## The Miller Volcanic Spark Discharge Experiment

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In 1953, Miller (1) published a short paper describing the spark discharge synthesis of amino acids from a reducing gas mixture thought to represent the atmosphere of the early Earth. This exper-

We were interested in the second apparatus because it possibly simulates the spark discharge synthesis by lightning in a steam-rich volcanic cruption (6) (Fig. 1A). Miller identified five different amino

Molar Ratio 10-2 10 Gly Ala β-Ala IsoSer a-AIB **β-AIB** α-ABA **B-ABA** Tungsten γ-ABA electrodes **HomoSer** 2-Me-Ser Asp Condenser **β-ОН-А**sp 5 liter Val Isoval flask Norval Orn Glu 2-Me-Glu a-AAA Steam Phe aspirator MA EA Ethanolamine Iso-PA 500 cc N-PA

**Fig. 1.** (A) Lightning associated with the 3 May 2008 eruption of the Chaiten volcano, Chile. [Photo credit: Carlos Gutierrez/UPI/ Landov] (B) The volcanic spark discharge apparatus used by Miller (3). Gas quantities added were 200 torr of  $CH_4$ , 200 torr of  $CH_4$ , and 100 torr of  $CH_4$ , 200 torr of  $CH_4$ , and 100 torr of  $CH_4$  (cc) flask and boiled, and the apparatus sparked with a Tesla coil for 1 week; (C) Moles (relative to glycine = 1) of the various amino acids detected in the volcanic apparatus vials [see (2) and table S1 for abbreviations]. Amino acids underlined have not been previously reported in spark discharge experiments. Values for amines are minimum values because of loss due to their volatility during workup.

iment showed that the basic molecules of life could be synthesized from simple molecules, suggesting that Darwin's "warm little pond" was a feasible scenario.

After Miller's death on 20 May 2007, we found several boxes containing vials of dried residues. Notebooks (2) indicated that the vials came from his 1953–54 University of Chicago experiments that used three different configurations (3, 4). One was the original apparatus used in (1). Another incorporated an aspirating nozzle attached to the water-containing flask, injecting a jet of steam and gas into the spark. The third incorporated the aspirator device but used a silent discharge instead of electrodes. Although Miller repeated his experiment in 1972 with use of the original architecture (5), the others were never tested again.

acids, plus several unknowns, in the extracts from this apparatus (3). Product yields appeared somewhat higher than those in the classical configuration, although Miller never confirmed this. We reanalyzed 11 vials in order to characterize the diversity of products synthesized in this apparatus.

The residues in the vials were resuspended in 1-ml aliquots of doubly distilled deionized water and characterized by high-performance liquid chromatography and liquid chromatography–time of flight mass spectrometry that allows for identification at the sub-picomolar (<10<sup>-12</sup> M) level (2). We identified 22 amino acids and five amines in the volcanic experiment (Fig. 1C), several of which had not been previously identified in Miller's experiments. Vials

from the other two experiments were also reanalyzed and found to have a lower diversity of amino acids (table S1). The yield of amino acids synthesized in the volcanic experiment is comparable to, and in some cases exceeds, those found in the experiments Miller conducted (1, 3, 5). Hydroxylated compounds were preferentially synthesized in the volcanic experiment. Steam injected into the spark may have generated OH radicals that reacted with either the amino acid precursors or the amino acids themselves (7).

Geoscientists today doubt that the primitive atmosphere had the highly reducing composition Miller used. However, the volcanic apparatus experiment

> suggests that, even if the overall atmosphere was not reducing, localized prebiotic synthesis could have been effective. Reduced gases and lightning associated with volcanic eruptions in hot spots or island arc-type systems could have been prevalent on the early Earth before extensive continents formed (8). In these volcanic plumes, HCN, aldehydes, and ketones may have been produced, which, after washing out of the atmosphere, could have become involved in the synthesis of organic molecules (3, 4, 8). Amino acids formed in volcanic island systems could have accumulated in tidal areas, where they could be polymerized by carbonyl sulfide, a simple volcanic gas that has been shown to form peptides under mild conditions (9).

## **References and Notes**

- 1. S. L. Miller, Science **117**, 528 (1953).
- Analytical details and additional data are available as supporting material on Science Online.
- 3. S. L. Miller, J. Am. Chem. Soc. 77, 2351 (1955).
- 4. A. Lazcano, J. L. Bada, *Origins Life Evol. Biosph.* **33**, 235 (2003).
- D. Ring, W. Yecheskel, N. Friedmann,
  L. Miller, *Proc. Natl. Acad. Sci. U.S.A.* 69, 765 (1972).
- S. R. McNutt, C. M. Davis, J. Volcanol. Geotherm. Res. 102, 45 (2000).
- 7. D. Ring, S. L. Miller, *Origins Life Evol. Biosph.* **15**, 7 (1984).
- 8. R. D. Hill, *Origins Life Evol. Biosph.* **22**, 277 (1991).
- L. Leman, L. Orgel, M. Reza Ghadiri, Science 306, 283 (2004).

## Supporting Online Material

www.sciencemag.org/cgi/content/full/322/5900/404/DC1 Materials and Methods

Figs. S1 and S2 Table S1

References and Notes

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