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basal of the two. Such a placement of the more terrestrially adapted *Ichthyostega* (16), taken together with the features indicating weight-bearing ability (ventrally facing radial and ulnar facets) of the very primitive ANSP 21350 (9), would suggest a scenario of rapid early terrestrialization rather different from the currently predominant “aquatic Devonian tetrapods” model.

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#### Supporting Online Material

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Materials and Methods

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## A Ferroelectric Oxide Made Directly on Silicon

Maitri P. Warusawithana,<sup>1</sup> Cheng Cen,<sup>2</sup> Charles R. Slesman,<sup>2</sup> Joseph C. Woicik,<sup>3</sup> Yulan Li,<sup>4</sup> Lena Fitting Kourkoutis,<sup>5</sup> Jeffrey A. Klug,<sup>6</sup> Hao Li,<sup>7</sup> Philip Ryan,<sup>8</sup> Li-Peng Wang,<sup>9,10</sup> Michael Bedzyk,<sup>6,11</sup> David A. Muller,<sup>5</sup> Long-Qing Chen,<sup>4</sup> Jeremy Levy,<sup>2</sup> Darrell G. Schlom<sup>1\*</sup>

Metal oxide semiconductor field-effect transistors, formed using silicon dioxide and silicon, have undergone four decades of staggering technological advancement. With fundamental limits to this technology close at hand, alternatives to silicon dioxide are being pursued to enable new functionality and device architectures. We achieved ferroelectric functionality in intimate contact with silicon by growing coherently strained strontium titanate (SrTiO<sub>3</sub>) films via oxide molecular beam epitaxy in direct contact with silicon, with no interfacial silicon dioxide. We observed ferroelectricity in these ultrathin SrTiO<sub>3</sub> layers by means of piezoresponse force microscopy. Stable ferroelectric nanodomains created in SrTiO<sub>3</sub> were observed at temperatures as high as 400 kelvin.

For decades, semiconductor device designers have envisioned numerous devices using ferroelectrics in combination with semiconductors. These concepts include non-volatile memories (1, 2), “smart” transistors that can be used as temperature or pressure sensors (3), and ferroelectric field-effect transistors whose logic states require no power to maintain (4, 5). Missing, however, has been the ability to integrate ferroelectrics directly with mainstream semiconductors. Our work bridges this gap, demonstrating ferroelectric functionality in a

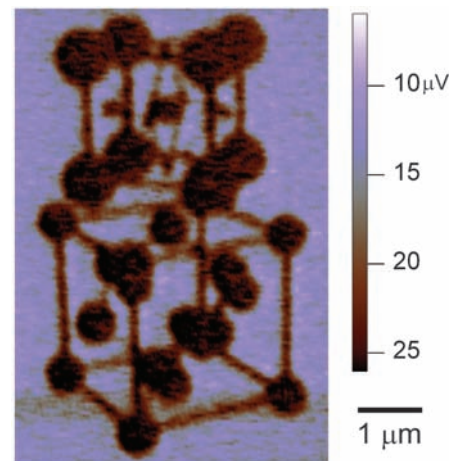
SrTiO<sub>3</sub> thin film grown directly, without any intermediate layers and free of reaction, on the workhorse of semiconductor technology, silicon.

Recent work has explored ways to use epitaxial strain to induce or enhance ferroelectricity in thin films (6–8). Ferroelectric responses that are distinct from naturally occurring bulk ferroelectrics have also been obtained through the growth of nano-engineered superlattices containing different dielectric and ferroelectric phases (9–11). In all of the above-referenced studies, the substrate and film are isostructural. For commensurate SrTiO<sub>3</sub>/(001) Si, the interface is structurally far more complex, connecting a diamond structure (silicon) with a perovskite (SrTiO<sub>3</sub>) (Fig. 1). The high reactivity of silicon with many elements and their oxides (12) presents a formidable challenge to the integration of functional oxides with silicon, as does the tendency of a pristine silicon surface to rapidly form its own oxide.

