SQUID–SIMS is a useful approach to uncover primary signals in the Archean sulfur cycle

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Many aspects of Earth’s early sulfur cycle, from the origin of mass-anomalous fractionations to the degree of biological participation, remain poorly understood—in part due to complications from post depositional diagenetic and metamorphic processes. Using a combination of scanning high-resolution magnetic superconducting quantum interference device (SQUID) microscopy and secondary ion mass spectrometry (SIMS) of sulfur isotopes ($^{32}$S, $^{33}$S, and $^{34}$S), we examined drill core samples from slope and basinal sediments. These textures record systematic spatial differences in both mass-dependent and mass-anomalous sulfur-isotopic composition over length scales of even a few hundred microns. Petrography and magnetic imaging demonstrate that mass-anomalous fractionations were acquired before burial and compaction, but also show evidence of post depositional alteration 500 million years after deposition. Using magnetic imaging to screen for primary phases, we observed large spatial gradients in $\Delta^{33}$S ($>$4‰) in nodules, pointing to substantial environmental heterogeneity and dynamic mixing of sulfur pools on geologically rapid timescales. In other nodules, large systematic radial $\Delta^{34}$S gradients ($>$20‰) were observed, from low values near their centers increasing to high values near their rims. These fractionations support hypotheses that microbial sulfate reduction was an important metabolism in organic-rich Archean environments—even in an Archean ocean basin dominated by iron chemistry.

In addition to the nature of the MAF that is so conspicuous in Archean strata, questions remain about what role, if any, biology played in the early sulfur cycle. Comparative molecular biology suggests that both sulfide-based photosynthesis and dissimilatory sulfate reduction (DSR) were important early autotrophic and heterotrophic metabolisms, respectively (9, 10). Similar interpretations about DSR have been garnered from modest but notable sulfur-isotope fractionations in Archean samples (11–13). These proxies rely on the premise that differences between isotope ratios captured in sedimentary S-bearing materials can be definitively linked to specific S metabolisms via their expected kinetic isotope fractionations. In general, however, $\delta^{34}$S variations in Archean pyrites are much smaller than observed in Proterozoic and Phanerozoic rocks, and have average values close to bulk silicate earth ($~0$‰; ref. 14). This pattern has plausible end-member interpretations that range from no biological cycling (8, 14) to some biological cycling but with little induced fractionation during DSR due to low seawater sulfate concentrations ($<200$ µM; ref. 15), high temperatures (16), or high electron donor concentrations (e.g., ref. 17). An exclusive test of these ideas is challenged by a mass-balance circumstance unique to the Archean sedimentary record—sulfate minerals are exceedingly rare. Early Archean barite deposits like those known from the Dresser Formation of Western Australia (1, 18) and chert-rich successions of similar age in the Barberton Greenstone Belt of South Africa.

Significance

A challenge to understanding ancient sulfur-cycle processes on Earth is the persistent observation that post depositional processes have affected all Archean-age rocks, impacting geochemical signals, and the quality of paleoenvironmental interpretations. To solve this problem we developed a combination of texture-specific microscale techniques—scanning high-resolution low-temperature superconducting quantum interference device microscopy and secondary ion mass spectrometry. We applied these techniques in a well-studied Archean-age sedimentary succession in South Africa to unravel the mineralization and isotopic history and reveal primary sulfur-cycle processes. We observed systematic patterns of isotope ratios at microscopic scales that inform the nature of enigmatic sulfur-isotope mass anomalies unique to this time interval and further support hypotheses for the early evolution of sulfate-reduction metabolisms.


