**"MIF IN BIF" provides unique clues to the atmosphere-hydrosphere system at the Hadean/Archean transition on Earth.** S.J. Mojzsis[1,2] and N.L. Cates[1]. [1]Department of Geological Sciences, Center for Astrobiology, University of Colorado at Boulder, 2200 Colorado Ave, UCB 399, Boulder, Colorado 80309-0399, USA, (mojzsis@colorado.edu); [2]Centre de Recherches Pétrographiques et Geochemiques (CNRS-CRPG), 15 rue Notre Dame des Pauvres, 54501 Vandoevre-les-Nancy, France.

**Introduction:** Banded iron-formations (BIFs) are common "early Earth" sediments found throughout the Precambrian from the Hadean/Archean transition at ~3.85 Ga [1] to the Paleoproterozoic, with a long hiatus before reappearing at the Neoproterozoic glaciations (0.9-0.7 Ga). These were chemical sediments that precipitated from seawater and serve as the principal records of the first terrestrial surface environments [2]. Although abiogenic and biogenic models for their origin have been put forward for over 50 years [3], BIF genesis has remained mysterious [4] because oxic conditions at the surface today preclude their deposition. Fe-isotopes have been used to bolster the case that the BIFs were biotically modulated [5-8]. Recent experiments [9] show that photochemically oxidated $Fe(II)_{aq}$ effused into shallow marine waters at seamounts could not have been a dominant mechanism for precipitation of ferro/ferric-hydroxides into BIF. These new data appear to favor Fe(II)-based bacterial photosynthesis for the origin of BIFs.

Pre-3.8 Ga BIFs [10-12] formed in the context of particular atmospheric and oceanic compositional regimes. If we could know more about those conditions, it may be possible to constrain the kinds of metabolisms which were feasible at the earliest times.

**BIF Sulfur.** Sulfur is an isotopic biomarker and redox sensor in sediments [13]. Sedimentary S-minerals in Archean rocks for which the minor sulfur isotope ($^{33}$S) does not lie on a mass-dependent fractionation line with other, younger terrestrial minerals have now been widely documented [14]. "Mass-independent" sulfur isotope fractionation (MIF) is characterized by non-zero values of $\Delta^{33}$S (where $\Delta^{33}$S=0‰ and $\Delta^{33}$S(‰)=1000•[(1+$\delta^{33}$S/1000)-(1+$\delta^{34}$S/1000)$^{\lambda}$; the term $\lambda$=the mass dependent fractionation relationship between $\delta^{33}$S and $\delta^{34}$S). MIF S isotopes arise from gas-phase reactions on sulfur gases in anoxic ($pO_2 \ll 10^{-6}$ present atmospheric level; PAL) atmospheres [15]. Many pre-2.4 Ga sedimentary sulfides and sulfates preserve large magnitude $\Delta^{33}$S deviations in contrast to almost all sulfides and sulfates younger than 2.32 Ga with $\Delta^{33}$S values typically from -0.30 to +0.30‰ (**Fig. 1;** [16]).

**"MIF in BIF" and the atmosphere.** MIF S in sediments is explicable by separation of the photochemically-processed sulfur into water-soluble ($^{33}$S-depleted; negative $\Delta^{33}$S) sulfate and water-insoluble elemental sulfur ($^{33}$S-enriched; positive $\Delta^{33}$S) fractions [14,15]. This prevents MIF S accumulation in

the oceans, where the various species would mix back together and the MIF signature would be lost [15].

Sulfides in BIFs sample sulfur from the water column ultimately acquired from atmospheric or magmatic exhalations. Data for the oldest BIFs show large +$\Delta^{33}$S values with separate arrays in $\Delta^{33}$S vs. $\delta^{34}$S space, consistent with deep UV photochemistry at different wavelengths and in the absence of ozone [17].
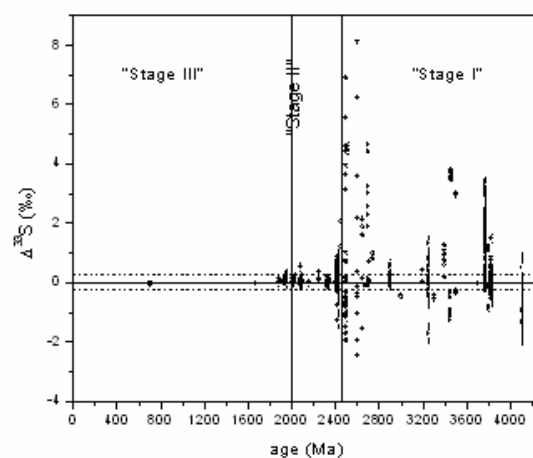


**Figure 1.** Compilation of $\Delta^{33}$S data for sedimentary sulfides and sulfates vs. age [16]. The small range in $\Delta^{33}$S values for samples < 2.42 Ga reflects change in atmospheric oxygen concentration past the $pO_2 = 10^{-6}$ PAL threshold. The oldest BIFs preserve MIF S. Data >4 Ga are for an Hadean zircon sulfide inclusion. Labeled "Stages" correspond to the evolution of atmospheric redox [17]. Error bars are reported at ($2\sigma$).

