slabs indicates that they may have been the result of a much larger scale operation, incorporating some technology derived from the ceramic and metallurgical industries.

Until we can return to Mashkan-shapir for further excavations, we can only surmise the process. The synthetic basalt must have been produced in large furnaces, at least 1 m in diameter given the size of our largest blocks. These furnaces probably had thick, chaff-tempered walls for maximum insulation and were charged with a combination of charcoal and lumps of silt (7). Once near melting of the silt had been achieved, the structure must have been left to cool for 20 to 40 hours, the time necessary for the crystal growth observed in the thin sections to have occurred (8).

The evidence of the production of synthetic basalt at Mashkan-shapir provides information on the technological achieve-

Fig. 1. Large slab of synthetic basalt in situ. Slab measures ~80 cm by 40 cm by 8 cm. (Photo: Paul Zimansky)

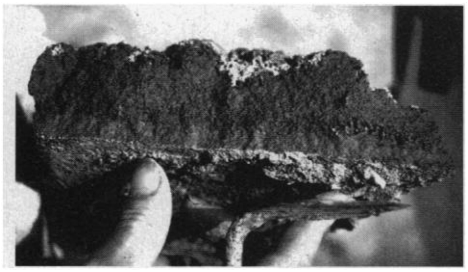

Fig. 2. Section (~30 cm by 8 cm) across slab of synthetic basalt. (Photo: Paul Zimansky)

Fig. 3. Thin section of the slab shown in Fig. 2. Microphenocrysts and elongate groundmass crystals of cpx (mainly light to medium gray) in a glassy matrix (black). The circular regions in the upper left corner are microvesicles. Crossed polarizers; width of field: 1 mm. (Photo: William Vernon)

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.

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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.
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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.
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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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