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Patterns emerging from multiple sulfur-isotope ratios in sedimentary rocks have provided powerful insights into the behavior of the Archean (>2.5 Ga) sulfur cycle and the timing of the rise of atmospheric oxygen (1). Sulfur-isotope data from Archean sedimentary successions show distinct differences from those contained in younger successions—in rocks older than ~2.32 Ga, S-bearing minerals display large deviations in isotope ratios from predicted mass-fractionation relationships, captured by the statistic $\Delta^{33}$S ($\Delta^{33}$S = $1000(\ln(1 + (\delta^{33}$S/1000)) – 0.515(ln(1 + (\delta^{34}$S/1000)), with $\delta^{34}$S = ($\delta^{34}$S/\delta^{32}$S$ _{\text{Samp}}$)/($\delta^{32}$S/\delta^{32}$S$ _{\text{Std}}$) – 1)1000; $\delta^{33}$S = ($\delta^{33}$S/\delta^{33}$S$ _{\text{Samp}}$)/($\delta^{33}$S/\delta^{33}$S$ _{\text{Std}}$) – 1)1000; $\Delta^{33}$S = $1000(\ln(1 + (\Delta^{33}$S/1000)) – 0.515(ln(1 + (\delta^{34}$S/1000))) and here termed mass-anomalous fractionations (MAF; refs. 1–3). The origin of Archean sulfur-isotope MAF remains imperfectly understood, although most hypotheses implicate atmospheric photochemistry involving SO$_2$ (1, 4, 5). If this interpretation is correct, photochemical and geochemical models can use stratigraphic sulfur-isotope data to provide quantitative constraints on the oxidative power of the Archean atmosphere (e.g., O$_2$ mixing ratio $\ll 10^{-5}$; ref. 6), continental crust growth, volatile fluxes from the solid earth (7), seawater chemistry, and the degree of biological cycling (8).
sedimentary basin that accumulated iron formation throughout its history (30, 36, 37).

Despite the high overall quality of preservation of these geological materials, petrographic textures (Fig. S5) indicate that the macroscopic sulfide-bearing phases display origins ranging from precipitation during early diagenesis (e.g., nodules with differential compaction, intraclast breccias, and soft sediment deformation) to late diagenesis and metamorphism (nodules without differential compaction, overgrowth rims and cements on early diagenetic chert nodules, millimeter-scale euhedral pyrites, and cross-cutting veins). In addition, the samples also contain abundant submillimeter finely disseminated sulfide-bearing minerals. Previous study of these materials by millimeter-scale sampling and bulk powders by gas-source mass spectrometry revealed variable $\delta^{34}$S values with an average close to 0‰ but strong and variable MAF values with $\Delta^{34}$S values, both positive and negative depending on petrographic texture (38, 39). Prior SIMS work on this succession also revealed substantial textural variation of $\Delta^{34}$S values, and a larger range of $\delta^{34}$S values (13, 29). These observations highlight a complex and protracted history of sulfur mineralization in this succession and the need for screening protocols to understand texture-specific analyses of multiple sulfur-isotope ratios.

Rock magnetics and paleomagnetism lend sensitive tools to query the chemical taphonomy of iron-bearing minerals and evaluate the quality of redox proxies derived from their abundance and isotopic ratios. Accordingly, core GKF01 was drilled at a 15° angle and geospatially oriented for paleomagnetic study. De Kock et al. (40) conducted an intensive paleomagnetic survey of both outcrop and drill core samples of Transvaal strata from the Griqualand West region as a part of the Agouron Drilling Project. All samples examined contain a very well developed and pervasive chemical remanence—referred to by its declination and inclination as north down—carried by ferromagnetic sulfide-bearing phases (i.e., pyrrhotite, Fe$_{1-x}$S where $x \approx 0.2$); this overprint is tied to extensive epigenetic Pb–Zn mineralization of Transvaal strata by craton-scale Mississippi Valley-type fluids driven by the emplacement of the ca. 2-Ga Bushveld Complex large igneous province (Fig. S1; refs. 40 and 41). Despite the ubiquity of this magnetic component even in strata from Griqualand West, the impact of this alteration on observed isotopic signals has remained unclear.

The presence of the late, metasomatic magnetic component is especially useful because it highlights geologic samples that otherwise appear well preserved, but nonetheless contain detectable sulfide-bearing mineral phases tied to later metasomatism. We used scanning high-resolution magnetic microscopy, using superconducting quantum interference device (SQUID) sensors to image the magnetization in room-temperature samples containing diverse sulfide mineral components at a 50-μm scale (Methods). The sensitivity and spatial resolution offered by this technique allow the opportunity to study how these rocks have preserved biogeochemical information through a complex 2.5-billion-year history. With insight from the SQUID images, we then measured $\delta^{34}$S from $\delta^{34}$S values, both positive and negative depending on petrographic texture (38, 39). Prior SIMS work on this succession also revealed substantial textural variation of $\Delta^{34}$S values, and a larger range of $\delta^{34}$S values (13, 29). These observations highlight a complex and protracted history of sulfur mineralization in this succession and the need for screening protocols to understand texture-specific analyses of multiple sulfur-isotope ratios.

