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## Paleoarchean carbonates on early Earth - microbial biosignature versus hydrothermal origin

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Paleoarchean carbonates from the Pilbara (Western Australia, WA) and Barberton Greenstone Belt (South Africa, SA) are almost the oldest known in Earth history, and compositionally variable. Their origin is mostly unclear - formed biologically and/or abiologically. Few stromatolites (e.g. 3.35 Ga Strelley Pool Fm, WA) are still preserved as a dolomite. These dolomites are zoned and exhibit a strong cathodoluminescence. The cores of the dolomites, however, are non-luminescent and represent the primary precipitate. Rare earth element characteristics are in part comparable to modern microbialites (e.g. negative Ce and positive Y anomalies).  $\delta^{13}\text{C}_{\text{VPDB}}$  signatures of these carbonates (ca. +3‰) are in good accordance with photoautotrophy. A fenestral chert from the same formation strongly resembles a typical microbial carbonate facies from the Upper Triassic of the European Alps, which was deposited in a carbonate lagoonal setting [1]. Within this facies, dolomite rhomboids and chert pseudomorphs after aragonite were observed [1], pointing to carbonate as general precursor material of the cherts. The majority of carbonates, however, are primary calcites within inter pillow spaces of the ca. 3.47 Mt. Ada Basalt, the 3.46 Ga Apex Basalt, and the 3.35 Ga Euro Basalt of the Pilbara (Fig. 1). In case of the Apex basalt, the calcite exhibits  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{SMOW}}$  values (0 ‰/+13‰) approximately to modern marine settings. Hydrothermal carbonates (e.g. kutnahorite and ankerite in the 3.5 Ga Dresser Fm, WA) are strikingly different. These carbonates exhibit elevated Fe, Sr and Ba concentrations, REE+Y patterns typical for a hydrothermal source (positive Eu anomaly), and distinct  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{SMOW}}$  values (-6‰/+21‰). Carbonate phases in hydrothermal chert veins and silicified 3.25 Ga sedimentary rocks of the Fig Tree Group (SA) are particularly interesting. These small carbonate crystals (10-20µm) exhibit a strong cathodoluminescence, pointing to enrichments of  $\text{Mn}^{2+}$  in the crystal lattice, and are linked to organic flakes (100-200µm), which have  $\delta^{13}\text{C}_{\text{VPDB}}$  values of ca. -25 to -30‰. Various microorganisms are able to precipitate rhodochrosite and kutnahorite [2, own experiments]. Mn-rich carbonates therefore



may precipitated within microbial EPS using reduced  $\text{Mn}^{2+}$  directly from anoxic seawater. While the validity as a microbial biosignature remains to be proven, multiple lines of evidence argue for early Archean carbonates as important environmental archives of microbial activity on early Earth [3].

*Figure 1: 3.46 Ga Apex basalt.*

*References:*

- [1] Duda et al. (2016) PLOS One, 11(1)
- [2] Kashefi K and Lovley D R (2000) *AEM*, 66, 1050-1056.
- [3] Reitner J. Fritz H-J and Duda J-P (2014) *Gaia Inform*, 7

