

# Direct dating of Archean microbial ichnofossils

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## ABSTRACT

Well-preserved Archean pillow lavas from the ca. 3.35 Ga Euro Basalt of the Pilbara Craton, Western Australia, contain micron-sized tubular structures mineralized by titanite (CaTiSiO<sub>6</sub>) with residual organic carbon preserved along their margins. Direct U-Pb dating of titanite in the tubular structures demonstrates an Archean age. These tubular microstructures are identical to microbial ichnofossils in modern basalts, ophiolites, and greenstone belts, and are interpreted as a biogenic signature in these ancient rocks. Microbial colonization of basaltic glass thus appears to have been part of a deep subsurface biosphere established early in Earth's history.

**Keywords:** early life, greenstone belt, Pilbara Craton, geochronology, ichnofossil, astrobiology.

## INTRODUCTION

Recent work in the Barberton Greenstone Belt of the Kaapvaal Craton, South Africa, has shown that volcanic rocks may have hosted life as far back as 3.5 Ga (Furnes et al., 2004; Banerjee et al., 2006). Most evidence for early life is the subject of ongoing debate because purported microfossils or biosignatures lack direct age constraints, modern analogues are commonly lacking, and alternative abiotic hypotheses exist. Here we show that ca. 3.35 Ga volcanic rocks from the Pilbara Craton, Western Australia, preserve early microbial ichnofossils similar to those of the Barberton Greenstone Belt and provide the first in situ radiometric age determination of these Archean microbial trace fossils. The microfossils are tubular structures mineralized by titanite with residual organic carbon preserved along their margins. These structures are identical to microbial ichnofossils in modern basalts, ophiolites, and greenstone belts for which no demonstrable abiogenic hypotheses exist. Direct U-Pb dating of titanite in the Pilbara Craton microfossils confirms their Archean age. Thus Archean pillow basalts may help reveal the conditions under which life began to flourish on Earth and, by analogy, other planets and moons.

## GEOLOGICAL BACKGROUND AND SAMPLE DESCRIPTIONS

The samples for this study come from exceptionally well preserved pillow lavas in the ca. 3.35–3.31 Ga Euro Basalt (lat 21°13.206'S; long 119°18.071'E) of the Kelly Group in the Pilbara Craton, Western Australia (Van Kranendonk et al., 2002; Van Kranendonk and Pirajno, 2004; Fig. 1A). The Kelly Group consists of the

basal Strelley Pool Chert, a silicified quartzite and stromatolitic carbonate succession, the 5–8-km-thick Euro Basalt, which has a basal komatiitic unit, the felsic volcanic Wyman Formation, and the Charteris Basalt (Van Kranendonk et al., 2002; Van Kranendonk and Pirajno, 2004). The Strelley Pool Chert is interpreted to have formed as an isolated, transgressive peritidal carbonate platform and contains evidence for early life in the form of several distinct stromatolite facies (Allwood et al., 2006), although a range of self-organizing structures resembling stromatolites can also be generated abiotically (Grotzinger and Rothman, 1996; Brasier et al., 2006). The Kelly Group unconformably overlies the ca. 3.53–3.43 Ga Warrawoona Group, in which traces of microbial life have also been inferred from stromatolites and microfossils in the ca. 3.49 Ga Dresser Formation (e.g., Walter et al., 1980), and microfossils of the Apex chert (e.g., Awramik et al., 1983; Schopf, 1993), although both examples are controversial (e.g., Brasier et al., 2002; Garcia-Ruiz et al., 2003).

A dark zone that represents the chilled, originally glassy rim defines the outermost 10–20 mm of most pillows (Figs. 1A, 1B). Parts of this glassy margin spalled off during pillow growth, forming interpillow hyaloclastite (Fig. 1B). These formerly glassy rims and original glass shards in interpillow hyaloclastites (Fig. 1C) now consist of a greenschist facies metamorphic mineral assemblage of extremely fine grained chlorite with quartz, calcite, titanite, and scattered epidote. Interpillow hyaloclastites commonly show very little evidence of deformation with preservation of original jigsaw breccia textures (Fig. 1C).

