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# Response to Comment on “Early Archaean Microorganisms Preferred Elemental Sulfur, Not Sulfate”

Pascal Philippot,<sup>1\*</sup> Mark Van Zuilen,<sup>1</sup> Kevin Lepot,<sup>1</sup> Christophe Thomazo,<sup>1</sup> James Farquhar,<sup>2</sup> Martin J. Van Kranendonk<sup>3</sup>

Our knowledge of the sulfur cycle on early Earth is still in its infancy. Nevertheless, there exist enough geochemical constraints from the rock record to show that the theoretical mixing models proposed by Bao *et al.* are highly unlikely to account for the range of  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  values recorded for the microscopic sulfides at the North Pole.

Bao *et al.* (1) propose that the relatively large range of  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  values reported for microscopic sulfides preserved in bedded barite from the Dresser Formation at the North Pole could be accounted for by mixing between photolytic elemental sulfur ( $+\Delta^{33}\text{S}$ ) and surface sulfides derived from inorganic or microbial sulfate reduction ( $-\Delta^{33}\text{S}$ ). Two main types of models have been considered to explain the observed range in  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  values of microscopic sulfides. The first supposes that there was a pool of atmospheric  $\text{S}^0$  that was temporally or spatially heterogeneous in  $\Delta^{33}\text{S}$ . This hypothesis is poorly constrained and not supported by the sulfur isotope data reported so far in ~3800- to 2700-million-year-old Archaean rocks. As shown in Fig. 1, more than 90% of Early to Mid-Archaean sulfides show a narrow range of  $\delta^{34}\text{S}$  values of  $\pm 5$  per mil (‰) and  $\Delta^{33}\text{S}$  values between +6 and -1‰. The only exception concerns the microscopic sulfides at the North Pole. Although a heterogeneous source of positive  $\Delta^{33}\text{S}$  sulfides cannot be excluded, it would imply that it developed only once in a time span of more than 1000 million years and was restricted to the microscopic pyrites but not the adjacent macroscopic pyrites surrounding the barite crystals hosting the microscopic sulfides, which seems highly unlikely.

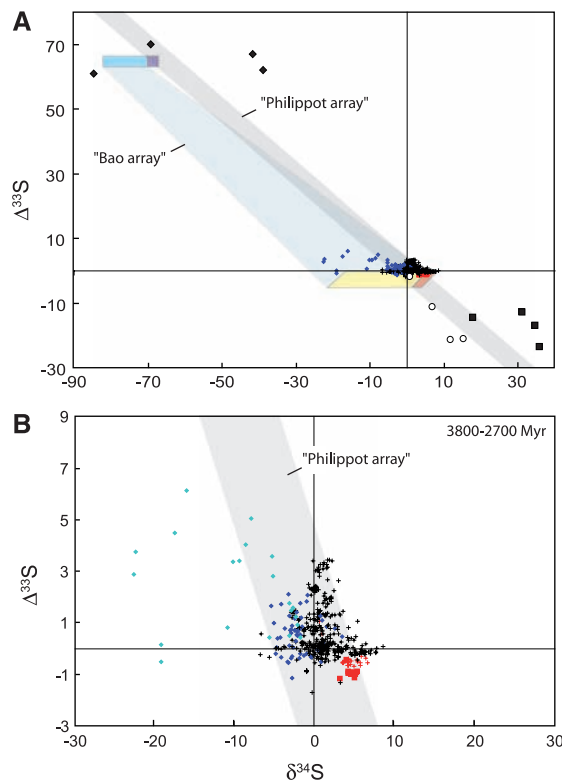
The second model envisions mixing a small pool of homogeneous atmospheric  $\text{S}^0$  with extreme  $\Delta^{33}\text{S}$  values of about +70‰ with a large pool of oceanic “sulfides” displaying negative  $\Delta^{33}\text{S}$  values of about 0 to -4‰ and a large range of  $\delta^{34}\text{S}$  values between +5 and -25‰. This model is based in part on geologically relevant