**Early Sun.** All models for the early atmosphere require adequate greenhouse gases at substantially higher concentrations than at present to offset the faint young Sun (FYS) and ensure that the Earth did not plunge into a deeply frozen state for the first half its history [18]. The most important candidate greenhouse gases that could have done this are $CO_2$ and $CH_4$.

**$CO_2$.** Most solutions the FYS problem invoke high proportions of $CO_2$ to keep the surface warm. Yet, MIF is inhibited by Rayleigh scattering of UV [19] at partial pressures of $CO_2$ (p$CO_2$) $\geq$0.5 bar (**Fig 2**). Hence, $CO_2$ must have been lower than this value, or $\leq$1.5$\times10^3$ PAL. The mineral phase relationships of BIFs provide a further constraint of <$10^{-1}$ bar $CO_2$ at pH below ~7.

**$CH_4$.** At p$CH_4$/p$CO_2 \geq$0.6 [21] methane aerosols form a UV-blocking haze [22] (**Fig. 3**) that shuts-down MIF production. It is difficult to bring average surface temperature above 50°C in the early Archean when p$CO_2$ had to have been below $10^{-1}$ bar, without

requiring methane $>10^4$ ppm. What was the origin of all this methane?
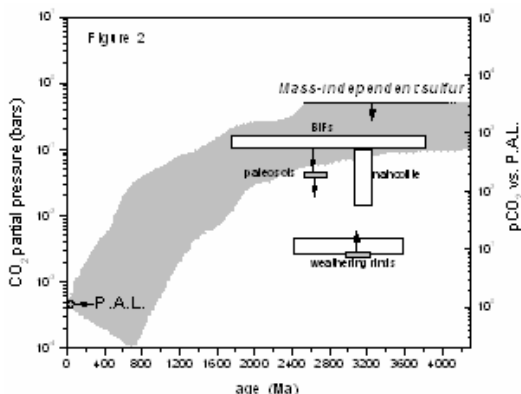


**Figure 2.** Changing $CO_2$ levels in the atmosphere over time in partial pressure of $CO_2$ in bars (left), and vs. PAL (right). Shaded region = range of concentrations required to stabilize liquid water and compensate for the FYS [modified from 20].
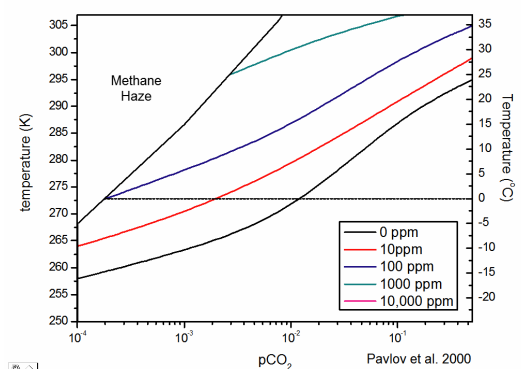


**Figure 3.** Surface temperature as a function of $pCO_2$ (in bars; x-axis) and $pCH_4$ (expressed in ppmv) for anoxic atmospheres. Horizontal dashed line shows the freezing point of water and the "Methane Haze" field corresponds to mixing ratios of $pCH_4/pCO_2 \geq 0.6$ which do not allow for production of MIF S isotopes because of UV-blocking. In this simple 1-D model (no clouds), the assumed solar flux is 0.8 times the present value corresponding to conditions in the late Archean [21]. At $pCH_4 = 10$ ppm (red line) and $pCO_2 = 0.5$ bar, mean surface temperature is about 20 ºC. Inset legend shows values for different $pCH_4$.

**H$_2$.** MIF S is sensitive to $pH_2$ (A. Pavlov, personal comm.). In a pre-biotic world where hydrogen abundance could have been high [23], the MIF S signal is much weaker compared to an anoxic "biological" atmosphere. Others [24] have argued that plentiful $H_2$ enables the reduction of S-bearing gases to $S_8$ that boosts the deposition of $S_8$ aerosols which in turn enhances the "positive" $\Delta^{33}S$ signal in sediments. Yet, with a biosphere the $H_2$ should be converted to $CH_4$.

These results are interesting, because they suggest that "MIF in BIF" may represent a passive signal of biological activity. A recent study [25] came to the independent conclusion that Archean $pH_2$ was very low. In that study, it was noted that at 25°C, magnetite is thermodynamically stable relative to the common BIF-hosted ferrous carbonate phase (siderite) only at $pCO_2 \sim 10^{-1.5}$ and $pH_2 < 10^{-10}$ bar. Based on existing physical models, it seems quite difficult to bring average surface temperatures well above 30ºC in the early Archean [26, 27]. Clearly more work is required to reconcile the models with the robust oxygen and silicon isotope data reported from the rock record.

**Conclusions.** The properties of mass-independent sulphur isotopes in the oldest BIFs provide unique solutions to the composition of the atmosphere at the Hadean/Archean transition on Earth. These results provide further fuel to the debate about whether BIFs were indeed biologically mediated, and important guiding principles in the spectroscopic search for Extrasolar Early Earths. From the first-order interpretations presented here, the atmosphere at 3.8-3.9 Ga had the following properties: (i) transparency to deep UV with effectively no ozone, in other words no significant UV blocking hazes; (ii) $pCO_2 < 1.5 \times 10^3$ PAL; (iii) $pCH_4 > 10^3$ ppmv; (iv) and $pH_2$ was below 0.1 ppbv.

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