Results and Discussion

Sample domains affected by late-stage (2.05 Ga) sulfide mineralization are highlighted in the scanning SQUID images (Figs. 1C, 2B and E, and 3B), by the presence of secondary ferromagnetic minerals of the pyrrhotite series. In general, early diagenetic pyrite nodules do not carry a remanent magnetization, but several nodules clearly contain magnetic domains (Fig. 1C).

We studied a well-preserved platform margin section of a Late Archean–age (ca. 2.6–2.52 Ga) carbonate platform found in the Griqualand West structural subbasin on the Kaapvaal Craton, Northern Cape Province, South Africa (Fig. S1). Core materials collected during the Agouron Scientific Drilling Project sample deep subtidal, slope, and basinal environments on the paleo-environmental processes.

The one-sink Archean sulfur cycle is currently underdetermined and it is not straightforward to use sulfur-isotope data to distinguish between a spectrum of sulfur-cycle processes. To test the interpretation that variability of $\delta^{34}$S values within a sample or paleoenvironment is the result of DSR (11, 13), we require a means to observe the isotopic composition of an environmental sulfur reservoir as it evolved along a known reaction path. Here we target pyrite nodules that grew in the sediments during early diagenesis to track the isotopic evolution of the fluid composition as a function of their radius and provide a targeted view into the microbial physiology once present in this environment.

Another and equally critical challenge to interpreting sulfur-isotope ratio data in Archean rocks is the persistent observation that the petrographic textures of sulfide-bearing minerals present in any given rock sample demonstrate complex origins that combine detrital, diagenetic, and metamorphic components. Indeed, a substantially different hypothesis was proposed wherein MAF arises during high-temperature diagenetic reactions involving the interaction of sulfur-bearing fluids with kerogen in the protolith (23, 24). Although this mechanism does not appear to explain the aforementioned secular MAF trends (25), it is important to note that all Archean successions have undergone diagenetic and, in most cases, metasomatic episodes of sulfur mineralization, which complicates interpretation of isotope records (e.g., ref. 26). To test these hypotheses and better capture the nature of MAF signals, we require a better understanding of how sedimentary successions preserve isotopic signatures through complex and protracted histories of sulfur mineralization. Secondary ion mass spectrometry (SIMS) has emerged as a powerful technique for measuring the sulfur-isotope compositions of Archean and Paleoproterozoic rocks, and this approach has demonstrated systematic isotopic differences tied to different pyrite textures (e.g., refs. 13 and 27–29). Here we build on this work using a combination of petrography and microscale magnetic imaging coupled to texture-specific sulfur-isotope measurements using SIMS to evaluate the effects of postdepositional mineralization and better constrain primary paleoenvironmental processes.

We studied a well-preserved platform margin section of a Late Archean–age (ca. 2.6–2.52 Ga) carbonate platform found in the Griqualand West structural subbasin on the Kaapvaal Craton, Northern Cape Province, South Africa (Fig. S1). Core materials collected during the Agouron Scientific Drilling Project sample deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes. In these environments, dolomite and deep subtidal, slope, and basinal environments on the paleo-environmental processes.
This is in contrast to finely disseminated sulfide mineral phases in the shale matrix, which are commonly magnetic (Fig. 1C). This is useful because the relationships revealed by SQUID microscopy are not readily determined by petrography alone. In particular, although finely disseminated sulfide mineral phases are often preferred for sulfur-isotope analysis, the scanning SQUID data suggests that, at least in this succession, they appear most impacted by the late mineralization and may not yield primary signals. This may reflect their greater surface area and higher reactivity with metamorphic fluids; and if this is true more broadly, a different sampling strategy may be required to derive higher quality proxy data from Precambrian successions.