Micron-sized tubular structures mineralized by titanite are observed in the formerly glassy rims and interpillow hyaloclastites of Euro

Basalt pillow lavas (Fig. 1D). These consist of fine-grained aggregates of titanite that form tubes, commonly 1–5 μm wide and as long as 150 μm. The tubes have vermicular and branching morphologies and are commonly segmented (Fig. 1). They consistently extend away from healed fractures (Figs. 1D, 1H). The size, shape, and distribution of these tubes are remarkably similar to those found in the Barberton Greenstone Belt (Furnes et al., 2004; Banerjee et al., 2006) and to features documented in glassy pillow rims and hyaloclastites in modern oceanic crust (e.g., Furnes et al., 2001; Banerjee and Muehlenbachs, 2003; Fig. 1C) and ophiolites (Furnes and Muehlenbachs, 2003). In particular, similarities in delicate textures such as apparent segmentation are readily observed (Figs. 1F, 1G). Further, the morphology of the tubes is inconsistent with inorganic precipitation of titanite during normal seafloor hydrothermal metamorphism, which forms either wedge-shaped crystals or “dusty” pseudomorphs of primary phases (e.g., Alt, 1995).

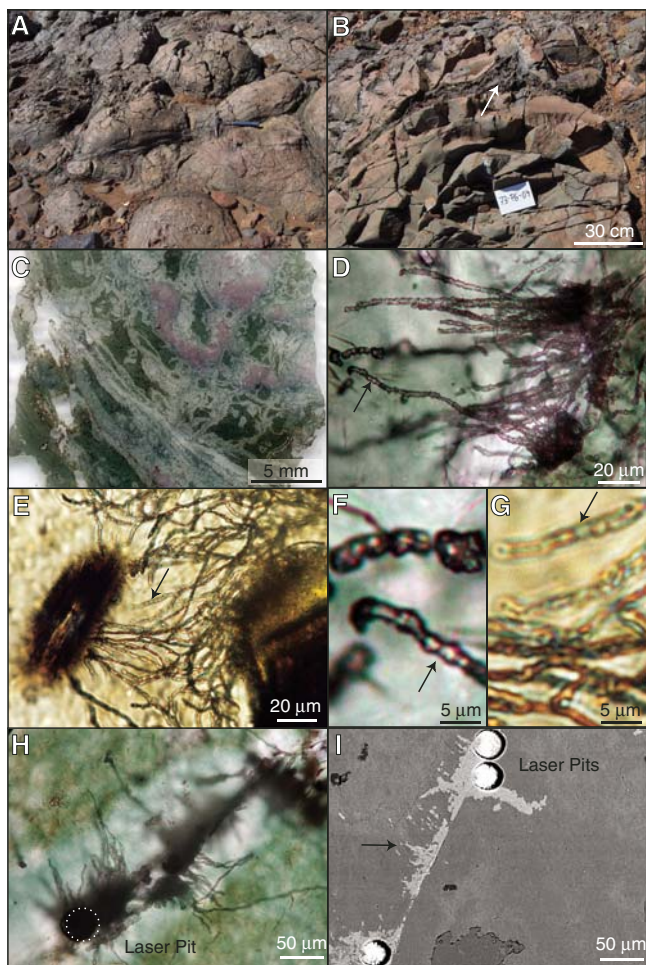
## X-RAY MAPPING

Volcanic glass is scarce throughout the rock record, and so evidence for bioalteration in ophiolites and greenstone belts is more commonly observed as geochemical fingerprints. Elevated levels of biologically important elements such as carbon (C), nitrogen (N), and phosphorus (P) are taken as markers of microbial activity. To prevent C contamination during sample preparation, special care was taken to avoid external carbon sources, and all grinding and polishing was performed with Al oxide powders. X-ray mapping reveals C along the margins of the tubular structures (Fig. 2; see GSA Data Repository Fig. DR1<sup>1</sup>). Smaller enrichments in N and P are also observed (Fig. 2; Fig. DR2). These enrichments are highly restricted to the immediate area of the titanite tubes and quickly diminish away from these areas. Fe and Mg maps from the

<sup>1</sup>GSA Data Repository item 2007119, Figure DR1 (carbon X-ray element maps), Figure DR2 (additional X-ray element maps), Figure DR3 (additional weighted average <sup>206</sup>Pb/<sup>238</sup>U plots), and Table DR1 (U-Pb dating results), is available online at [www.geosociety.org/pubs/ft2007.htm](http://www.geosociety.org/pubs/ft2007.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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**Figure 1. A:** Pillow lavas from ca. 3.35 Ga Euro Basalt from Pilbara Craton, Western Australia. Note hammer is ~30 cm long. **B:** Dark 10–20-mm-thick zone marks originally chilled, glassy rims. Arrow indicates where triangular intersection of three pillows is filled with interpillow hyaloclastite. **C:** Thin-section image showing angular fragments with jigsaw breccia textures that were originally glass. **D:** Photomicrograph of interpillow hyaloclastite (sample 74-PG-04) from Euro Basalt. Original glass exhibits healed fractures along which numerous tubular structures mineralized by titanite are rooted. Arrow points to well-developed segmentation visible at ends of one of tubes. **E:** Modern microbial tubular structures (Deep Sea Drilling Project sample 46–396B–20R–4, 112–122 cm) are remarkably similar to those found in Euro Basalt (D). Dark object on left is variole, quench texture defined by central swallow-tail plagioclase crystal onto which clinopyroxene needles have grown perpendicularly. Arrow points to well-