Using molecular beam epitaxy (MBE), we have deposited epitaxial SrTiO<sub>3</sub> films on (001) Si substrates via a kinetically controlled growth process (13, 14) (fig. S1), which synchrotron diffraction measurements reveal to be commensurately strained up to a thickness of ~24 Å. The growth method used differs substantially from those reported previously (15–17) for the epitax-

ial integration of SrTiO<sub>3</sub> with silicon (13) (figs. S1 and S2). Although bulk SrTiO<sub>3</sub> is not ferroelectric at any temperature, the large compressive strain (~1.7%) induced on commensurately strained SrTiO<sub>3</sub>/Si is predicted to result in ferroelectricity (13, 18) with a Curie temperature (T<sub>C</sub>) near room temperature (fig. S3 and table S1) and an out-of-plane polarization (6, 8, 19). Films whose thickness exceeds the equilibrium critical thickness (20), however, are unstable to relaxation, which would lower the transition temperature and produce nanoscale heterogeneity.

We discuss data from five SrTiO<sub>3</sub> films identified by their nominal thickness in molecular layers (ML): 5 ML, 6 ML, 8 ML, 10 ML, and 20 ML. These SrTiO<sub>3</sub> films were grown on (001) Si substrates by MBE, in layers of one to a few molecular strata at a time, until the desired thickness was reached (13). The silicon substrates used in this study were doped with n-type phosphorus (1 × 10<sup>15</sup> to 5 × 10<sup>15</sup> phosphorus atoms/cm<sup>3</sup>) having a resistivity of 1 to 4 ohm-cm. Each layer that was grown involved a controlled sequence of



**Fig. 1.** Structure of the SrTiO<sub>3</sub>/Si interface, written and imaged on a 6 ML SrTiO<sub>3</sub>/Si sample by PFM. With the 45° in-plane rotational offset between the unit cells (15), the epitaxial orientation relationship is (001) SrTiO<sub>3</sub> // (001) Si and [110] SrTiO<sub>3</sub> // [100] Si.

<sup>1</sup>Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA. <sup>2</sup>Department of Physics and Astronomy, University of Pittsburgh, Pittsburgh, PA 15260, USA. <sup>3</sup>National Institute of Standards and Technology, Gaithersburg, MD 20899, USA. <sup>4</sup>Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802, USA. <sup>5</sup>School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853, USA. <sup>6</sup>Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208, USA. <sup>7</sup>Applied Research and Technology Center, Motorola Inc., Tempe, AZ 85284, USA. <sup>8</sup>Ames Laboratory, Ames, IA 50011, USA. <sup>9</sup>Intel Corporation, Santa Clara, CA 95052, USA. <sup>10</sup>TricornTech, San Jose, CA 95129, USA. <sup>11</sup>Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA.

\*To whom correspondence should be addressed. E-mail: schlom@cornell.edu

steps (13, 14) that kinetically suppress the oxidation of the substrate and reduce the tendency of the film to form islands (21) (fig. S4).

