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Sulfur isotope analysis of microcrystalline iron sulfides using SIMS imaging: Extracting local paleo-environmental information from modern and ancient sediments

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RATIONALE: Sulfur isotope ratio measurements of bulk sulfide from marine sediments have often been used to reconstruct environmental conditions associated with their formation. In-situ microscale spot analyses by secondary ion mass spectrometry (SIMS) and laser ablation multiple-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) have been utilized for the same purpose. However, these techniques are not often suitable for small ($\leq$10 μm) grains or for detecting intra-grain variability.

METHODS: Here, we present a method for the physical extraction (using lithium polytungstate heavy liquid), and subsequent sulfur isotope analysis (using SIMS; CAMECA IMS 7f-GEO) of microcrystalline iron sulfides. SIMS sulfur isotope ratio measurements were made via Cs^+ bombardment of raster squares with sides of 20-130 μm, using an electron multiplier (EM) detector to collect counts of $^{32}S^-$ and $^{34}S^-$ for each pixel (128x128 pixel grids) for between 20 and 960 cycles.

RESULTS: The extraction procedure did not discernibly alter pyrite grain-size distributions. Apparent inter-grain variability in $^{34}S/^{32}S$ in 1-4 μm-sized pyrite and marcasite fragments from isotopically homogeneous hydrothermal crystals was ~ ±2‰ (1σ), comparable to the standard error of the mean for individual measurements ($\leq$ ±2‰, 1σ). In contrast, grain-specific $^{34}S/^{32}S$ in modern and ancient sedimentary pyrites and marcasites can have inter- and intra-grain variability >60‰. Distributions of intra-sample isotopic variability are consistent with bulk $^{34}S/^{32}S$ values.

CONCLUSIONS: SIMS analyses of isolated iron sulfide grains yielded distributions that are isotopically representative of bulk $^{34}S/^{32}S$ values. Populations of iron sulfide grains from sedimentary samples record the evolution of the S-isotopic composition of pore water sulfide in their S-isotopic compositions. These data allow past local environmental conditions to be inferred.

39Iron sulfide minerals, particularly pyrite (FeS_2), represent a substantial geologic reservoir of 40sulfur. Pyrite is a key constituent of many iron sulfide ore deposits,[1] a common accessory 41phase in an array of igneous and metamorphic rocks,[2,3] and a nearly ubiquitous mineral in 42marine sedimentary rocks of all ages.[4] Sedimentary pyrites have diverse morphologies, 43crystal sizes, and S-isotope compositions, and these characteristics have proven to be 44invaluable archives for reconstructing local environmental conditions as well as global-scale 45changes in biogeochemistry.[5–8] The S-isotopic composition of pyrite is expressed here in the 46standard delta notation (in units of per mil, ‰) relative to the Vienna Canyon Diablo Troilite 47(VCDT) reference standard for sulfur,[9]

$$48 \qquad \delta^{34}S_{sample} = \left(\frac{R_{sample}}{R_{VCDT}} - 1 \right) \qquad\qquad (1)$$

49where R represents $^{34}S/^{32}S$ ratios.

50   Pyrite $\delta^{34}S$ values are commonly obtained by bulk extraction of chromium-reducible 51sulfur (CRS), using Cr^{2+} to reduce and volatilize FeS_2 to H_2S gas, which can subsequently be 52trapped as zinc or silver sulfide.[10,11] Isotope ratios for the isolated CRS can be measured by 53combustion elemental analysis isotope ratio mass spectrometry (EA-IR-MS),[12–17] or by 54solution multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS).[18–21] 55Such approaches yield an integrated $\delta^{34}S$ value for the CRS pool and are thus blind to patterns 56of isotopic variability within the pyrite pool. In addition, the CRS pool can potentially also 57include marcasite (FeS_2), elemental S, organic polysulfides, and other metal sulfides in 58addition to multiple morphologies or generations of pyrite.[8,10,11]

59   The degree of isotopic variability within the pyrite pool is hypothesized to reflect 60depositional conditions and may record critical information about the location(s) and 61condition(s) of pyrite formation.[8,22] For example, if pyrite in a sample is isotopically 62homogeneous, this would suggest that all grains formed from the same fluid. In contrast, a 63bimodal pyrite $\delta^{34}S$ distribution might indicate two distinct sulfide sources, e.g., from 64successive exposure to distinct sulfide-bearing fluids. Pyrites from a single source may also 65have a range of $\delta^{34}S$ values, representing their continuous formation in the presence of an 66evolving sulfide reservoir.[23,24] In diffusively limited environments like marine sediments, pore 67water sulfate can be drawn down by microbial sulfate reduction (MSR). Sulfate reducers have 68a strong preference for the lighter isotopes of S in sulfate,[25,26] which leads to increasingly ^{34}S- 69enriched sulfate and sulfide with depth in the sediment.[27] As a result, later-formed pyrite 70crystals or the outer layers of large pyrite crystals may be more ^{34}S-enriched than pyrite that 71formed earlier.[23] These distinct scenarios (unimodal distribution, bimodal distribution, or 72evolved source) would not be distinguishable using bulk $\delta^{34}S$ values. Therefore, there is great 73potential for a grain-specific method for pyrite S-isotope measurements to enhance our 74understanding of pyrite $\delta^{34}S$ records, providing a new dimension of information to inform our 75interpretations of this powerful archive.