developed segmentation visible at ends of one of tubes. **F:** Enlarged view of segmented tubes from D. **G:** Enlarged view of segmented tubes from E. Note striking similarity in segmented structures between F and G. **H:** Photomicrograph showing size and location of laser pit (white dotted circle) at root zone of titanite tubes after in situ laser ablation dating analysis. **I:** Backscattered electron image showing size and location of laser pits at root zone of titanite tubes. Titanite shows up as light gray; chlorite and quartz are darker shades. Arrow identifies approximate location of area mapped in Figure 2.

same region show opposite trends to C, indicating the C is not bound in carbonate (e.g., Fig. 2; Fig. DR2). The CI map shows no enrichment, eliminating epoxy as the carbon source (Fig. DR2). The presence of C and other biologically important elements associated with biofilms and organic remains containing nucleic acids have been well documented from microbial etching textures in modern basaltic glass (Torsvik et al., 1998; Furnes et al., 2001; Banerjee and Muehlenbachs, 2003). In ancient rocks, the association of C with microbial ichnofossils is interpreted as residual organic material trapped along the interior surfaces of the tubes and preserved by later titanite mineralization (Furnes et al., 2004, 2005; Banerjee et al., 2006).

#### U-Pb DATING

To directly determine the age of the titanite-mineralized microfossils in the Pilbara Craton samples, we conducted U-Pb dating of titanite

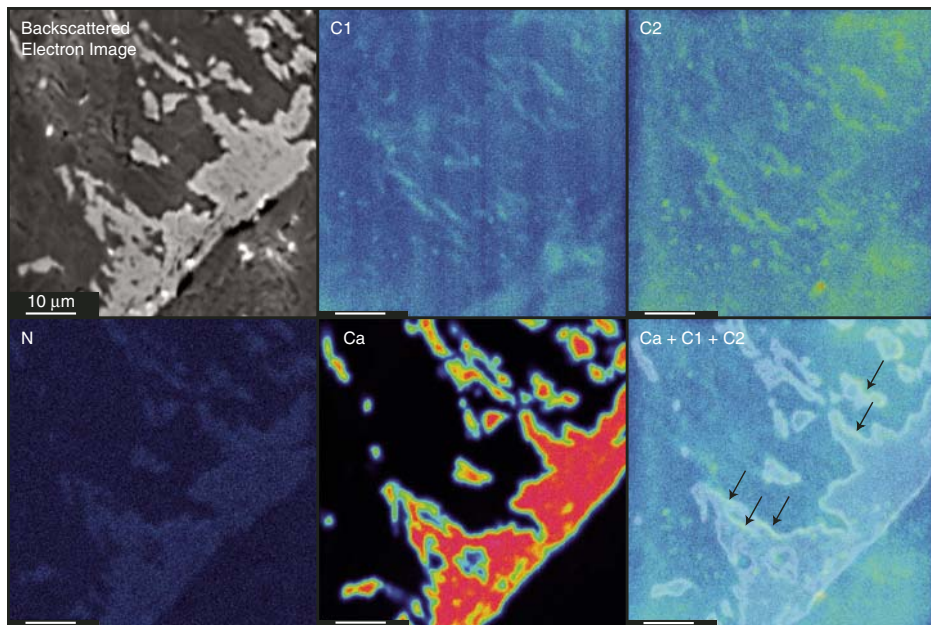
in the tubes using a novel in situ laser ablation multicollector-inductively coupled plasma-mass spectrometry (LA-MC-ICP-MS) technique. Unlike most laser ablation U-Pb studies that analyze separated, handpicked grains, the U-Pb analyses in this study were conducted in situ, on the same (30–50- $\mu\text{m}$ -thick) petrographic thin sections of interpillow hyaloclastite used for optical microscopy and X-ray mapping. This allowed precise targeting of areas of interest with the laser (Figs. 1H, 1I). A spot size of ~40  $\mu\text{m}$  was used to acquire U-Pb contextual age information and maximize the mass spectrometer ion signal. In most cases the root zones of the tubes rather than individual tubes were targeted, because most tubes are only a few microns wide (Fig. 1). This approach helped avoid contamination from adjacent minerals during laser analysis. To our knowledge, this is the first direct in situ radiometric age determination of an Archean microfossil.