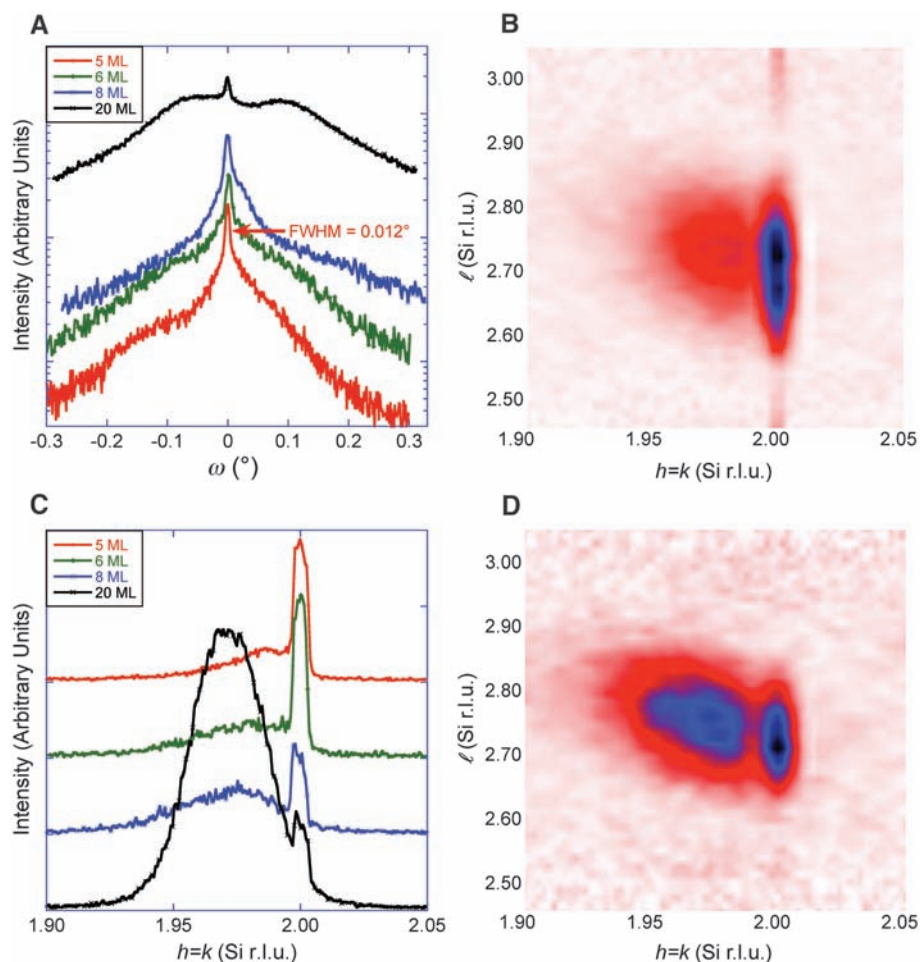
X-ray diffraction reveals the structural quality and strain relaxation that occurs in the SrTiO<sub>3</sub> films as thickness is increased. Rocking curves in  $\omega$  [where the angle of incidence ( $\theta$ ) between the

x-ray beam and the sample is rocked while leaving the detector position ( $2\theta$ ) fixed] of the out-of-plane SrTiO<sub>3</sub> 002 reflection are shown in Fig. 2A. Each curve displays an intense and narrow central peak due to coherently strained SrTiO<sub>3</sub> on top of a broad background peak (13). The height of the sharp central peak in relation to

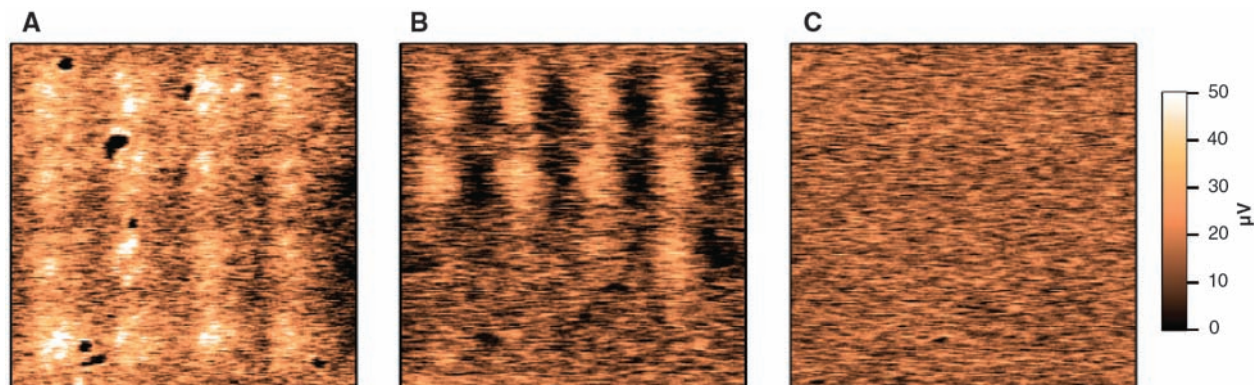
the background on this log intensity scale gives an indication of the fraction of the SrTiO<sub>3</sub> film that is coherently strained. The coherently strained fraction of the SrTiO<sub>3</sub> films decreases as the film thickness is increased. The full width at half maximum (FWHM) of the 5 ML sample, 0.012°, is representative of the sharpness of the coherent peaks (fig. S5).

