

## Species-specific intracellular iron biomineralization in a 1.9-Ga microfossil assemblage

KEVIN LEPOT<sup>1,2\*</sup>, AHMED ADDAD<sup>3</sup>, ANDREW H. KNOLL<sup>4</sup>,  
ARMAND BÉCHÉ<sup>5</sup> AND EMMANUELLE J. JAVAUX<sup>2</sup>

<sup>1</sup>Laboratoire d'Océanologie et de Géosciences, Université de Lille, CNRS UMR8187, 59655 Villeneuve d'Ascq, France.

\*kevin.lepot@univ-lille1.fr

<sup>2</sup>Paléobiogéologie, Paléobotanique & Paléopalynologie, Département de Géologie, Université de Liège, 4000 Liège, Belgium

<sup>3</sup>Unité Matériaux et Transformations, Université Lille 1, 59655 Villeneuve d'Ascq, France.

<sup>4</sup>Department of Organismic and Evolutionary Biology, Harvard University, Cambridge, MA 02139, USA

<sup>5</sup>Electron Microscopy for Material Science, University of Antwerp, 2020 Antwerp, Belgium

Gunflint-type Paleoproterozoic (2.45-1.6 Ga) microfossil assemblages are dominated by spherical (*Huroniospora*) and filamentous (*Gunflintia*) microfossils with phylogenetically ambiguous morphologies. Based on depositional environment, mineral associations (carbonates, Fe-oxides, sulfides), and Fe-, S- and C-isotopes, microfossils have been interpreted variously as cyanobacteria, Fe-oxidizing bacteria, or S-oxidizing bacteria.

We studied microfossils in shallow water stromatolites of the 1.9 Ga Gunflint Iron Formation using a combination of Focused Ion Beam sectioning, Scanning Transmission Electron Microscopy, Electron Energy Loss Spectroscopy, nanobeam electron diffraction, and Scanning Transmission X-ray Microscopy. Taphonomic transformations and primary taxonomic features were distinguished by organic micro- to nanostructures. This defined two populations (thick- and thin-walled) of *Huroniospora*. Moreover, intracellular Fe-oxide minerals were systematically found in thick-walled *Huroniospora*, but not in thin-walled *Huroniospora* or in filaments (*Gunflintia*). Nanoscale distribution of iron oxidation states ( $\text{Fe}^{2+}$  vs  $\text{Fe}^{3+}$ ), petrographic relationships, and crystallography provide constraints on the diagenetic fate of the initial Fe-bearing phases in these microfossils. We propose that these Fe-oxides formed after primary  $\text{Fe}^{3+}$ -bearing intracellular biominerals in *Huroniospora*. The species-specific Fe-mineralization rules out secondary processes affecting all organic fossils. Moreover, the intracellular locus of Fe-mineralization, coupled with the large size (7-12  $\mu\text{m}$ ) of the microfossils put constraints on the metabolism of thick-walled *Huroniospora* and on the chemistry of their environment.