Multiple sulfur-isotope ratios vary between textures, within textures, and with millimeter-scale changes in rock magnetics—and these relationships document isotopic history of sulfur mineralization. For example, sample 264.05 m contains at least four S-bearing phases: early diagenetic nodules, later overgrowth cement, and finely disseminated crystals in the shale matrix, as well as magnetic finely disseminated crystals in the shale matrix. SIMS data shows a sharp contrast in isotope ratios (resolved by our grids to within 60 μm) at the contact between nonmagnetic nodules and the overgrowth cement (Fig. 1D; and Fig. S6); this is still greater than expected length scales for self-diffusion of sulfur isotopes in sulfide-bearing minerals given the thermal history of this succession (43). The nodules in this sample record negative Δ33S values and systematically varying δ34S values; whereas, the overgrowth cement has Δ33S and δ34S values closer to zero per mil. These observations demonstrate that the sediments acquired their MAF before burial diagenesis and rule out a class of hypotheses positing a high-temperature burial origin for the isotope effects (23).

Our SIMS data also reveal that sulfur-isotope ratios of the sample were altered at 2.05 Ga. Five spot measurements on magnetic finely disseminated phases in the matrix show a δ34S mean and variance of −0.07‰ and 1.45‰², respectively, and a Δ33S mean and variance of 1.09‰ and 0.54‰², respectively. These magnetic Δ33S values represent a distinct isotopic composition from the other textures (Fig. S7), and demonstrate the impact of metasomatic alteration. Several nodules also show distinct magnetic anomalies; for example, an analytical grid
through a triangle-shaped nodule captures a continuous trend from magnetic nodule to nonmagnetic nodule to overgrowth cement (Fig. 1E and Fig. S6). Sulfur isotopes are distinct between these three phases (Fig. S7), in particular the magnetic nodule is characterized by higher $\Delta^{33}$S values than the nonmagnetic parts of the nodule and both are distinct from the overgrowth cement. The isotopic composition of the magnetic nodule (Fig. 1E) is also distinct from the nonmagnetic portion of the nodule and overgrowth cement (Fig. S7), but could reflect mixing of a primary nodule composition and later fluids. This protracted history of sulfur mineralization shows that the minor isotopic compositions of late phases varied and do contain MAF, but were also higher than the negative $\Delta^{34}$S values that characterize the primary phases. In principle, pyrrhotite can form from the decomposition of pyrite and loss of sulfur or with the addition of iron at high temperatures. However, either of these scenarios would imply little to no change of multiple sulfur-isotope composition. Pyrrhotite is also commonly a primary phase that acts as an important sulfur and redox buffer during metamorphism (44). The 2.05-Ga alteration event on the Kaapvaal Craton is widely reflected by epigenetic ore mineralization and the metals were transported and precipitated in sulfide-bearing...
minerals from low temperature fluids (41). The isotopic composition of late phases could record intratropical or intrasublimal redistribution of sulfur and need not require the introduction of new sulfur from fluid earth reservoirs (e.g., Paleoproterozoic seawater sulfate). This highlights a style of isotopic mixing due to late fluid flow processes that will tend to alter the MAF signal originally held by these sediments, as these processes are expected to be (largely) mass dependent.

This ability to identify and target nodules unaffected by late diagenetic and metasomatic processes provides fresh insights into biotic and abiotic sulfur-cycle processes, as they offer samples of pore fluid evolution with time. Several of these primary nodules show remarkable isotopic gradients as a function of their spherical segment radius, from negative δ34S values near the center to positive δ33S values near the rim (Figs. 1D and 2); whereas, δ18S values do not vary systematically over the same length scale (Fig. S8). This pattern implies significant sulfur-isotope fractionations (ca. 10–20‰, to produce the range in values observed in Figs. 1D and 2) occurred during DSR in these organic-rich shallow sedimentary paleoenvironments during growth of early diagenetic pyrite nodules. These data strongly support hypotheses that DSR was an important respiratory metabolism on early Earth (11–13, 16). Deep seawater in this marine basin was iron rich throughout its history (30), but even so, these δ34S fractionations illustrate that sulfur metabolisms were operating in environments with insufficient ferric iron to respire the organic matter present. These fractionations are larger than anticipated and imply that either sulfate concentrations in Archean seawater were greater than ~200 μM (15) or DSR fractionations are more physiologically plastic and/or poorly predicted by sulfate concentration alone. These observations demonstrate biological participation in the Archean sulfur cycle; however, despite the large systematic fractionations revealed by the SIMS data, on average and in bulk, these rocks have δ34S values near zero per mil (38, 39). From a mass-balance perspective, this suggests at least partially closed system behavior—most sulfate entering organic-rich marine sediments was converted to pyrite. This contrasts with sulfur cycling in marine sediments today wherein reoxidation of sulfate is important, and suggests that pyrite precipitation in Archean sediments was limited by sulfide rather than reactive iron (45).

