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# Early Archaean oxygenic photosynthesis and the stabilization of the continents

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3800 Ma metasedimentary rocks from Isua, West Greenland, contain large concentrations of carbon with  $\delta^{13}C$ values ranging down to -25 per mil [PDB] and trace element signatures that suggest that oxygenic photosynthesis was already active at 3800 Ma. The rate of activity for an early Archaean biosphere is unknown, but it might well have been comparable to the present, when first oxygenic photosynthesis was introduced. The present photosynthetic primary production brings ca  $10^{16}$  mol y<sup>-1</sup> of carbon to the level of glucose. If this is averaged over the surface of Earth it translates to ca 300 mWm<sup>-2</sup>of chemical free energy production. This contrasts to the heat flow from Earth interior, which is ca 87 mWm<sup>-2</sup>. The emergence of oxygenic photosynthesis thus increased the transfer of energy through Earth surface environment considerably. Although most of the primary photosynthetic free energy production is dissipated within the biosphere itself, there is a leak from the biosphere to the lithosphere, which is characterized by oxidation of minerals and burial of biomass. One of the geochemical consequences of an active photosynthesising biosphere is the biologic forcing of the disequilibrium between the atmosphere and the rock substrate, which enhances rock weathering. In effect photosynthesis transforms solar energy into chemical free energy that can perform work in the form of weathering and fractionation of surface components. Weathering is and essential link in the chain of geochemical processes that ultimately leads to the formation of granite. It can be speculated that the free energy contribution from photosynthesis was the cause that allowed the rate of granite formation to exceed the rate of destruction during the early Archaean, and caused an end to the Hadean by the rise of the continents.

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## Carbonaceous matter in early Archean rocks; how to recognize a biosignature

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The rock record of the early Archean has been poorly preserved and the very few exposed formations that date back beyond 3 Ga have all been subject to greenschist to granulite facies metamorphism. Since ancient microfossils could easily have lost their original shape, mineralogical, chemical and isotopic indicators have been used to infer the presence of life. However, recent controversies have highlighted the need for a critical assessment of these indicators.

Several abiogenic processes have been recognized that can create the very tracers that scientists use in order to search for ancient life. Carbonaceous microfilaments in the 3.5 Ga old Warrawoona Group (Western Australia) were suggested to be the result of Fischer-Tropsch type reactions associated with hydrothermal activity[1]. In addition, it was shown in laboratory experiments that abiotic and morphologically complex microstructures can be synthesized which closely resemble the kind of carbonaceous, fossil-like structures that are found in early Archean metasediments [2]. In the 3.8 Ga old Isua Supracrustal Belt (southern West Greenland) some graphite was found to have formed by thermal disproportionation of metasomatic Fe-carbonate [3]. Abundant graphite in this belt was also found in highly altered ultramafic rocks, suggesting an origin from reactions related to serpentinization. The future of early life detection depends heavily on the understanding of these abiogenic processes and especially on the characteristics of the resulting carbonaceous material. In addition, an intriguing question is whether some of these abiogenic processes could have been involved in the production of organic precursor molecules for life.

A critical assessment is presented of the specific chemical, structural, and isotopic characteristics of carbonaceous material found in early Archean deposits. Materials of putative abiogenic and biogenic origin are compared. Results are presented of nitrogen and carbon isotope analysis by stepped combustion/pyrolysis mass spectrometry.

#### References

- [1] Brasier et al. (2002) Nature 416, 76-81.
- [2] Garcia-Ruiz et al. (2003) Science 302, 1194-1197.
- [3] van Zuilen et al. (2002) Nature 418, 627-630.