76   Progress has been made using spot analyses by SIMS,[1,23,28–38] or LA-MC-ICP- 77MS,[20,39,40] to make spatially resolved $\delta^{34}S$ measurements. Some have already attributed

78detectable intra-sample pyrite δ^{34}S variability to temporal changes in the S-isotopic 79composition of the fluids from which the pyrites precipitated.[24,28] The method described here, 80scanning ion imaging by SIMS, is designed to address several of the limitations of currently 81available methods for micro-scale analysis of δ^{34}S in sedimentary pyrite. First, by rastering 82over grains, scanning ion imaging can generate a continuous record of isotope variations,[29] 83one that can be interrogated at variable spatial resolution after data collection. Previously, 84most SIMS studies of pyrites relied on analyses of fairly large ($\geq$10 µm-diameter) spots 85within grains.[1,23,28–38] This precludes analyses of many sedimentary pyrites (i.e., those with 86diameters <10 µm). Moreover, while spot analyses can be sufficient to determine the 87presence of inter-grain isotopic variability on larger grains, they are not able to discern intra-88grain variability,[31–37] except for the case of unusually large (diameters > ~100 µm) pyrites.[23]

89   Additionally, by reducing the primary beam current, we achieve the spatial resolution 90necessary to measure inter- and intra-grain δ^{34}S variability in microcrystalline pyrites. In 91comparison, spot analyses are not ideal for many micro-sized pyrites or necessarily even for 92larger pyrites that are composed of many small parts (e.g., framboids). Relatively high 93primary beam currents (e.g., $\geq$ 1 nA) inherently limit the three-dimensional resolution of 94isotopic measurements.[28,38] As scanning ion imaging requires the use of very low primary 95beam currents (e.g., $\leq$ 20 pA) to prevent the saturation of the electron multiplier detector,[29] 96the associated low sputter rates and small diameter of the focused primary beam ($\leq$1 µm) 97result in excellent three-dimensional resolution.[29]

98   Finally, we introduce a physical extraction procedure to enable pyrite to be 99concentrated for optimized SIMS analyses for samples where pyrite is a trace phase. As 100pyrite is not a high abundance phase in most sedimentary rocks, and grains are often broadly 101disseminated,[41] this limits the number of grains likely to be present at the polished surface of 102a 1-inch round thin section. Additionally, when grains are close to the edge of the sample 103holder, this adversely affects precision.[42] Therefore, the physical extraction of pyrites from 104sedimentary samples is in many cases a necessary precondition for efficient SIMS analysis on 105a sufficient number of grains to characterize the population. Most early physical extraction 106procedures for pyrite used magnetic separation, although because pyrite is only paramagnetic, 107these approaches are inefficient.[43] Alternative separation procedures utilize heavy liquids,[44–48] 108as these represent an opportunity to separate dense phases like pyrite (5.01 g/cm^3) from less 109dense, but common insoluble minerals like quartz (2.65 g/cm^3) and clays (2-2.7 g/cm^3). For 110this study, lithium polytungstate (LST; working density of 2.85 g/cm^3) is preferred due to its 111low toxicity and high recyclability.

112   In the following, we present the details of our SIMS scanning ion imaging-based 113sulfur isotope analysis procedure. We first test the validity of the method on micron-scale 114fragments of cm-scale isotopically homogeneous hydrothermal pyrite and marcasite crystals. 115By comparing SIMS results to bulk ^{34}S/^{32}S ratio data obtained via EA-IR-MS, we quantify 116overall analytical biases associated with the method and determine its general limitations in 117order to provide a robust platform for future grain-specific SIMS analyses of modern and 118ancient microcrystalline iron sulfides. By generating continuous ^{34}S$^-$ and ^{32}S$^-$ ion maps for

119inter/intra-grain variability and probing variation in hydrothermal crystals, we increase our
120confidence that the observed variation in sedimentary samples is environmentally meaningful
121and not an analytical artefact. Lastly, we apply the method to a set of extensively studied
122sediment samples that are thought to represent distinct styles and histories of pyritization,
123demonstrating its applicability and value to investigations of modern and ancient marine
124sediments.