Early diagenetic core minerals also document an evolving fluid with regard to minor sulfur-isotope composition (Fig. 3). Large systematic gradients in δ34S (>4‰, both positive and negative values) exist within single nodules and intraclasts—trends that, intriguingly, do not correlate strongly with δ34S (Fig. S8). Further, δ34S values within these single nodules cover much of the range seen in bulk throughout the entire sedimentary succession (38). These observations imply at least partially open system isotope mass-balance behavior during the growth of these nodules and intraclasts, with the sedimentary pore fluid sampling different sulfur pools on geologically short timescales. This environmental heterogeneity of δ34S values underscores the importance of incomplete but variable mixing due to sulfur-cycle processes, including microbial metabolisms and the possibility of rapid secular changes in the processes producing MAF.

Altogether, observations from this succession document the importance of mixing processes (both biotic and abiotic) at a wide range of length and timescales, including the impacts of post depositional mineralization. The magnitudes of these mixing processes are difficult to identify simply—in consequence, the observed microscale isotopic heterogeneity challenges the use of bulk rock δ33S data as a robust stratigraphic proxy for sulfur-cycle processes. However, by leveraging information from petrography and magnetic imaging, it is possible to untangle the complex history of sulfide mineralization and arrive at a more accurate understanding of sulfur-cycle function on Earth.

**Methods**

We used the scanning SQUID microscope to produce images of pyrite nodules highlighting the relative differences in magnetic field strength. The relative differences in field strength captured by the SQUID microscope images uncover otherwise cryptic magnetic domains within preserved sulfide-bearing minerals. Unlike a standard SQUID rock magnetometer that measures the magnetic moment of a sample, a scanning SQUID microscope measures the vertical component of the magnetic field on a prepared surface of a sample as it is rastered across a stationary microfabricated sensor, producing a high-resolution map (46–49). The SQUID sensor on the Caltech microscope is held at superconductor temperatures (2.6–3.8 K) on a sapphire bobbin, thermally linked with a vibration-stabilized Cryotech PT-403 pulse-tube cryocooler, eliminating the need for liquid helium. A 25-μm-thick sapphire window separates the room-temperature sample from the SQUID sensor. The SQUID apparatus remains fixed while the sample is rastered in small steps in an x,y grid using a nonmagnetic scanning stage; 50-μm steps were used in this study, with a resolution somewhat coarser than our SIMS spots. We collected oriented cylindrical 2.5-cm samples from the core (referenced using a ballmark system and wireline geophysical tools) using a drill press with a nonmagnetic bit. The cylindrical core was subsampled and stepwise hybrid demagnetization techniques (50) were applied to splits to confirm the presence of the north-down component magnetization vector (40). The samples were subsequently given a known isotropical remanent magnetization (IRM) of ~300 mT perpendicular to the sample surface, either into, or out of, the page. The IRM was subsequently imaged using the scanning SQUID microscope. As the IRM flowed through a thin, linear wire film) was run in between samples as a standard to monitor sensitivity, mainly as a measure of distance from the room-temperature sample to the superconducting sensor. Because of small differences in the height of the SQUID sensor to the sample surface from sample to sample, and because the strength of the field decays as 1/r², the absolute values of field strength measurements are difficult to compare between samples; however relative values within one scan can be used to precisely distinguish regions of differing magnetic properties within a sample. After obtaining SQUID images, samples were sputter coated with 30 nm of Au for SIMS analysis.