We performed 13 titanite U-Pb laser ablation analyses in three thin sections; the results are listed in Table DR1 (see footnote 1) and plotted in Figure 3. The LA-MC-ICP-MS analyses yield a lower intercept age of  $2949 \pm 250$  Ma on a Tera-Wasserburg plot and define a well-defined mixing line between the radiogenic and common Pb components (Fig. 3A). To obtain valid U-Pb dates, the common Pb component of the titanite was calculated using a method applied to Pb dating of perovskite (Williams, 1998). The  $^{207}\text{Pb}/^{206}\text{Pb}$  value ( $1.256 \pm 0.11$ ) is given by the y-intercept on the Tera-Wasserburg plot (Fig. 3A) and is used to calculate the proportion of common Pb for each analysis, using well-established U-Th-Pb equations (Compston et al., 1984). The titanite data yield a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $2921 \pm 110$  Ma (Fig. 3B).

The low  $^{206}\text{Pb}$  ion signal intensities (cps; Table DR1 [see footnote 1]) from the Pilbara Craton titanite analyses are similar in magnitude to those reported for titanite used to test the accuracy of the analytical protocol (sample CL-2 in Simonetti et al., 2006). This indirectly confirms minimal (if any) contamination from adjacent minerals during laser analysis of the Pilbara titanite. The changes in the calculated  $^{206}\text{Pb}/^{238}\text{U}$  ages are less than their associated  $2\sigma$  uncertainties when varying the common  $^{207}\text{Pb}/^{206}\text{Pb}$  values from 1.256 to 1.14 (Fig. DR3; see footnote 1).

#### DISCUSSION AND CONCLUSIONS

Investigations of titanite microtubules in the Barberton Greenstone Belt have concluded that these represent the ancient mineralized traces of microbial activity formed during biogenic etching of the originally glassy pillow rims and hyaloclastites (Furnes et al., 2004; Banerjee et al., 2006). Comparable microbial corrosion of natural basaltic glass has been well documented over the past decade in modern oceanic crust and well-preserved ophiolites worldwide (e.g., Thorseth et al., 1992; Fisk et al., 1998; Furnes et al., 2001, 2005; Banerjee and Muehlenbachs, 2003). Early studies (Thorseth et al., 1992) suggested that microbes colonizing natural glass surfaces actively dissolve them to extract nutrients, and this mechanism was later verified experimentally (Thorseth et al., 1995; Staudigel et al., 1995, 1998). One abiotic mechanism for the formation of similar-looking tubular structures, known as ambient inclusion trails and formed by pressure solution, has already been negated as a viable option for titanite mineralized tubular structures in Archean pillow lavas (Banerjee et al., 2006). Based on the size, shape (e.g., straight, curved, bifurcating, budding), and distribution of the tubular structures, coupled with the presence of residual organic carbon preserved along their margins, we suggest that the Pilbara Craton examples represent mineralized



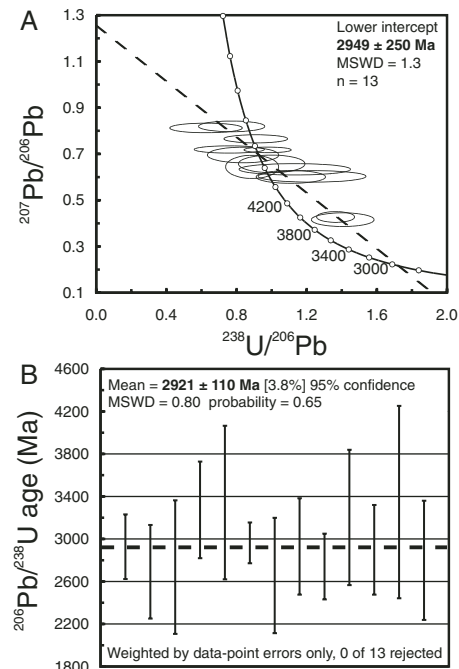
**Figure 2.** Backscattered electron image and X-ray element maps of carbon from two spectrometers (C1 and C2), nitrogen, and calcium associated with tubular structures from area identified by arrow in Figure 1. Two carbon maps (C1 and C2) were then superimposed on gray-scale version of Ca map showing association of carbon with margins of tubular features (identified by arrows). This association also demonstrates that carbon is not bound as calcium carbonate. X-ray mapping was performed at University of Alberta using JEOL JXA-8900R microprobe with accelerating voltage of 15kV and probe current of  $3 \times 10^{-8}$  on iridium-coated thin section.

microbial ichnofossils formed during biogenic etching of basaltic glass beneath the Archean seafloor. We emphasize that the etch-generated, now mineralized tubular bioalteration textures described here have a higher preservation potential than structures claimed to be fossilized microorganisms in sedimentary rocks.