125**Materials & Methods**

126*Samples*
127For use in density separation procedure tests, and as a S-isotopic standard for SIMS
128experiments, we obtained a single large (~2cm-diameter) euhedral pyrite crystal from Ward's
129Science (Rochester, NY), sourced from the San Jose de Huanzala Mine, Peru. The pyrite at
130this locality is of hydrothermal origin, and has been shown in previous studies to be
131stoichiometric FeS_2.[49] For use as an additional S-isotopic standard for SIMS experiments, we
132obtained a single large (~1cm-diameter) euhedral marcasite crystal from Ward's Science,
133sourced from the Jiří open-pit lignite mine in the Czech Republic. For use in further SIMS S-
134isotope experiments, we selected a modern sediment sample from Santa Barbara Basin,[50] and
135two mid-Cretaceous, Cenomanian-Turonian Ocean Anoxia Event (OAE 2) shale samples
136from the Cismon section in Italy,[51] and the Demerara Rise.[52]

137*Extraction of microcrystalline pyrite from geologic samples*
138A ~0.5g fragment of the hydrothermal pyrite crystal was ground to a fine powder by mortar
139and pestle, and homogenized. The resulting grain size distribution of the powdered crystal
140('pre'; Table S1) was characterized using a combination of optical microscopy and image
141processing in ImageJ.[53] This involved suspending ~0.001 g of powder in ethanol and
142dispersing the sample on a glass microscope slide, then capturing 20 focused images of
143unique parts of the slide through a 40× optical objective. These images were overlain by
14420×20 μm grids, and a random number generator was used to select 5 grid squares to analyze
145per image. In ImageJ, images of grid squares were scale-calibrated, converted to grayscale,
146and a bandpass filter (filtering large structures down to 10 pixels) and threshold were applied
147to highlight grains. Overlapping/touching grains, or grains with a circularity of <0.9 were
148removed, to approximate the near-sphericity of natural pyrite grains. Grain areas were
149calculated for the remaining particles using the 'Analyze Particles' function in ImageJ, and
150grain sizes were estimated by assuming that each grain was perfectly circular in cross-section.

151   A separation procedure was then carried out on subsamples of the powdered crystal.
152Three 0.01 g aliquots of powder were added to 45 mL of LST in three 50 mL centrifuge
153tubes. These tubes were mixed for a minute using a vortex mixer at the highest speed, then
154placed in an ultrasonic bath (35 kHz) for 15 minutes. Tubes were then spun in a centrifuge for
15538 minutes at 3000 rpm, as these conditions were estimated (see equation 2) to allow ≥0.5 μm
156diameter spherical pyrite fragments to settle in LST. Particle settling time (t_s) was estimated
157using Stokes' Law[54,55]:

$$t_s = \frac{9\,\mu h}{2\left(\rho_p - \rho_l\right) R_p^2\, a} \qquad (2)$$

158

159where μ is the dynamic viscosity of the fluid (0.011 Pa·s for LST), h is the height of the liquid
160in the centrifuge tube (10 cm in our setup), ρ_p and ρ_l are the mass densities of the particles and
161the fluid (5.01 and 2.85 g/cm^3 for pyrite and LST), R_p^2 is the radius of the settling particle
162squared, and a is the centrifugal acceleration (in m/s^2), given by:

$$a = \omega^2 r \qquad (3)$$

163

164where r is the centrifuge radius (18 cm in our setup), and ω is angular velocity (in radians/s),
165given by:

$$\omega = 2\pi f \qquad (4)$$

166

167where f is the rotational frequency (50/s in our setup). It should be noted that the settling time
168calculated using equation 2 is likely an underestimate due to hindering effects such as
169particle-particle and particle-container interactions. After centrifugation, settled fragments
170were removed from the tubes using a plastic micro-pipette, placed in new 50 mL centrifuge
171tubes, rinsed and spun down (5 minutes at 2000 rpm) five times in deionized water. This
172process was repeated three times sequentially (Table S1, 'a-c') for each 0.01 g portion of
173powder. In order to more closely approximate insoluble residues from marine sediments, the
174extraction procedure was also repeated for a 1:99 mixture of pyrite and ~300 µm-sized quartz
175grains (0.01 g pyrite, 0.99 g quartz), and a 1:99 mixture of pyrite and ~50 µm-sized quartz
176grains. Each extract was dried and weighed, and grain size distributions were calculated for
177the first sequential extracts for the pure pyrite ('post'), pyrite with large quartz grains
178('postQz'), and pyrite with small quartz grains ('postSmQz').

179   A shatter box was employed to powder the Cretaceous-age shale samples, for no
180longer than one minute. There was no obvious sign of sulfide mineral fragmentation after this
181procedure. For the Santa Barbara Basin sediment sample, one gram of dried sediment was
182powdered gently in a mortar and pestle. For the Cretaceous shales and modern Santa Barbara
183Basin sediment, carbonate minerals were removed by three sequential 10-minute treatments
184with 6M hydrochloric acid, before the insoluble residue was rinsed five times with deionized
185water and dried in an oven at 60°C for 24 hours. The insoluble residues were then powdered
186by mortar and pestle prior to performing a single density separation as described above on
1870.25 g aliquots of each.

