Introduction: Sulfur isotopes (32S, 33S, 34S and 36S) are used as tracers for igneous, hydrothermal and biological processes on Earth. Sulfur is abundant in marine systems and has been utilized as a biomarker in ancient sediments. Fundamental questions related to the early Earth such as the evolution of life, oxygenation of the atmosphere and lithosphere-atmosphere interactions could be addressed by using the sulfur isotopic compositions of ancient sediments. Mass-dependent sulfur isotope fractionations expressed in δ34S_{CDT} (δ^{34}S=([^{34}S/^{32}S]_{sample}/[^{34}S/^{32}S]_{standard}−1)×1000) for S-containing minerals exhibit a small range centered at ~0‰ for terrestrial igneous (0±5‰) and hydrothermal (0±10‰) systems [1]. Bacterial sulfate reduction has been linked to the >150‰ range in δ34S from sulfate and sulfide in the rock record. Atmospheric chemical reactions on early Earth are implicated in non-mass-dependent sulfur isotope anomalies (Δ33S=δ^{33}S–0.52δ^{34}S) reported from whole-rock analyses of S-containing phases in Precambrian sediments [2]. To explore these in detail, a new ion microprobe technique was developed [3] to obtain precise 32S, 33S and 34S measurements of sulfide grains in situ from a suite of Precambrian (1.8-3.8 Ga) marine sediments.

Materials and methods: All sulfides analyzed in this study were characterized by light microscopy and electron microprobe. To analyze the isotopic compositions of these sulfides, we used the UCLA Cameca ims1270 high-resolution ion microprobe in multi-collector mode with a 2.9-nA, 20 KeV Cs⁺ primary ion beam focused to a ≤30 μm spot; this new method simultaneously measures 32S, 33S and 34S on adjacent detectors and uniquely provides the spatial resolution to determine isotopic heterogeneity at the subgrain scale. Pre-sputtering times were 500 s; analyses comprised 15 cycles of 10 s measurements; including spot-to-spot setup time, total time per analysis was ~12 min. Negative secondary ions with initial energies in the range 0–25 eV were analyzed and a normal-incidence electron flood gun was used to neutralize positive charge build-up in the analysis area. Faraday cups were used to detect 32S, 33S and 34S beams and signals amplified by Finnigan electrometers housed in a temperature-controlled evacuated chamber. Secondary beam currents are quoted here in counts-per-second (Hz). A mass resolving power of 4000 was sufficient to maintain the 32S contribution to the 33S peak to <10 ppm. Repeat measurements of the detection system baseline were made throughout each analysis session and were reproducible to ~1000 Hz (2σ, n=20) for the 33S and 34S detectors. Integration time for each baseline measurement was 650 s. Count rates on 33S were in the range 7.3–31.0 MHz. Instrumental drift was not apparent over separate analytical sessions and no correlation between Δ33S and count rate of 33S was observed. Instrumental mass fractionation (IMF) was corrected for by means of measurements made on standards of the same sulfide phases as the unknowns. The measured δ34S/Δ33S IMFs were: pyrite, -17.3‰; pyrrhotite, -21.9‰; trolite, -25.5‰. The terrestrial mass-dependent fractionation (TF) line for S on a 3-isotope plot was determined by 282 separate analyses on sulfide standards interposed with the unknowns. Measured 33S/32S ratios were corrected for IMF assuming an exponential mass fractionation law. We defined the 33S/32S of CDT by the intersection of the experimentally determined TF line and the accepted value of (33S/32S)_{CDT}=4.50045×10^{-3} [4] to obtain (33S/32S)_{CDT}=7.9573×10^{-3}. Reported δ33S and δ34S data use these reference ratios. The slope of our TF line in δ33S vs. δ34S is 0.520, hence Δ33S = δ33S–δ34S. The range in Δ33S for our sulfide standards including CDT was -0.2±0.05 to +0.4±0.08‰.

Results: Our data (Figure 1) reveal well-resolved non-mass-dependent Δ33S anomalies in an early Archean (ca. 3.8 Ga) banded iron-formation (IM23: Δ33S=+1.3±0.16‰ to +2.0±0.08‰, 2σ) and metapelite (IM43: Δ33S=+1.1±0.08‰ to +1.2±0.03‰, 2σ) from Isua, West Greenland. An exploratory study of sulfides in a diverse suite of late Archean to Proterozoic (3.2–1.8 Ga) stromatolithic cherts, banded iron-formation and shales documented only mass-dependent (Δ33S≠0‰) sulfur isotope relationships within the precision of our measurements. Our results reveal that non-mass-dependent S isotope anomalies (i.e. Δ33S ≠ 0‰) are preserved in sulfide phases contained in ca. 3.8 Ga sediments. That these rocks contain Δ33S anomalies from gas-phase reactions in an early atmosphere lends support the interpretation that atmospheric partial pressures of oxygen were low and the effects of UV-photolysis on atmospheric sulfur from a UV-active young Sun mediated non-mass-dependent fractionations in the sulfur cycle. We are continuing to explore the preservation of these non-mass-dependent effects in ancient sedimentary sulfides; such Δ33S signals may be commonplace in early to mid Archean sedimentary rocks.