We used x-ray diffraction to determine the in-plane strain of the SrTiO<sub>3</sub> films (13, 22). Because the out-of-plane lattice constant of SrTiO<sub>3</sub> is distinct from that of silicon, the in-plane lattice constant of SrTiO<sub>3</sub> can be obtained by measuring an off-axis SrTiO<sub>3</sub> reflection where there is no overlap with a substrate peak. Figure 2C shows scans made through the SrTiO<sub>3</sub> 202 peak for the 5 ML, 6 ML, 8 ML, and 20 ML samples. The sharp peak observed at  $h = k = 2.00$  Si reciprocal lattice units (r.l.u.) is due to the commensurate portion of the SrTiO<sub>3</sub> films with in-plane lattice constant  $= a_{\text{Si}}/\sqrt{2} = 3.840$  Å. As the film thickness increases, the relative integrated intensity of the sharp peak decreases while that of a broad peak at  $h = k < 2.00$  Si r.l.u. increases. The plot clearly shows the transition from mostly commensurate SrTiO<sub>3</sub> to mostly relaxed SrTiO<sub>3</sub> as the film thickness is increased. Reciprocal space maps of the SrTiO<sub>3</sub> 202 peak for the 6 ML and 8 ML samples are shown in Fig. 2, B and D, respectively. The 6 ML sample (Fig. 2B) has its diffracted intensity mostly centered at  $h = k = 2.00$  Si r.l.u., whereas for the 8 ML sample (Fig. 2D), more spectral weight is observed at lower values of  $h = k$  (i.e., at larger in-plane lattice constants) because of relaxation of the SrTiO<sub>3</sub>. The reciprocal space map for the 8 ML sample also shows how the spectral weight tails off to higher  $\ell$  with smaller  $h = k$  as strain relaxation sets in. From  $\ell$  scans made across the coherent peak at  $h = k = 2.00$  Si r.l.u., we find that the coherent peak occurs at  $\ell \sim 2.71$  Si r.l.u.

To check for ferroelectricity in these strained SrTiO<sub>3</sub>/(001) Si films, we used piezoresponse force microscopy (PFM), a technique that has been demonstrated on ferroelectric films as thin as 28 Å (23–26). With strain relaxation occurring for SrTiO<sub>3</sub>/(001) Si film thickness as small as 8 ML ( $\sim 32$  Å), measurement of the piezoelectric

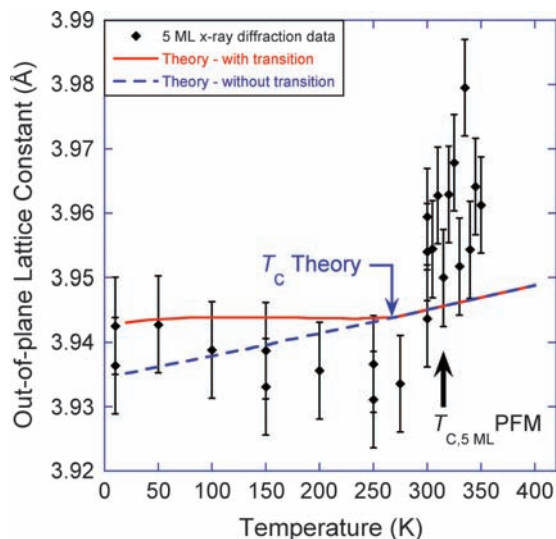


**Fig. 2.** The strain state of the SrTiO<sub>3</sub> films revealed by x-ray diffraction. (A) Rocking curves in  $\omega$  of the out-of-plane SrTiO<sub>3</sub> 002 reflection. (B) Reciprocal space map of the 202 SrTiO<sub>3</sub> peak for the 6 ML sample. Note the beating along the  $\ell$  direction. (C) Off-axis scans through the 202 SrTiO<sub>3</sub> peak. (D) Reciprocal space map of the 202 SrTiO<sub>3</sub> peak for the 8 ML sample. In (B) and (D), the intensity increases from white to red to blue to black.



**Fig. 3.** PFM images (1  $\mu\text{m}$  by 1  $\mu\text{m}$ ) of a 4  $\times$  4 pattern of domains written on the 5 ML SrTiO<sub>3</sub>/Si sample at different temperatures. (A)  $T = 298$  K. (B)  $T = 314$  K. (C)  $T = 323$  K.