188*Mounting of samples*
189Dried iron sulfide samples were carefully transferred onto the surface of the base of a 1-inch
190round acrylic mould that had been coated with a release agent, isooctane. After adding iron
191sulfide samples and powdered hydrothermal pyrite and marcasite for use as internal S-
192isotopic standards (kept separate using a Parafilm M grid), the upper half of the mould was

193then attached and filled with epoxy (2:1:13.63 ratio mixture of 1-(2-aminoethyl) piperazine;
1941,-8-diamino-p-menthane; and Araldite 506 epoxy resin). After degassing in a vacuum oven
195for 10 minutes, and removing any remaining bubbles with a 21G needle, the epoxy was cured
196for 72 h at 60°C in an oven. The epoxy was then removed from the mould and sequentially
197polished with a 6 µm polishing pad, 3 µm diamond paste, and 1 µm diamond paste, in order
198to expose the standards and sample, and minimize surface topography and roughness. After
199using Raman microprobe analysis (1 mW laser power and 50x objective)[56] and optical
200microscopy (50x objective, plane-polarized light) to confirm the presence and mineralogy of
201analyte at the surface of the polished epoxy pucks, the pucks were coated with ~50 nm thick
202Au to ensure conductivity for SIMS analysis.

203**Sample imaging**
204For iron sulfide extracts from the Cismon and Demerara shale samples, ~20 µg aliquots were
205mounted on carbon tape, coated with 5 nm Au by physical vapor deposition using a Kurt J.
206Lesker PVD 75 (Jefferson Hills, PA, USA), before representative mineral textures were
207imaged by Scanning Electron Microscopy (SEM) using a JEOL JSM-7100 LVF Field
208Emission SEM (Tokyo, Japan).

209**Bulk sulfur isotope analyses**
210To determine $\delta^{34}S$ values for the hydrothermal pyrite and marcasite crystals, and to assess
211their degrees of isotopic homogeneity, three fragments of each crystal were randomly
212selected, and powdered in an agate mortar. Small (~125 µg) aliquots of powdered FeS_2 were
213loaded into tin capsules with 1-2 mg V_2O_5, combusted in a Costech ECS 4010 Elemental
214Analyzer (Valencia, CA, USA); $^{34}S/^{32}S$ ratios were then measured in a Thermo Scientific
215Delta V Plus isotope ratio mass spectrometer (Waltham, MA, USA), and corrected to VCDT
216by bracketing analyses of in-house VCDT-calibrated ZnS, BaS and $BaSO_4$ standards. For the
217fragments of pyrite and marcasite, the average $\delta^{34}S$ values measured by EA-IR-MS were –1.0
218± 0.1‰ (1σ, n=3) and 4.6 ± 0.2‰ (1σ, n=3), respectively. The same analytical procedure was
219used to generate 'bulk' $\delta^{34}S$ data for the pyrite physically extracted from the Cismon section
220sample.

221**SIMS sulfur isotope analyses**
222After pre-sputtering by Cs^+ bombardment for 300 seconds with a 1 nA beam current at the
223desired raster size, sulfur isotopic ratio experiments were performed in "scanning ion imaging
224mode" by Cs^+ bombardment (beam diameter of <1 µm, current of ~10 pA) of raster squares
225of 20-130 µm, using an electron multiplier (EM) detector on a CAMECA IMS 7f-GEO
226(Fitchburg, WI, USA) at Washington University in St. Louis to collect counts of $^{32}S^-$ and $^{34}S^-$
227for each pixel (grids of 128x128 or 256x256 pixels) for between 20 and 960 planes (1 minute
228per plane).

229   The size of each exposed grain analyzed was measured using calibrated optical
230microscope images before analyses. The SIMS stage was x-y calibrated to a stitched optical
231microscope image of the epoxy puck using digital video camera footage of the gold-coated
232sample surface in the analysis chamber. Raw isotope ratios for each grain were calculated by
233taking the mean $^{34}S^-/^{32}S^-$ ion count ratio of a central area of the grain over the multiple

234analysis planes. Various corrections were applied to data, including a dead-time correction, an 235interpolation of $^{34}S^-$ counts to align in time with those on $^{32}S^-$, and a quasi-simultaneous 236arrival (QSA) effect correction.[57] The magnitude of the QSA undercounting correction is 237proportional to instrument transmission, i.e., the number of secondary ions reaching the 238detector per incident primary ion. However, it is not possible to determine primary currents 239<50 pA very accurately on the 7f-GEO instrument. Therefore, the ratio of the QSA coefficient 240(β) to the primary ion flux (J) was used to facilitate the correction.[57] β/J values were 241determined for each session, via data obtained from the internal standard grains, using the 242relationship:

243
$$R_{exp} = R_{cor} + (\beta/J) \times {}^{34}S_{exp}$$
(5)

244where R_{exp} and $^{34}S_{exp}$ are dead time corrected $^{34}S/^{32}S$ ratio and ^{34}S count rate, respectively, and 245R_{cor} is the QSA corrected $^{34}S/^{32}S$ ratio. The instrumental mass fractionation was then corrected 246for by calculating the mineral-specific fractionation factor ($^{34}\alpha$) based on the mean raw (from 247SIMS) and expected (from EA-IR-MS) $\delta^{34}S$ value of the population of internal hydrothermal 248pyrite or marcasite fragments and dividing the average $^{34}S^-/^{32}S^-$ ratio of each environmental 249iron sulfide grain by the appropriate $^{34}\alpha$.

