A COMBINED As K-EDGE XANES AND µ-XRF ELEMENTAL MAPPING APPROACH TO INDIRECTLY ASSESS THE BIOGENICITY OF ARSENIC IN FE-RICH PALEOARCHEAN SEDIMENTS.

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Introduction: Arsenic is hypothesized to be abundant and important to microbial life in Archean environments [1-4]; however, due to the high mobility of $H_3AsO_3^0$, the probable dominant form of As^{III} in a reduced, HCO_3^- buffered Archean ocean, little evidence of its journey through sedimentary environments is preserved in the rock record prior to the great oxidation event. This work examines a test case for a complete microbial As cycle preserved in the 3.26 Ga Mapepe Formation (Fig Tree Group, Barberton greenstone belt, South Africa). The distribution and mineralogy of As was mapped by µ-XRF and As K-edge x-ray absorption near-edge spectroscopy (XANES).

Results: Arsenopyrite (FeAsS) inclusions were found within hematite-rich (Fe_2O_3) jasper clasts in fan-delta conglomerates (Fig. 1). FeAsS are distributed diffusely throughout the interior of jaspers, or concentrated on pre-erosion surfaces within the clasts (Fig. 1A, B), strongly suggesting its introduction during the deposition or early diagenesis of jasper precursor sediments. In contrast, other more reduced clasts in fan delta deposits possess FeAsS or orpiment (As_2S_3) lining the outer edges of clasts, implying post-erosional introduction (Fig. 1C).

Hematite and arsenopyrite are not stable at the same pH and pe; therefore, we propose that As^{III}, As^{V}, or both were introduced to these sediments by adsorption to amorphous Fe-oxy-hydroxides during episodic Fe-oxidation in a transiently oxidized environment. Once buried, conditions in the sediment became very reducing, similar to modern marine sediments, mobilizing As^{III} and retaining more tightly adsorbed As^{V}, a process observed during reductive dissolution of iron oxides in modern reducing aquifer sediments. Subsequent reduction of As^{V} may have occurred due to the activity of a consortium of sulfate, Fe-, and As^{V}-reducing microorganisms in the presence of trace amounts of sulfide or sulfate, resulting in the microbially mediated precipitation of FeAsS, also observed in modern reducing sediments [5]. The presence of thick bedded barite deposits in the same unit imply the availability of sulfate on the fan delta.

Conclusions: µ-XRF imaging provides critical textural evidence for early As cycling. Indeed, the scarcity of As relative to Fe in typical surface environments likely implies that the sedimentary record of As cycling will commonly be preserved in lamination-scale features and thin linings observable primarily by *in situ* fine-scale techniques like µ-XRF. Similar geochemical imaging by PIXL (Planetary Instrument for X-ray Lithochemistry) or SHERLOC (Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals) will be important for detecting signatures of ancient (bio)geochemical cycles during the Mars 2020 rover mission.

We argue that As^{V} had to be present in the Fig Tree depositional basin in order for As to be retained and explain the distribution of FeAsS that was observed through µ-XRF imaging of these samples. This study provides indirect yet compelling evidence that microorganisms were oxidizing As^{III} to As^{V} and that other organisms or consortia were reducing As^{V} to As^{III}.

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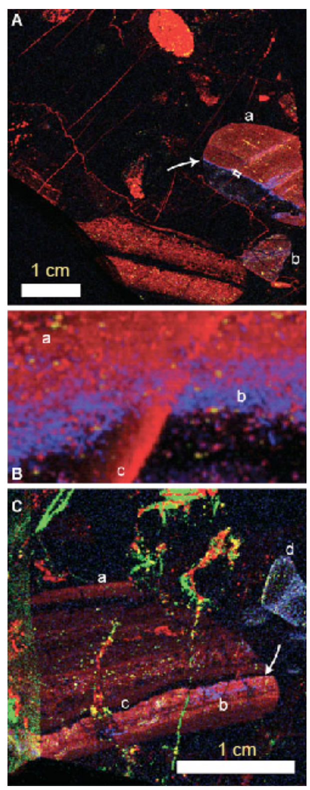

Figure 1. Fluorescence intensities of Fe (red), As (blue), and sulfur (green) in Fig Tree conglomerates. (A) Pebble (a) with FeAsS lined jasper band (arrow). White box from (A) enlarged in (B) shows FeAsS lining (a) jasper band with cross-cutting reduced phase vein (c). (C) Pebble with jasper band with internal FeAsS linings (a), and hematitic laminations (b) truncated by early erosion surface (arrow). Pebble containing Fe in pyrite and siderite with diffuse FeAsS lining pebble margins.