**Fig. 4.** Temperature dependence of the out-of-plane lattice constant of SrTiO<sub>3</sub> strained commensurately to the underlying silicon substrate. Theoretical prediction from thermodynamic analysis is shown, along with experimental data obtained from x-ray diffraction measurements of the 5 ML sample. The error bars reflect the maximum error expected considering systematic errors and variation in sample thickness. Some hysteresis between data taken on heating and cooling is evident. Also indicated is the transition temperature observed from PFM measurements for the 5 ML sample ( $T_{C,5\text{ ML PFM}}$ ).



response of such thin layers is challenging. The large  $d_{33}$  coefficients predicted for strained SrTiO<sub>3</sub>/(001) Si (fig. S6), however, make it a reasonable signal to probe. Local electric fields were applied across the SrTiO<sub>3</sub> layer by means of a biased, conducting atomic force probe, and the resulting piezoelectric response of the strained SrTiO<sub>3</sub> film was subsequently imaged using the same probe (13). At room temperature, we found that domains of both polarities could be patterned on the 5 ML, 6 ML, 8 ML, and 10 ML samples, but not on the 20 ML sample. Figure 1 shows a PFM image written on the 6 ML sample at room temperature. In all of the samples that exhibited ferroelectricity via piezoresponse, a preferred downward polarization was observed (fig. S7). This agrees with reported x-ray fine structure measurements (27) and indicates that strained SrTiO<sub>3</sub> films on (001) Si are prepoled in their as-grown state. The lack of observable ferroelectricity in the 20 ML sample is consistent with x-ray diffraction measurements showing that the 20 ML sample is mainly relaxed (Fig. 2C) and helps rule out other possible mechanisms, such as changes in surface chemistry, for the observed piezoelectric response in other samples. A retention study of the written domains was also carried out for the 6 ML sample at room temperature (13) (figs. S8 and S9). The domain pattern was observed to be stable over a 72-hour period, at which point the pattern was erased by rastering the atomic-force probe with a constant voltage over the patterned area.

PFM measurements performed as a function of temperature revealed a rather sharp phase transition, above which ferroelectric domains are unstable. Figure 3 shows a series of three PFM measurements made on the 5 ML sample at different temperatures. Each image was acquired ~30 min after writing a  $4 \times 4$  array of square domains. Although some features that are associated with imperfections on the sample surface also showed up on these images, at  $T = 298$  K each of the 16 domains could be observed (Fig.

3A). The temperature was increased, and at  $T = 314$  K only 9 of the 16 domains could be seen (Fig. 3B). The existence of a single domain on the third row from the top rules out a variety of possible measurement artifacts, such as a “wandering” cantilever resonance frequency. At  $T = 323$  K (Fig. 3C) or at higher temperatures, no stable domains could be observed. These PFM measurements provide a lower bound on the paraelectric-to-ferroelectric transition temperature ( $T_C$ ):  $T_{C,5\text{ ML}} > 314$  K.

Measurements performed on the 6 ML sample, however, show that ferroelectric domains written on it are stable at even higher temperatures:  $T_{C,6\text{ ML}} > 410$  K (fig. S10). Such temperatures are much higher than that predicted by thermodynamic analysis (fig. S3). The theoretical calculation assumes an infinitely thick SrTiO<sub>3</sub> slab with complete polarization charge screening and with a uniform biaxial compressive strain equivalent to that obtained by growing commensurately strained SrTiO<sub>3</sub> on (001) Si. By leaving out surface effects such as structural and electronic discontinuities and the possibility of incomplete screening of the polarization charge, the thermodynamic analysis does not take into account the finite film thickness, which presumably would lead to a substantially reduced transition temperature, as has been shown for the related ferroelectrics PbTiO<sub>3</sub> (28) and BaTiO<sub>3</sub> (29). Thus, the observed experimental results indicate a substantially higher transition temperature than that predicted by theory. In the case of a metal in contact with a ferroelectric (30, 31), polarization screening at the interface has been shown to enhance the ferroelectric  $T_C$ . Screening of the polarization charge as well as structural and electronic discontinuities at this heteroepitaxial SrTiO<sub>3</sub>/Si interface, not considered in the present thermodynamic analysis, could play a role in understanding the quantitative differences between experiment and theory.

