

## EARLY ARCHEAN CARBONATES ON EARLY EARTH - MICROBIAL BIOSIGNATURE VERSUS HYDROTHERMAL ORIGIN.

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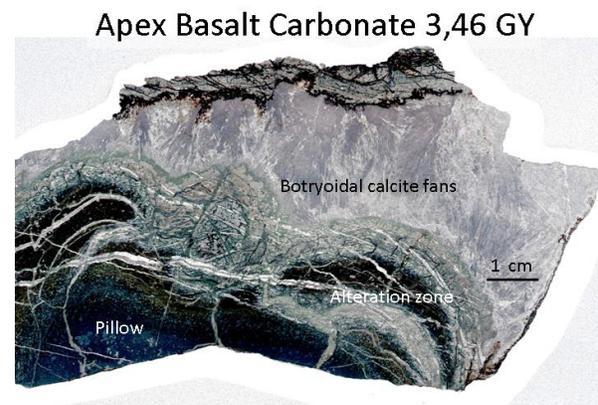
Early Archean carbonates from the Pilbara (Western Australia (WA)) and Barberton Greenstone Belt (South Africa (SA)) are amongst the oldest in the geological record and vary in composition from different settings. Their origin, however, is mostly unclear - are they biological or abiological precipitates? Early Archean environments were anoxic and many were strongly influenced by hydrothermal vents. A few stromatolites (e.g. 3.35 Ga Strelley Pool Fm, WA), however, are still preserved as dolomite, suggesting microbial precipitation. These dolomites are zoned and exhibit strong cathodoluminescence. The cores of the dolomites, however, are non-luminescent and interpreted to represent the primary precipitate. REE+Y analyses of these cores show patterns (negative Ce & positive Y anomalies) similar to modern microbialites and exhibit  $\delta^{13}\text{C}_{\text{VPDB}}$  values (ca. +3‰) that are in accordance with carbonates precipitated via photoautotrophy. A primary sedimentary carbonate-chert from the Dresser Formation has cm-scale bedding that strongly resembles a typical microbial carbonate facies from the Upper Triassic Dachsteinkalk of the European Alps deposited in a lagoonal setting. Within this facies, dolomite rhomboids, as well as chert pseudomorphs after aragonite, point to carbonate as the general precursor material of the cherts. Taken together, these results confirm that the microbial mat facies of the Pilbara were initially formed in a carbonate setting [1].

These characteristics are strikingly different to those of hydrothermal carbonates (kutnahorite, ankerite in the 3.5 Ga Dresser Fm, WA), which exhibit high Fe, Sr and Ba concentrations, a REE+Y pattern 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‰). Another distinct carbonate occurrence is bladed, pink calcite precipitated within inter-pillow spaces of 3.5-3.35 Ga basalts of the Pilbara (Fig. 1). For the Apex Basalt, these calcites exhibit  $\delta^{13}\text{C}_{\text{VPDB}}$  and  $\delta^{18}\text{O}_{\text{smow}}$  values (0‰/+13,5‰) similar to modern marine settings.

The most intriguing Archean carbonates, however, are linked to small organic flakes (100-200µm) within Pilbara hydrothermal chert veins and silicified 3.25 Ga sedimentary rocks of the Fig Tree Group (SA). The organic flakes have  $\delta^{13}\text{C}_{\text{VPDB}}$  values of ca. -25 - 30‰ and are commonly associated with small (10-20µm), high-luminescent, Mn-rich carbonates, e.g. rhodochrosite. Hyperthermophile archaea like *Pyrobaculum is-*

*landicum* was reported to be able to reduce  $\text{MnO}_4$  at 100°C while precipitating rhodochrosite [2, and our own experiments]. Archean rhodochrosite and other Mn-rich carbonates (kutnahorite) may therefore be the product of archaeal activity. 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].

**References:** [1] Van Kranendonk M.J. et al. (2008) *Precamb. Res.*, 167, 93-127. [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



### Apex Basalt Carbonates:

Carbonate mineralogy (XRD+Raman):

Fe(II)/Mn-rich Calcite 78%  
 Ankerite 3%  
 Dolomite 2%

$\delta^{13}\text{C}$ : 0,004 to 0,947‰  
 $\delta^{18}\text{O}_{\text{smow}}$ : 13,5‰

Basalt:  $^{87}\text{Sr}/^{86}\text{Sr}$  0,702636

Calcite:  $^{87}\text{Sr}/^{86}\text{Sr}$  0,703312

### Mt Ada Basalt Carbonates

$\delta^{13}\text{C}$ : -0,39 to -0,66‰  
 $\delta^{18}\text{O}_{\text{smow}}$ : 11,34 to 11,56‰

### Euro Basalt Carbonates:

$\delta^{13}\text{C}$ : 0,21 to -0,17‰  
 $\delta^{18}\text{O}_{\text{smow}}$ : 10,35 to 10,59‰

**Fig. 1: Bladed Mn-rich calcite precipitated within the cavity space between pillows; these textures are typical of boiling.**