For multiple sulfur isotope analyses, we used a Cameca 7F-GEO ion microprobe housed within the Center for Microanalysis in the Division of Geological and Planetary Sciences at California Institute of Technology. We used a focused primary Cs⁺ ion beam of ~4 nA rastered over an area for a final spot size of ~25 × 25 μm². This configuration makes the 7F-GEO ideally suited for identifying isotope ratio trends within and between different textures revealed by petrography and scanning SQUID microscopy using closely and regularly spaced spot analyses (41, 51), although the small size of the disseminated pyrites present in many samples precludes reliable analysis of this type (41). While the instrument can analyze a large number of grains (50) that makes element-specific objective in SIMS analysis is operating at sufficient mass-resolving power (MRP) to separate ions of similar mass, but also allowing enough transmission of secondary ions to make precise measurements. When measuring multiple sulfur isotopes (δ31S, δ32S, δ33S), the minimum MRP is ~3,900 to separate δ32S from the δ34S ion. Operating with these analytical conditions, we typically achieve ~10⁻⁵ counts per second of δ32S and ~10⁻⁶ and ~10⁻⁷ counts per second for δ31S and δ33S, respectively. We used regularly spaced analytical grids of spot analyses collected incrementally from end to end (back and forth) to identify isotopic trends on a length scale greater than a millimeter. Analysis of sample unknowns were bracketed by measurements of standards every 10–15 measurements. We used a Caltech internal pyrite standard—grains of igneous pyrite from Peru (Orocamo district)—for which the multiple sulfur-isotopic composition was determined by gas source mass spectrometry of SF₆ (as in ref. 52; δ34S 1.024‰, δ32S 0.608‰, Vienna Canyon Diablo Troilite). Our standards were embedded within the samples close to the desired analytical region, and polished to obtain a flat surface (either as a thin section or thick section). This provides similar beam conditions for measurements of both standards and sample unknowns, a widely recognized challenge that must be met to produce accurate data (53). The isotope ratio data were corrected for Faraday cup yield differences and instrumental mass fractionation (Dataset S1). External precision, defined as the SD of multiple adjacent measurements of standards, is typically better than δ33S = 0.4%, δ32S = 0.3%, Δδ34S = 0.15‰ (1σ).

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Supporting Information

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Geological Context
The Late Archean Transvaal Supergroup occurs across much of the Kaapvaal Craton, broadly divided into Griqualand West and Transvaal structural subbasins (Fig. S1). The succession is remarkably well preserved and largely undeformed across much of the craton. Steeper dips occur in the Transvaal subbasin around the Bushveld Igneous Complex, and acute folding and faulting appears along the far western edge of the craton where Proterozoic red beds of the Olifantshoek Group are thrust over Transvaal rocks (1–4). Significant metamorphism is limited locally to areas of stratigraphic overlap and the Bushveld complex and the western fold-and-thrust belt; other regions remained below greenschist-equivalent facies (3, 5). However, surficial oxidative weathering is extensive in South Africa. To obtain fresh unweathered material for analysis, we sampled from deep diamond drill core materials taken northeast of Prieska in the Northern Cape Province, South Africa as a part of the Agouron Institute South African Drilling Project (Fig. S1). Core GKF01 captures a diverse range of siliciclastic and authigenic lithologies (carbonates, shales, and banded iron formation) within a well-studied sequence stratigraphic framework (6–8) that provides useful insight into the vectors of time and environment (Figs. S2 and S3). This succession has been studied extensively for its sedimentology, stratigraphy, paleontology, U–Pb geochronology, organic and carbonate C isotopes and contents (9), bulk rock multiple S isotopes (10, 11), paleo- and rock magnets (12), and bulk and trace element geochemistry (6, 13).

The sedimentary geology of the Transvaal Supergroup in Griqualand West with special attention to relationships in GKF01 is described in detail (6). This succession has been studied extensively for its sedimentology, stratigraphy, paleontology, U–Pb geochronology, organic and carbonate C isotopes and contents (9), bulk rock multiple S isotopes (10, 11), paleo- and rock magnets (12), and bulk and trace element geochemistry (6, 13).