As an independent check of the ferroelectric phase transition, temperature-dependent x-ray

diffraction measurements of the out-of-plane lattice constant were performed on the 5 ML sample (Fig. 4) to sense the structural transition (7, 8, 32) that should coincide with  $T_C$ . The average out-of-plane lattice constant was extracted from scans made of the SrTiO<sub>3</sub> 002 peak. With the in-plane lattice constant clamped to the silicon substrate and changing only by the thermal expansion of silicon, which is much smaller than that of SrTiO<sub>3</sub>, the out-of-plane lattice constant should continuously expand with temperature in the absence of a structural transition. The measured out-of-plane lattice constant with temperature for the 5 ML sample shows a clear deviation from what is expected for thermal expansion with the in-plane lattice constant constrained to that of silicon. This deviation coincides in temperature with the transition temperature observed by PFM. The “kink” feature observed in the out-of-plane lattice constant with temperature (7, 8, 32) is qualitatively consistent with thermodynamic analysis of commensurate SrTiO<sub>3</sub>/Si undergoing a ferroelectric transition (Fig. 4), although the agreement with  $T_C$  is likely to be coincidental.

A ferroelectric in direct contact with silicon invites hybrid ferroelectric-semiconductor devices (1–5). Although the low or almost nonexistent conduction band offset predicted (33) and measured (34) between SrTiO<sub>3</sub> and silicon could lead to practical difficulties in implementing such ferroelectric devices, it has been proposed that this problem can be overcome by carefully constructing the interface between SrTiO<sub>3</sub> and silicon (35, 36).

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Materials Sciences. Diffraction data were taken at sector 33BM of the Advanced Photon Source, which is supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science under contract W-31-109-ENG-38.

### Supporting Online Material

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Materials and Methods

SOM Text

References

Figs. S1 to S10

Table S1

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# Anomalous Fractionations of Sulfur Isotopes During Thermochemical Sulfate Reduction

Yumiko Watanabe,<sup>1\*</sup> James Farquhar,<sup>2</sup> Hiroshi Ohmoto<sup>1</sup>

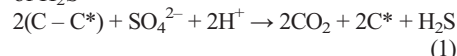
Anomalous fractionated sulfur isotopes in many sedimentary rocks older than 2.4 billion years have been widely believed to be the products of ultraviolet photolysis of volcanic sulfur dioxide in an anoxic atmosphere. Our laboratory experiments have revealed that reduced-sulfur species produced by reactions between powders of amino acids and sulfate at 150° to 200°C possess anomalously fractionated sulfur isotopes:  $\Delta^{33}\text{S} = +0.1$  to  $+2.1$  per mil and  $\Delta^{36}\text{S} = -1.1$  to  $+1.1$  per mil. These results suggest that reactions between organic matter in sediments and sulfate-rich hydrothermal solutions may have produced anomalous sulfur isotope signatures in some sedimentary rocks. If so, the sulfur isotope record of sedimentary rocks may be linked to the biological and thermal evolution of Earth in ways different than previously thought.

Large anomalous fractionations of sulfur isotopes (1–5) are present in many sedimentary rocks older than 2.4 billion years and are virtually absent in younger rocks (6–10). It has been argued that sulfur-bearing minerals [such as pyrite ( $\text{FeS}_2$ ) and barite ( $\text{BaSO}_4$ )] in sedimentary rocks older than 2.4 billion years formed from native sulfur ( $\text{S}^0$ ) and/or sulfate ( $\text{SO}_4^{2-}$ :  $\text{S}^{6+}$ ) produced by ultraviolet (UV) photolysis of volcanic sulfur dioxide ( $\text{SO}_2$ ) in an  $\text{O}_2$ -poor atmosphere (6, 8, 10), and thus that the record of anomalously fractionated S isotopes is evidence for the transition from an anoxic to oxic atmosphere about 2.4 billion years ago (7, 11). These arguments have been based on the assumption that the only processes producing anomalously fractionated S isotopes for both  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  (2, 6) are photochemical reactions involving gaseous S-bearing species [such as hydrogen sulfide ( $\text{H}_2\text{S}$ ) and  $\text{SO}_2$ ] (6, 12). Laboratory experiments performed with UV photolysis of  $\text{SO}_2$  under an  $\text{O}_2$ -free condition produced  $\text{S}^0$  and  $\text{SO}_4^{2-}$  with large anomalous fractionations of S isotopes (13). A theoretical study also suggests