observations and therefore must be considered with caution. The sulfate endmember used is typical of North Pole barite [negative  $\Delta^{33}\text{S}$  anomaly of about -1‰ (2)]. The range of  $\delta^{34}\text{S}$  values considered for the “surface” sulfides are similar to the data reported by Shen *et al.* (3) and our original study (see Fig. 1 in (4)). Following our data interpretation, Bao *et al.* (1) considered that such strongly  $^{34}\text{S}$ -depleted microscopic sulfides with negative  $\Delta^{33}\text{S}$  values could have formed from inorganic or microbial sulfate reduction. In contrast, the extreme positive  $\Delta^{33}\text{S}$  values of

atmospheric  $\text{S}^0$  used by Bao *et al.* are derived from the experimental results of (5). Such extreme values were not found in the rock record. The highest positive  $\Delta^{33}\text{S}$  anomaly reported so far does not exceed 10‰ (6). Product sulfate in equilibrium with this experimentally determined atmospheric endmember shows lower negative  $\Delta^{33}\text{S}$  values of about -25‰ (see Fig. 1) than the one used by Bao *et al.* in their mixing model (0 to -4‰). To satisfy their model, they introduced the notion of “poor” mixing of small amounts of extremely fractionated atmospheric  $\text{S}^0$  raining down in a vast sulfide reservoir derived from the reduction of oceanic sulfate. Although conceptually feasible, this scenario does not fit with the geological observations.

Figure 2 shows a general framework of sulfur cycling during the Early Archaean. The diagrams in inset compare the sulfur isotope results recorded in North Pole drill cores with the prediction of the Bao *et al.* poor-mixing model. The small pool of particulate atmospheric  $\text{S}^0$  with extreme  $\Delta^{33}\text{S}$  anomalies should affect the entire rock sequence and should not be restricted to the microscopic sulfides lining barite overgrowth zones. Adjacent macroscopic pyrite laminae should show the same type of  $\Delta^{33}\text{S}/\delta^{34}\text{S}$  variation. In addition, sulfides located higher up in the sequence—namely the macroscopic sulfides in the bedded barite and the sedimentary sulfides