The accepted ca. 3.35 Ga U-Pb zircon age for the Euro Basalt (Nelson, 2005) is more than 400 m.y. older than the age determined here for the tubular titanite microstructures. This titanite date corresponds to the age of regional metamorphism related to the last phase of deformation and widespread granite intrusion (North Pilbara orogeny) that affected our sample site in the western part of the East Pilbara terrane ca. 2930 Ma (Van Kranendonk et al., 2002). Given that chlorite overprints the titanite tubules, and that the chlorite formed ca. 2930 Ma, or earlier (ca. 3.24 Ga; Wijbrans and McDougall, 1987), we interpret the age obtained here to represent a minimum estimate for titanite formation. Titanite growth during regional metamorphism likely overprinted an older, probably older than 3.24 Ga, episode of titanite mineralization formed soon after eruption of the lavas. Early titanite mineralization on or beneath the seafloor likely occurred slowly, at subgreenschist facies or lower conditions. Later titanite growth was probably accelerated by greenschist facies conditions, yielding the apparent age determined here.

Early titanite mineralization of microbial ichnofossils is not a unique occurrence, since titanium can be passively accumulated during microbial etching of glass (Banerjee and Muehlenbachs, 2003). For example, Ti enrichments in tubular microbial ichnofossils are observed in the glassy pillow margins of the ca. 160 Ma Mirdita ophiolite (Albania; Furnes and Muehlenbachs, 2003) and the Late Jurassic Stonyford Volcanics (California; Shervais and Hanan, 1989). In these rocks, zeolite minerals have begun to replace the glass, and open or clay-filled tubular microfossils are mineralized by titanite as they pass into the zone of zeolite alteration (Furnes and Muehlenbachs, 2003). This direct link between open or clay-filled tubes with titanite-mineralized tubes suggests that the mineralization process follows a step-wise sequence during progressive alteration. This mineralization of the originally open tubes is essential if the microbial ichnofossils are to be preserved through geologic time. This mineralization hypothesis is consistent with the presence of Ti-rich nodules associated with microbial alteration of Pleistocene Hawaiian basaltic glass at low temperatures (Walton and Schiffman, 2003).

We suggest that microbial alteration of Pilbara Craton volcanic rocks occurred penecontemporaneously with pillow formation, but may have continued for a protracted length of geologic time. We propose that originally glassy basaltic pillow lavas from both South Africa and



**Figure 3.** Tera-Wasserburg diagram (A) and weighted average  $^{206}\text{Pb}/^{238}\text{U}$  plot (B) for laser ablation results obtained for titanite tubes from three thin sections of sample 74-PG-04. Error ellipses in A are at  $2\sigma$  level. U-Pb dating of titanite-mineralized microfossils was conducted using 213 nm laser ablation system coupled to NuPlasma multicollector-inductively coupled plasma-mass spectrometer (MC-ICP-MS). Instrument configuration (both laser and MC-ICP-MS), analytical protocol, and data reduction procedure employed in this study were summarized elsewhere (Simonetti et al., 2005, 2006). Large single crystals of titanite from copper-mineralized pegmatite, Khan mine (Namibia), were used as external standard. Kinny et al. (1994) reported isotope dilution-thermal ionization mass spectrometry (ID-TIMS) concordant U-Pb age of  $518 \pm 2$  Ma based on six analyses from splits of two crushed fragments. Repeated laser ablation analyses of Khan titanite (Simonetti et al., 2006) obtained during identical analytical sessions as for samples from Pilbara Craton, Western Australia (PWA), yield an age of  $517 \pm 4$  Ma that is indistinguishable compared to its accepted age. Accuracy of analytical protocol was further verified with in situ laser ablation U-Pb results of titanite grains from two samples of 1109 Ma Coldwell Complex, Ontario, previously dated by ID-TIMS and described in Simonetti et al. (2006). MSWD—mean square of weighted deviations.

Australia hosted similar microbial communities that left biomarkers ca. 3.3–3.5 Ga.

This and previous studies (Furnes et al., 2004; Banerjee et al., 2006) demonstrate that a deep subsurface biosphere hosted in volcanic rocks was well established and possibly widespread early in Earth's history. Pillow lavas are the most common rock type in Archean greenstone belts,

so perhaps volcanic environments were not only one of the earliest places where life began, but also where life first flourished, warmed by geothermal energy and protected from harmful radiation. Thus Archean microbial biosignatures preserved in pillow basalts from greenstone belts may help to elucidate not only the presence of early life on Earth, but also possibly the conditions under which life began.

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