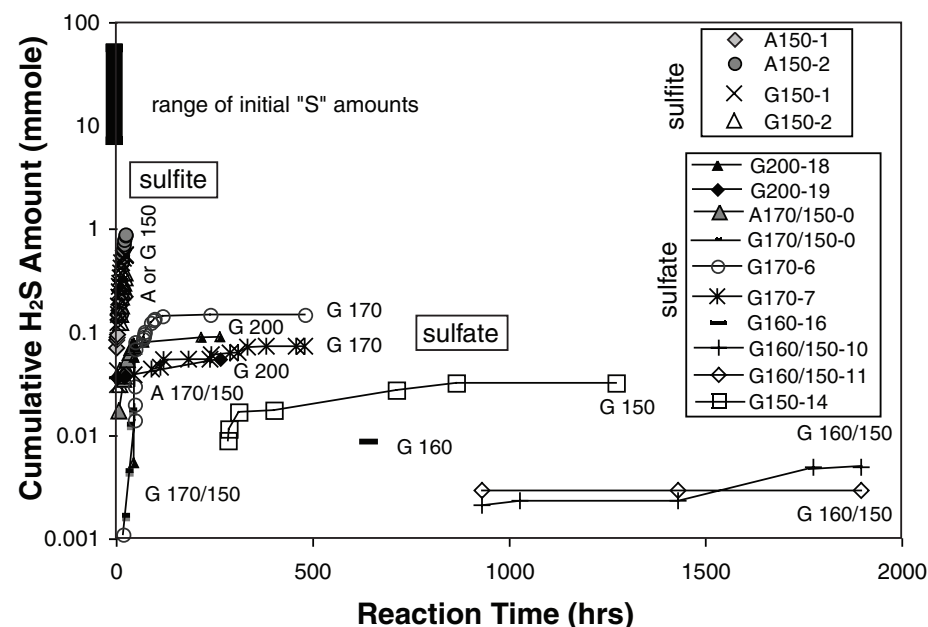
a maximum partial pressure of oxygen ( $P_{\text{O}_2}$ ) of  $\sim 10^{-6}$  atm in order for the UV photolysis of  $\text{SO}_2$  to produce  $\text{S}^0$  and  $\text{SO}_4^{2-}$  (14). Here, we present

experiments showing that reactions between powders of amino acids and  $\text{SO}_4^{2-}$  can also produce anomalous fractionations of S isotopes.

$\text{FeS}_2$ , the most abundant sulfide mineral in sedimentary rocks, forms from a variety of reactions involving  $\text{H}_2\text{S}$  and Fe in sediments and solutions (15). Both bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR) using  $\text{SO}_4^{2-}$  and organic matter in waters and sediments are important in the production of  $\text{H}_2\text{S}$



where C and C\* refer, respectively, to reactive and nonreactive (residual) carbon atoms in organic compounds. This reaction typically results in positive correlations between the  $\text{FeS}_2$  and C\* contents of sedimentary rocks (15). The C/C\* ratio and reaction rate vary depending on the type and maturation degree of organic compounds (for example, carbohydrates, hydrocarbons, amino acids, bitumen, and type I, II, and III kerogens). BSR is carried out by sulfate-reducing bacteria (SRB),



**Fig. 1.** Cumulative amounts of  $\text{H}_2\text{S}$  produced from  $\text{SO}_3^{2-}$  or  $\text{SO}_4^{2-}$  reductions by amino acids (alanine or glycine). Gray symbols represent the experiments using alanine (A) and solid, open, cross, or bar symbols represent those using glycine (G). The three-digit numbers (150, 160, 170, and 200) represent experiment temperatures, and the hyphenated numbers represent the run numbers.

<sup>1</sup>The NASA Astrobiology Institute and Department of Geosciences, Pennsylvania State University, University Park, PA 16802, USA. <sup>2</sup>Department of Geology and Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20742, USA.

\*To whom correspondence should be addressed. E-mail: yumiko@geosc.psu.edu