Archean 'whiffs of oxygen' tied to post-depositional processes

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The origin of Cyanobacteria remains controversial because of the absence of a robust Archean body and molecular fossil record. A separate, widely applied, approach to date the evolution of Cyanobacteria centers on proxies for their metabolic product: O_2. A broad range of geological and geochemical observations support a minimum age for their origin to a time between 2.45 and 2.32 Ga, however a number of studies have argued for much earlier appearance of O_2 and oxygenic photosynthesis, some based on subtle elemental and isotopic signatures in drill core ABDP-9 through the Late Archean Mt. McRae Formation. Here we use light and electron microscopy, electron microprobe and synchrotron XRF for elemental composition, synchrotron X-ray spectroscopy for redox state, and secondary ion mass spectrometry (SIMS) to make trace metal and S isotope ratio measurements and inform bulk rock isotope data measured from ABDP-9. Altgoether this combination of tools is essential to untangle the complex mineralization and recover accurate paleoenvironmental signals. We observe five key results that impact prior hypotheses developed from ABDP-9.

1. Light and electron microscopy and X-ray imaging data show at least four generations of pyrite mineralization, some of which are tied to compressional deformation features.

2. Metamorphic phosphate minerals intergrown with late sulfides and fibrous chlorite group minerals in metasomatic veins reveal U-Pb SHRIMP ages that capture five distinct events of alteration that postdate the deposition of the Mt. McRae Formation at 2.31, 2.21, 2.05, 2.10, and 1.66 Ga.

3. Both SIMS and synchrotron imaging show that Mo is abundant in late pyrite phases and is strongly correlated with As (up to 4%), Cu, and Co—related to metasomatic fluids.

4. SIMS sulfur isotope data show early pyrite phases are characterized by negative ^{33}S mass anomalies. Vice versa is true for late pyrite phases which have very strong positive ^{33}S anomalies. This explains observed stratigraphic trends.

5. The 'whiff interval' is notably fissile and S redox maps show laminations of sulfate salts due to the impact of oxidizing fluids along these flowpaths. Fe redox imaging also reveals distinct oxidation fronts in underlying iron formation.