The sedimentary geology of the Transvaal Supergroup in Griqualand West with special attention to relationships in GKF01 has been previously described (6–9, 14), the observations important to this study are highlighted briefly here. The Transvaal sits conformably atop volcanics and intercalated sedimentary rocks of the Ventersdorp Supergroup (felsic volcanics from the upper Ventersdorp yielded a U–Pb ion microprobe age from zircon of 2.714 ± 8 Ma; ref. 15). Three subgroups, Schmidtsdrif, Campbellrand, and Asbestos Hills, make up the Transvaal Supergroup. These record the initial transgression of the Kaapvaal Craton and development of a marine sedimentary ramp flanking the basement highs, the flooding of the entire craton and the progradation of a thick carbonate platform, and drowning of the carbonate platform followed by iron-formation deposition, respectively. The Vryburg Formation was deposited during the first post-Ventersdorp marine transgression of the Kaapvaal Craton in Griqualand West. Based on correlation with units in the Transvaal Basin, the Vryburg was deposited between 2,642 ± 3 Ma and 2,664 ± 1 Ma (16, 17). The lower Vryburg consists primarily of ripple-laminated sandstones that deepen upward into organic-rich and pyritic shales and turbidites. The upper contact is gradational, with increasing carbonate content up section that eventually gives way to the shallower water stromatolites and oolitic grainstones of the Boomplas Formation. Another transgression separates the top of the Boomplas from the low-energy organic-rich and pyritic shales of the Lokammona Formation. Again, carbonate content increases toward the gradational upper contact with the overlying Monteville Formation, a steepened carbonate ramp that developed during presumed highstand. Following Monteville deposition, the entire Kaapvaal Craton was flooded and followed by widespread carbonate deposition and development of the steep-margined ~2,588–2,520 Ma (17, 18) Campbellrand Platform, represented by the Lower Nauga/Reivilo and Upper Nauga formations. A major transgression led to the eventual demise of the Campbellrand Platform and the deposition of the ~2,460 Ma (19) Kuruman Formation. Altogether the Transvaal Supergroup in Griqualand West, during the development of Campbellrand platform and Kuruman Iron Formation, reflects the passive accumulation of chemical precipitates and minor siliciclastics on thinned continental crust adjacent to a major ocean basin in Late Archean through earliest Paleoproterozoic time (Fig. S2).

South Africa
Prieska
100 km
Griqualand West
Transvaal
Johannesburg
Doornberg fault zone
A
A'
Katlani
Kalkdam
Bushy Park
ADP-GKF01
Bushveld Complex
Penge Iron Formation
Kuruman Iron Formation
Malmani Platform
Campbellrand Platform
Schmidtsdrif Group
Wolkberg Group
Griqualand West
Transvaal
South Africa
Johannesburg

Fig. S1. Geologic map of Kaapvaal Craton showing the surface exposures of the Late Archean Transvaal Supergroup, broadly divided into two structural subbasins: Griqualand West and Transvaal proper (modified from ref. 8). The location of drill core GKF01 is marked. Stars denote widespread locations of Pb–Zn deposits in Transvaal Supergroup strata; names are shown for those being mined in the Griqualand West subbasin. This episode of sulfide mineralization was felt craton-wide, tied to the circulation of hydrothermal fluids related to the emplacement of the Bushveld Igneous Complex at 2.05 Ga (20).