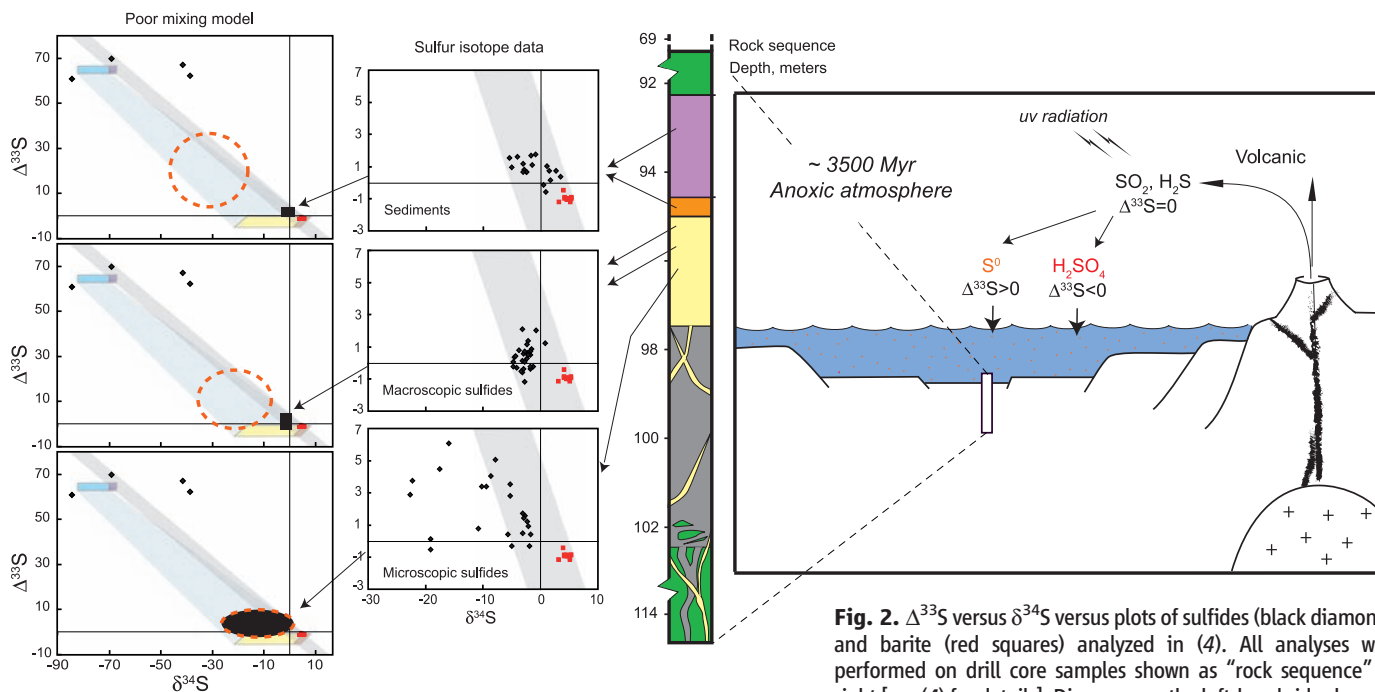
**Fig. 1. (A)** Experimental results of photolyzed sulfur dioxide to elemental sulfur ( $+\Delta^{33}\text{S}$ , large black diamonds) and sulfate ( $-\Delta^{33}\text{S}$ , large black squares) (large empty circles correspond to the residual  $\text{SO}_2$ ) when it is exposed to ultraviolet radiation at a wavelength of 193 nm (5, 7). Superposed onto this diagram is the range of sulfide pools and array used in (1) (“Bao array”). These include: (i) photolyzed  $\text{S}^0$  (dark blue) formed from interaction with ultraviolet at 193 nm and associated sulfide (light blue) formed from atmospheric  $\text{S}^0$  reduction or disproportionation and (ii) “surface” oceanic sulfate pool (red) and associated sulfides formed from sulfate reduction of microbial or inorganic origin (yellow). The light gray array labeled “Philippot array” represents the range of the photolyzed sulfur pool considered in (4). This array passes through the mean of the photolyzed  $\text{S}^0$  and sulfate-residual  $\text{SO}_2$  pools defined by (5, 7). Also shown are S isotope data from the literature covering the period 3800 to 2700 million years ago [data from (2, 4, 5, 7–17)].



**(B)** S isotope systematics of Archaean sulfides for the period 3800 to 2700 million years ago. Blue diamonds and red squares correspond to North Pole sulfides and barites, respectively. Strongly  $^{34}\text{S}$ -depleted microscopic sulfides are shown in light blue. Black and red crosses correspond to sulfides and barites from other localities. More than 90% of the S isotope data are comprised within the 193-nm array used in (4).

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**Fig. 2.**  $\Delta^{33}\text{S}$  versus  $\delta^{34}\text{S}$  versus plots of sulfides (black diamonds) and barite (red squares) analyzed in (4). All analyses were performed on drill core samples shown as “rock sequence” on right [see (4) for details]. Diagrams on the left-hand side show the

effect of mixing small amounts of extremely fractionated ( $\Delta^{33}\text{S} \sim +70\%$ ) atmospheric sulfur with a large volume of sulfides derived from the reduction of oceanic sulfates. The highest amount of particulate atmospheric  $\text{S}^0$  aerosols will be stored in the sedimentary layers located on the sea floor. This in turn should result in increasing mechanically the  $\Delta^{33}\text{S}$  scatter of the sedimentary sulfides (large dashed orange circle evolving toward the “ $\text{S}^0$  atmospheric pool”) compared with the macroscopic and microscopic sulfides present in the underlying bedded barite. The range of measured  $\Delta^{33}\text{S}$  versus  $\delta^{34}\text{S}$  values of North Pole sulfides are shown for comparison (black areas). Recognition that the sedimentary sulfides show systematic positive  $\Delta^{33}\text{S}$  anomalies indicates that the source of sedimentary sulfur was indeed almost exclusively derived from atmospheric  $\text{S}^0$ , which agrees with the sulfide source defined in (1). However, the limited range of  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  values of sedimentary sulfides argue against their mixing scenario.