250**Results**

251*Extraction procedure*
252The grain size distribution of the powdered hydrothermal pyrite crystal ('pre') suggested that 25392.5% of grains were >0.5 μm, the smallest size expected to settle in our setup, so this was 254set as the expected maximum level of recovery. Recovery of initial pyrite (summarized in 255Table S1) was highest for 'post' (58±12%, 1σ) and for 'postSmQz' (57%), but lower for 256'postQz' (23±4%, 1σ). Initial extractions ('a') recovered most pyrite, and subsequent 257extractions ('b' and 'c') were generally not effective in recovering the remaining pyrite. At 258grain sizes larger than 1.1 μm (close to the lower limit of what can be precisely measured on 259the 7f-GEO; Figure 1), grain size distributions of pre, post, postSmQz and postQz ('1a') were 260all similar, within the power of our technique to resolve differences (Figure 1, inset). 261Therefore, the extraction procedure does not impose a grain-size bias for grains ≥1.1 μm.

262[insert Figure 1]

263   Recovery of pyrite for the Santa Barbara Basin sediment sample was estimated to be 26441.3% by comparing extract mass to previously measured total S abundance.[50] Extract purity 265for the Cismon section FeS_2 was estimated using EA to be 61% and by comparing extract 266mass to CRS abundance, FeS_2 recovery was estimated to be 54.5%, which again closely 267matches measured recovery for our synthetic sediment samples. In addition, the physically 268extracted iron sulfides had a bulk $\delta^{34}S$ value of −42.5 ± 0.2‰, whereas the bulk untreated 269sample had a $\delta^{34}S$ value of −42.1 ± 0.2‰.[51] The agreement between the isotopic compositions 270of the chemically and physically extracted iron sulfides indicates that the physical extraction 271procedure did not impart any isotopic bias on the population of iron sulfides in the sample.

SIMS sulfur isotope experiments

273*Hydrothermal pyrite*
274Sub-angular, randomly oriented 1-3 µm diameter fragments of the hydrothermal pyrite
275(Figure 2A) were analyzed in a 50 um raster over 375 cycles (30 seconds integration time per
276ion, per cycle; Figure 2B; see Jones et al[58] for justification). The fragment-to-fragment
277reproducibility (n=14, 1σ) was ±1.9‰ (Figure 1C; Figure S1A), and using the EA-IRMS
278bulk δ^{34}S value of −1.0 ± 0.2‰, $^{34}\alpha_{pyrite}$ was calculated to be 0.9964 (Table S2). The standard
279error associated with individual fragments was ±0.9 to ±3.3‰ (1σ; Figure 2C), with an
280average of ±2.1‰ (Figure S1A), and was better for larger fragments due to better counting
281statistics (Figure S2). Lateral intra-fragment reproducibility in the largest fragment (Figure
282S3A) was ±2.8‰ (n=8, 1σ; Figure S3B, C), with an average standard error of ±3.0‰ (1σ;
283Figure S3C).

284[insert Figure 2]

285*Hydrothermal marcasite*
286Sub-angular, randomly oriented 1-5 µm diameter fragments of the hydrothermal marcasite
287crystal (Figure 3A) were analyzed in a 50 um raster over 375 cycles (30 seconds integration
288time per ion, per cycle; Figure 3B). The fragment-to-fragment reproducibility (n=25, 1σ) was
289±2.3‰ (Figure 3C; Figure S1B), and using the EA-IRMS bulk δ^{34}S value of +4.6 ± 0.2‰,
290$^{34}\alpha_{marcasite}$ was calculated to be 1.0014 (Table S2). The standard error associated with
291individual fragments was between ±1.1 to ±5.2‰ (1σ; Figure 3C), with an average of ±2.6‰
292(Figure S1B), and was better for larger fragments due to improved counting statistics (Figure
293S2). Lateral intra-fragment variability in the largest fragment (Figure S4A) was ±1.9‰ (n=6,
294 1σ; Figure S4B, C), with an average standard error of ±3.6‰ (1σ; Figure S4C).

295[insert Figure 3]