Fig. S2. Cross-section through the Cambellrand carbonate platform (oriented from A to A’ showing the distribution of iron-rich minerals as a function of facies (modified from ref. 14). Fine-grained siliciclastics were delivered across the platform to form lowstand wedges (8) that commonly accumulated substantial concentrations of sedimentary organic matter (9) as well as reactive iron (13). These black shales constitute the lithologic host for substantial accumulations of pyrite and other sulfide-bearing minerals. The location and approximate stratigraphic position of drill core GKF01 is marked.
Fig. S3. Lithostratigraphy and generalized sedimentology of drill core GKF01. Group and formation names, with geochronological constraints are shown alongside. Superscripts denote references: 1) ref. 21; 2) ref. 16; 3) ref. 18; and 4) ref. 17.
Fig. S4. Boxplots showing quartile ranges of organic carbon concentrations (in weight percent) in the dominant lithofacies from slope and basinal paleoenvironments on the Campbellrand carbonate platform. Data from refs. 9, 22, and 23. The amount of residual organic matter correlates with relative sedimentation rate, the overall valence state of iron, and the amount of sulfur (23) in these diagenetically stabilized lithologies (e.g., ref. 24). Early diagenetic pyrite nodules are common in the black shales and, to a lesser degree, carbonates, are essentially absent from either oxide or siderite facies iron formation.
Fig. S5. Photographic plate of pyrite textures from carbonate and shale lithologies in Griqualand West. Core slabs shown are NQ (47.6 mm) diameter and oriented for stratigraphic up. Note the conspicuous dipping laminations, which along with a ballmark system and geophysical wireline data, allow core samples to be georeferenced. (A) Multiple types of early diagenetic pyrite nodules show differential compaction and plastic deformation; (B) pyrite intraclast breccia surrounded by black shale; (C) early diagenetic chert nodules and lenses surrounded by rims of later pyrite; (D) pyritized subtidal fenestral microbialite (with void-filling sparry calcite cement) overlain by finely laminated detrital carbonate into siderite facies banded iron formation. (E) Early diagenetic pyrite nodules preferentially grew along beds of detrital carbonate surrounded by black shale. (F) Early diagenetic pyrite nodules and lenses in black shale. (G) Late diagenetic pyrite nodule composed of coarse euhedral pyrite grains concentrated along laminations; note the lack of differential compaction. (H) Early diagenetic chert nodules in black shale with pyrite rims; note the late euhedral pyrites developed at the contact between the black shale and siderite-facies iron formation in the center of the sample. (I) Black shale with abundant pyrite nodules grading into fenestral microbialite with pyritized microbial roll-up structures.

Fig. S6. Reflected light photomicrographs of analytical grids showing the location of analysis spots across nodules and cement shown in Fig. 1 D and E on the Left and Right, respectively. Annotated images are shown alongside to mark interpretations. Closed circles denote nodules and open circles denote cement; spots that mix textures are shown as half circles. For scale, the size of the spots is 25 μm.
Magnetic sulfur-bearing phases have a unique isotopic signature. (A) Kernel-smoothing probability density estimates of $\delta^{34}S$ vs. $\Delta^{33}S$ for the isotope ratio grids shown in Fig. 1E. The data are divided into spatial categories based on petrographic texture (shown in Fig. S6) and field strength $>30$ nT (shown in Fig. 1). (B) Pairwise Kolmogorov–Smirnov tests on $\Delta^{33}S$ reject the null hypothesis ($P << 0.05$) that the data in these distinct petrographic textures derive from the same underlying distributions.

![Fig. S7](image)

**Fig. S7.** Magnetic sulfur-bearing phases have a unique isotopic signature. (A) Kernel-smoothing probability density estimates of $\delta^{34}S$ vs. $\Delta^{33}S$ for the isotope ratio grids shown in Fig. 1E. The data are divided into spatial categories based on petrographic texture (shown in Fig. S6) and field strength $>30$ nT (shown in Fig. 1). (B) Pairwise Kolmogorov–Smirnov tests on $\Delta^{33}S$ reject the null hypothesis ($P << 0.05$) that the data in these distinct petrographic textures derive from the same underlying distributions.

Cross-plots of multiple sulfur-isotope ratio data ($\delta^{34}S$ vs. $\Delta^{33}S$) for 264.05 m (A), 1,419.40 m (B), and 290.28 m (C). Data from late sulfide-bearing phases (determined by either petrography, magnetics, or both) are distinguished from early phases by different symbols, pluses versus empty circles, respectively. VCDT, Vienna Canyon Diablo Troilite.

**Fig. S8.** Cross-plots of multiple sulfur-isotope ratio data ($\delta^{34}S$ vs. $\Delta^{33}S$) for 264.05 m (A), 1,419.40 m (B), and 290.28 m (C). Data from late sulfide-bearing phases (determined by either petrography, magnetics, or both) are distinguished from early phases by different symbols, pluses versus empty circles, respectively. VCDT, Vienna Canyon Diablo Troilite.

**Other Supporting Information Files**

Dataset S1 (TXT)