in the volcano-sedimentary layer (orange layer) and cherty carbonate (pink layer) —should be increasingly exposed to the atmospheric  $\text{S}^0$  derived from the overlying water column. This should have resulted in a progressive increase in  $\Delta^{33}\text{S}$  values and a progressive decrease in  $\delta^{34}\text{S}$  values (indicated as a large dashed orange circle along the “Bao Array”). Although the sedimentary sulfides at the North Pole show a systematic positive  $\Delta^{33}\text{S}$  value, which indicates that the main sulfur component involved in their formation is indeed derived from atmospheric  $\text{S}^0$  aerosols, they display a narrow range of  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  values close to the origin.

Although we agree with Bao *et al.* (1) that our understanding of the Early Archaean sulfur cycle is limited, a number of basic observations should be kept in mind before developing complex mix-

ing models. The basic premise of their model is that the original pool of oceanic sulfate with negative  $\Delta^{33}\text{S}$  anomaly is to be reduced microbially or inorganically into strongly  $^{34}\text{S}$ -depleted sulfides. This interpretation forms the crux of the reasoning of Shen *et al.* (3) and Philippot *et al.* (4). We see no need of invoking a complex mixing scenario at this stage.

#### References

- H. Bao, T. Sun, I. Kohl, Y. Peng, *Science* **319**, 1336 (2008); [www.sciencemag.org/cgi/content/full/319/5868/1336b](http://www.sciencemag.org/cgi/content/full/319/5868/1336b)
- J. Farquhar, H. Bao, M. H. Thiemens, *Science* **289**, 756 (2000).
- Y. Shen, R. Buick, D. E. Canfield, *Nature* **410**, 77 (2001).
- P. Philippot *et al.*, *Science* **317**, 1534 (2007).
- J. Farquhar, J. Savarino, S. Airieau, M. H. Thiemens, *J. Geophys. Res.* **106**, 32829 (2001).
- B. S. Kamber, M. J. Whitehouse, *Geobiology* **5**, 5 (2007).
- J. Farquhar, B. A. Wing, *Earth Planet. Sci. Lett.* **213**, 1 (2003).
- H. Bao, D. Rumble III, D. R. Lowe, *Geochim. Cosmochim. Acta* **71**, 4868 (2007).
- N. L. Cates, S. J. Mojzsis, *Geochim. Cosmochim. Acta* **70**, 4229 (2006).
- J. Farquhar *et al.*, *Nature* **449**, 706 (2007).
- G. X. Hu, D. Rumble, P. L. Wang, *Geochim. Cosmochim. Acta* **67**, 3101 (2003).
- D. Johnston *et al.*, *Am. J. Sci.* **305**, 645 (2005).
- S. J. Mojzsis, C. D. Coath, J. P. Greenwood, K. D. McKeegan, T. M. Harrison, *Geochim. Cosmochim. Acta* **67**, 1635 (2003).
- H. Ohmoto, T. Watanabe, H. Ikemi, S. R. Poulson, B. E. Taylor, *Nature* **442**, 908 (2006).
- S. Ono, B. Wing, D. Johnston, J. Farquhar, D. Rumble III, *Geochim. Cosmochim. Acta* **70**, 2238 (2006).
- D. Papineau, S. J. Mojzsis, *Geobiology* **4**, 227 (2006).
- M. J. Whitehouse, B. S. Kamber, C. M. Fedo, A. Lepland, *Chem. Geol.* **222**, 112 (2005).

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