296*Modern sedimentary pyrites (Santa Barbara Basin)*
297Optical microscope images (Figure 4A) suggest that the majority of pyrites in this modern
298sediment sample are 1-80 µm-diameter irregular aggregates of intergrown euhedral-to-
299anhedral microcrystals. A minority of pyrites are framboidal (i.e., 5-10 µm-diameter pseudo-
300spheroidal aggregates of equant, equidimensional, non-intergrown microcrystals), while some
301grains display a mixture of the framboidal and irregular textures (Figure 4A). The one
302pristine framboid measured by SIMS (Grain 27; Figure 4B-C) had a δ^{34}S$_{pyrite}$ value of −42.7 ±
303 1.5‰ (1σ; Figure 4C), the irregular aggregates (Figure 4B) had an average δ^{34}S$_{pyrite}$ value of
304+24.2 ± 2.9‰ (1σ, n=47; Figure 4C), and five grains displaying mixed textures (Grains 1–2,
305 17, 19, and 22; Figure 4B) had δ^{34}S$_{pyrite}$ values between +0.1 ± 0.8‰ (1σ) and +16.4 ± 0.7‰
306(1σ; Figure 4C; Table S2). Within the mixed textured grains, the framboidal areas were
307usually depleted in ^{34}S with respect to the irregular areas (Figure S5). Within the solely
308irregular aggregates, variability in δ^{34}S was minimal (±3.5‰, 1σ, n=11; Area 14 in Figure 4;
309Figure S6) and comparable to the average standard error associated with measurements
310(±2.6‰, 1σ; Figure S6D). Where present, the apparent variability had no consistent
311directionality (Figure S6). The average standard error associated with individual fragments
312was ±1.5‰ (1σ; Figures 4C, D). The sample average δ^{34}S$_{pyrite}$ value was +21.7 ± 10.3‰ (1σ;

313n=53; Figure 4D). The $\delta^{34}S_{pyrite}$ variability in this sample (Figures 4C, D) overlaps the bulk

314$\delta^{34}S_{CRS}$ value for the sample of +16.1‰,[50] and is not normally distributed (Figure 4D).

315[insert Figure 4]

316*Ancient sedimentary pyrites and marcasites (Cismon and Demerara Rise)*

317Optical microscope images of mounted extract from Cismon (Figure S7) display the presence

318of both euhedral marcasite and framboidal pyrite, as supported by laser Raman microprobe

319spot analyses and SEM (Figure S8). Pyrite and marcasite grains from Cismon measured by

320SIMS had average $\delta^{34}S$ values of −41.9 ± 5.2‰ (1σ; n=113) and −48.5 ± 5.1‰ (1σ; n=161;

321Figure 5), and cemented pyrite aggregates had an average $\delta^{34}S$ value of −42.2 ± 0.6‰ (1σ;

322n=2), as compared with the bulk $\delta^{34}S$ composition of −42.1‰.[51] There was little intra-grain

323$\delta^{34}S$ variation in marcasite grains (average 1σ = ±2.9‰, compared to an average intra-grain

324standard error of ±3.5‰, 1σ; Figure S9A-D), and very little intra-grain $\delta^{34}S$ variation in pyrite

325grains (average 1σ = ±3.7‰, compared to an average intra-grain standard error of ±2.9‰, 1σ;

326Figure S9E-H).

327[insert Figure 5]

328   As with the Cismon section sample, optical microscope images of mounted extract

329from Demerara (Figure S10) display the presence of both euhedral marcasite (in this case

330mostly in irregular aggregates) and framboidal pyrite, as supported by laser Raman

331microprobe spot analyses and SEM (Figure S8). Pyrite and marcasite grains measured by

332SIMS had average $\delta^{34}S$ values of −24.9 ± 11.2‰ (1σ; n=45) and −26.1 ± 6.1‰ (1σ; n=19;

333Figure 6), as compared with a bulk $\delta^{34}S$ composition of −24.4 ± 0.2‰.[52] In contrast to those

334from the Cismon section sample, pyrites from the Demerara sample sometimes featured

335larger, more easily-resolved intra-grain variation in $\delta^{34}S$ (average 1σ = ±6.0‰, compared to

336an average intra-grain standard error of ±1.6‰, 1σ; Figures 6, S11A-D). This was even more

337obviously the case for the marcasites (average 1σ = ±13.3‰, compared to an average intra-

338grain standard error of ±2.1‰, 1σ; Figures 6, S11E-H). Generally, the largest relative

339enrichments in ^{34}S were found near the edges of pyrite framboids (Figure S11A-B), and in the

340extremities of irregular aggregates of both minerals (Figure S11C-H).

341[insert Figure 6]

342**Discussion**

343*Evaluating the method*

344Despite incomplete recovery (reasons for which are discussed in the Supplement), the

345similarity between artificial pyrite grain size distributions before and after being treated with

346the extraction procedure (Figure 1) suggests that this protocol does not bias pyrite grain size

347distributions, even when grains are at the lower end of sizes that can be measured using a 7f-

348GEO SIMS instrument (~1 µm) or when they are mixed with large proportions of quartz

349grains. This is important because where grain size variability exists in populations of iron

350sulfide grains in sedimentary samples, such variability may be coupled to isotopic

351variability;[28] thus, a size bias in extraction protocol could produce an isotopic bias in the 352measured results relative to the parent sample.

