IMAGING OF VANADIUM AND NICKEL IN MICROFOSSILS: A NEW POTENTIAL BIOSIGNATURE.

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Introduction: Being able to distinguish unambiguously the biogenicity of microfossil-like structures in the ancient rock record is a fundamental predicament facing Archean paleobiologists and astrobiologists. Therefore, novel methods for discriminating biological from non-biological chemistries of microfossil-like structures are of the utmost importance in the search for evidence of early life on Earth and also possible life on Mars, either *in situ* by rovers or sample return missions back to Earth for future analysis. Here we report that synchrotron X-ray fluorescence imaging of vanadium and nickel within thermally altered organic walled microfossils of *bona fide* biological origin afford a new way forward to gain an insight into the nature and origin of ancient microfossil-like objects, and hence shed light on their biogenecity.

Vanadium and Nickel as a fossil chemical biosignature: It has been well established that the elements V and Ni are contained within crude oils, asphalts and organic matter contained in black shales, which are all unambiguously biological in origin [e.g., 1,2]. In these substances the V and Ni are strongly bound to metallo-organic complexes in the form of tetrapyrroles that form covalent bonds with divalent V and Ni cations, which consequently result in a high thermal stability of these macromolecules [e.g., 3,4]. Structurally, these V and Ni porphyrins are composed of four polypyrrole macrocyles interconnected together by methine bridges that contain four heterocyclic pyrrole-nitrogen atoms acting as ligands. It is has been conclusively demonstrated that these macromolecules are a product of diagenetic alteration of precursor chlorophyll and heme porphyrin pigment compounds from living organisms [e.g., 5,6].

Results:

Thermal alteration of Microfossils. Most organic walled microfossils, including acritarchs, investigated here, show sequential color and structural changes in response to increasing depth of burial related to the thermal history of the enclosing sediment. The acritarchs analyzed in this study are brown in color, corresponding to a TAI range 4, which indicates an overmature thermal alteration history.

X-ray microprobe analysis. The 2-D elemental map acquired from acritarchs *C. buickii*, *S. favosa* and a leiosphaerid reveal the presence of P, S, K, Ca, Ti, V, Fe, Co, Ni, Cu, and Zn. The quantitative analyses of these microfossils show they contain a significant quantity of V and Ni, particularly located in hotspots throughout the acritarchs. The quantitative data also demonstrate some interesting results, particularly the high P, S and Cl content, as well as low Cu and Fe concentrations.

Discussion:

Interpretation of vanadium and nickel data. The V and Ni may be attributed to remnant chlorophyll-containing chloroplasts within the organic-walled actritarchs. Alternatively, however, many marine algae contain a haloperoxidase in which vanadate is covalently linked to a histidine of the protein matrix [7]. However, the V content is too low to perform V XANES in order to determine the nature of the V environment. Further work will concentrate on performing V XANES if material allows.

Method assessment: Can V and Ni in association within carbonaceous microfossil-like objects be used as a biosignature? It is well accepted that morphology alone is not a useful criteria for distinguishing biologically and non-biologically derived carbonaceous microfossil-like objects. For example, carbonaceous microstructures resembling terrestrial microfossils have been observed and isolated from carbonaceous meteorites [8]. Furthermore, abiotic carbonaceous microstructures resembling morphologies of microfossil-like objects can also be synthesized by high-temperature heating of inorganic compounds, inorganic precipitation from hydrothermal fluids, and redox reactions during serpentinization [9]. However, the combination of morphology, carbonaceous composition, and V and Ni content distributed throughout the organic microfossil-like structure may form the basis a of protocol for the unequivocal identification of carbonaceous microstructures as biogeneic in origin.

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