353   Analysis of fragments of hydrothermal pyrite and marcasite crystals, used as S-354isotopic standards for our other SIMS experiments, resulted in little inter- (Figures S1-2) or 355intra-fragment (Figures S3-4) variability in δ^{34}S (i.e., the standard deviation of measurements 356between or within fragments was always smaller than the average standard error associated 357with those inter- or intra-grain measurements). Therefore, the method is suitable for the 358detection of the potentially large variations in δ^{34}S that may exist within or between 359sedimentary iron sulfide grains.[23,24,28,29,37]

360   The average SIMS δ^{34}S values for iron sulfides from samples from the Cismon section 361(–45.8 ± 6.1‰, 1σ; n=274; Figure 5) and the Demerara Rise (–25.3 ± 11.2‰, 1σ; n=45; 362Figure 6) are close to the previously reported bulk δ^{34}S$_{CRS}$ values (–42.1‰, and –24.4‰, 363respectively).[51,52] The Santa Barbara Basin pyrites' average δ^{34}S value (+21.7 ± 10.3‰, 1σ; 364n=53; Figure 4) is 5.6‰ higher than the bulk δ^{34}S$_{CRS}$ value (+16.1‰),[50] but the large range of 365grain-specific values (–42.7‰ to +28.9‰) overlaps with the bulk value, and corresponds to a 366textural dichotomy between isotopically light framboids and isotopically heavy irregular 367aggregates. Accordingly, the discrepancy between bulk and average grain-specific δ^{34}S values 368is likely the result of insufficiently representative sampling of the two textural components 369for SIMS analysis. The extraction and analytical procedures introduced in this study are not 370likely to give rise to any isotopic biases, though areas analysed by SIMS may not always be 371entirely representative of the bulk iron sulfides in a sample. In the future, this could be 372rectified by ensuring that SIMS analyses of each texture are in proportion to their relative 373abundances.

374   Importantly, the method documents δ^{34}S variability within a sample, which is critical 375for interpreting bulk 'CRS' δ^{34}S values. Inter-grain (Figures 4-7), intra-grain (Figures S5-6, 376S9, S11), and inter-mineralogy (Figures 5-6) variability all contribute to a single bulk δ^{34}S 377value from CRS extraction (which integrates both pyrite and marcasite, as well as potentially 378other reduced S phases). Each type of variability should be considered and investigated when 379making environmental interpretations based on δ^{34}S data.

380[insert Figure 7]

381***Interpreting sedimentary δ^{34}S data***
382The three samples studied here are distinct in terms of their bulk δ^{34}S values and internal δ^{34}S 383variability (Figure 7). Thus, they can be used to map out the environmental phase space that 384can be explored using this SIMS ion imaging method. The first step to this process is to 385consider that iron sulfide minerals formed in marine sediments record the δ^{34}S composition of 386reduced sulfur-bearing aqueous phases (e.g., hydrogen sulfide or polysulfides) in the fluid 387from which they nucleate or grow.[8,41] In most cases, this fluid is likely to be pore water in 388marine sediments, but pyrites can also precipitate from sulfide-rich water columns.[59] 389Secondly, iron sulfide mineral growth requires a source of iron. Different sources (i.e., 390mineral or aqueous) are differentially reactive to aqueous reduced sulfur species,[60] and

391therefore the extent to which iron sulfide minerals record spatio-temporal changes in the δ^{34}S
392composition of aqueous sulfur is highly dependent on the abundance, mineralogy, and
393speciation of available iron.[8]

394   The sample from Santa Barbara Basin comprises silt-clay sized material from one of
395the "gray layers" that have been hypothesized to represent extremely rapid deposition
396associated with major flood events.[61–63] Rapid deposition results in pore water sulfate being
397consumed faster than it is supplied.[22] We predict a broad range of pyrite δ^{34}S values
398corresponding to progressive pyrite precipitation in such a scenario. Berelson et al[50] found
399that iron disulfides from the sample are highly ^{34}S-enriched in bulk, and are predominantly
400irregular aggregates of pyrite. In this study, we found that the irregular aggregates noted by
401Berelson et al[50] are even more highly-enriched in ^{34}S than the bulk sample (Figure 4), and
402feature very little intra-grain δ^{34}S variability (Figure S6). Conversely, framboidal pyrites are
403depleted in ^{34}S, and feature irregular overgrowths that are usually relatively enriched in ^{34}S
404(Figure S5). This clearly implies a spatial or temporal separation in the growth of these two
405textures. The ^{34}S-depleted framboids likely formed in a relatively open, sulfate-replete
406system, such as pore waters close to the sediment-water interface, or in the water column
407(e.g., in sinking particles harboring anoxic microenvironments[64]). In contrast, the ^{34}S-enriched
408irregular aggregates likely formed in a system in which rapid MSR led to ^{34}S-enriched
409aqueous sulfate and sulfide.[22,65] MSR must have greatly outpaced pyrite formation, leading to
410the build up of an aqueous reduced sulfur pool in pore fluids with a similar S-isotopic
411composition to the initial sulfate reservoir. The majority of pyrite in the sample precipitated
412from this aqueous reduced sulfur pool. The high rate of MSR relative to the rate of pyrite
413formation was very likely a result of the slow kinetics of iron reduction.[60]

414   Sediments from the Cismon section are thought to represent nearly the opposite end-
415member case to Santa Barbara Basin, with very low bulk CRS δ^{34}S values (avg. –42.7‰).[51,52]
416These values have been interpreted to represent pyrite formation in a system that was open to
417the diffusive supply of sulfate,[66,67] so a narrow intra-sample range of δ^{34}S values is expected.
418Accordingly, we find that the sample lacks both inter-grain (Figures 5, 7) and intra-grain
419(Figure S9) δ^{34}S variability. Individual pyrite grain δ^{34}S values (−41.9 ± 5.2‰, 1σ; n=113)
420and marcasite grain δ^{34}S values (−48.5 ± 5.1‰, 1σ; n=161; Figure 5) cluster close to the bulk
421CRS δ^{34}S value, suggesting that the S-isotopic composition of aqueous reduced sulfur species
422in the fluid from which the iron sulfides formed was not highly variable. This is consistent
423with a scenario in which all iron sulfides (pyrite framboids, pyrite cements and marcasite
424euhedra) formed either in the water column or in sediments where the rate of sulfate diffusion
425from the water column exceeded the rate of sulfate consumption by MSR.

426   Finally, sediments from the Demerara Rise are thought to represent an intermediate
427case between the Cismon section and Santa Barbara Basin, with a corresponding bulk CRS
428δ^{34}S value of –24.4‰ for our sample. This black shale sample (422.8 m depth, ODP Leg 207,
429Hole 1258a) was deposited under a euxinic water column, so sulfate consumption by MSR
430very likely outpaced the diffusive replenishment of sulfate.[52] Therefore, a larger intra-sample
431range of δ^{34}S values relative to the Cismon section sample is expected. Accordingly, the

432sample from Demerara Rise features a large amount of δ^{34}S variability – both inter- (Figures
4336, 7) and intra-grain (Figure S11), in pyrites and marcasites. The mean δ^{34}S values of
434marcasite and pyrite grains (Figure 6) are very similar. However, unlike in the Cismon
435section sample, both pyrite framboids (Figure S11A), and pyrite (Figure S11C) and marcasite
436clusters (Figure S11E, G), have large internal ranges in δ^{34}S, of ~10‰ to 65‰, with more ^{34}S-
437enriched material on the outer layer of framboids or in discrete zones in the extremities of
438clusters. This pattern is evidence for the formation of these grains over a time interval with
439evolving pore fluid δ^{34}S. As in the case of the Santa Barbara Basin sample, these results
440suggest that MSR led to ^{34}S-enrichment of aqueous sulfate and sulfide with time in the
441sediment.[22,65] We also see a 'tail' of relatively ^{34}S-enriched pyrites in the δ^{34}S distribution
442(Figure 7), which suggests that there must have been sufficiently abundant and reactive iron
443available to sustain iron sulfide mineral growth as pore waters became progressively ^{34}S-
444enriched.[8,60]

445 Marcasite is thought to be a relatively rare mineral in sedimentary rocks, most notably
446occurring in black shales.[68,69] The environmental implications of its presence are still poorly
447understood. Experimental work suggests that a very low pH is required for its formation.[70]
448Given that pyrite oxidation can give rise to acidic conditions,[71] this has led to the suggestion
449that the partial oxidation of pre-existing pyrite led to the formation of marcasite in black
450shales.[68,69] However, given that black shales are thought to represent low pO$_2$ conditions in
451water column, it is unclear how early diagenetic pyrite oxidation could have occurred in these
452sediments. In addition, the general isotopic similarity between the highly abundant marcasite
453in the Demerara and Cismon samples used in this study, and the coexisting pyrite (Figures 5-
4546), suggests that the two minerals share a formation history. Therefore, marcasite formation
455was probably not a result of low pH conditions created by pyrite oxidation. Another way to
456generate more acidic pore waters than are typical for marine sediments is oxic organic matter
457respiration.[71] This process could have been exacerbated by the high organic loading at both
458sites.[52] Future work using SIMS will provide further constraints on the relative abundance of
459marcasite and the genetic relationship(s) between pyrite and marcasite in black shales.

460 In conclusion, the methods detailed here provide a basis for the physical extraction
461and accurate and precise sulfur isotopic measurement of microcrystalline iron sulfide grains
462within a range of sediments and sedimentary strata. The minimal size-biasing during the
463extraction procedure suggests that the iron sulfide extracts obtained should be isotopically
464representative of the bulk sample, as confirmed by our samples. The low apparent inter-grain
465variability between isotopically identical pyrite (and marcasite) micro-fragments implies that
466the sulfur isotope composition of diverse environmental populations of ≥ 1 μm-sized pyrites
467and marcasites can be measured accurately and precisely by SIMS ion imaging. Micrometer-
468scale intra-grain variability in δ^{34}S can also be measured. Ultimately, it is possible to use this
469approach to unpack local environmental (geochemical and depositional), metabolic, and
470diagenetic signals recorded in iron sulfide grains in both unlithified sediments and rocks.
471With this in mind, the method could be applied to the both the modern and ancient bulk
472sedimentary records of δ^{34}S to test previous wide-ranging interpretations of apparent
473excursions in bulk data.[72–74]

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