



Occurrence of gigantic biogenic magnetite during the Paleocene-Eocene Thermal Maximum

D. Schumann (1,2), T.D. Raub (3), R.E. Kopp (4), J.L. Guerquin-Kern (5,6), T.D. Wu (5,6), I. Rouiller (7), A.V. Smirnov (8), S.K. Sears (2,7), U. Lücken (9), S. M. Tikoo (3), R. Hesse (1), J. L. Kirschvink (3), H. Vali (1,2,7)

(1) Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montréal, Québec, H3A 2A7, Canada. (hesse@eps.mcgill.ca), (2) Facility for Electron Microscopy Research, McGill University, 3640 University Street, Montréal, Québec, H3A 2B2, Canada., (3) Division of Geological and Planetary Sciences, California Institute of Technology, MC 170-25 1200 E California Blvd, Pasadena, CA 91125, USA., (4) Department of Geosciences and Woodrow Wilson School of Public & International Affairs, 210 Guyot Hall, Princeton University, Princeton, NJ 08544, USA., (5) INSERM, U759, Institut Curie, Imagerie intégrative de la molécule à l'organisme, Orsay, 91405, France., (6) Institut Curie, Laboratoire de Microscopie Ionique, Orsay, 91405, France., (7) Department of Anatomy and Cell Biology, McGill University, 3640 University Street, Montréal, Québec, H3A 2B2, Canada, (8) Department of Geological and Mining Engineering and Sciences, Michigan Technological University, Houghton, MI 49931-1295, USA., (9) FEI Company, Nanobiology Marketing, Eindhoven, 5600KA Eindhoven, The Netherlands.

The Paleocene-Eocene Thermal Maximum (PETM) is one of the most severe climatic events of the Cenozoic Era. A massive injection of light carbon into the oceans and atmosphere over a few thousand of years triggered drastic perturbation of Earth's climate resulting in abrupt global warming of $\sim 5\text{--}9^\circ\text{C}$ [Sluijs et al., 2007] that persisted for $\sim 180,000$ years. This episode is marked by the diversification and radiation of terrestrial plants and mammals while in the marine realm numerous deep-sea benthic foraminifera species disappeared and new forms evolved. Sediments deposited during the PETM are clay-rich and contain distinct evidence of these climatic changes. Kopp et al., (2007) and Lippert & Zachos (2007) report an extraordinary magnetofossil 'Lagerstätte' in lowermost Eocene kaolinite-rich clay sediments deposited at subtropical paleolatitude in the Atlantic Coastal Plain of New Jersey, USA. Magnetofossils are magnetic particles produced most abundantly by magnetotactic bacteria.

Kopp et al. (2007) and Lippert & Zachos (2007) used ferromagnetic resonance (FMR) spectroscopy, other rock magnetic methods, and transmission electron microscopy (TEM) of magnetic separates to characterize sediments from boreholes at Ancora (ODP Leg 174AX) and Wilson Lake, NJ, respectively. These sediments contain abundant $\sim 40\text{--}300\text{-nm}$ cuboidal, elongate-prismatic and bullet-shaped magnetofossils, sometimes arranged in short chains, resembling crystals in living magnetotactic bacteria. Despite the scarcity of intact magnetofossil chains, the asymmetry ratios of the FMR spectra reflects a profusion of elongate single domain (SD) crystals and/or chains.

Here we address both conundrums by reporting the discovery from these same sediments of exceptionally large and novel biogenic magnetite crystals unlike any previously reported from living organisms or from sediments. Aside from abundant bacterial magnetofossils, electron microscopy reveals novel spearhead-like and spindle-like magnetite crystals up to $4\text{ }\mu\text{m}$ long (eight times larger than magnetite produced by magnetotactic bacteria) and elongated hexaoctahedra up to $1.4\text{ }\mu\text{m}$ long. Similar to magnetite produced by magnetotactic bacteria, these single-crystal particles exhibit chemical composition and lattice perfection consistent with a biogenic origin. The oxygen isotopic composition of individual particles supports a low temperature aquatic origin. Electron holography indicates single-domain magnetization despite the large crystal size. In a few cases, we observed apparently intact, tip-outward spherical assemblages of spearhead-like particles that possibly represent the preserved original biological arrangement of these crystals in a hitherto unknown magnetite producing organism. The discovery of these exceptionally large biogenic magnetite crystals that possibly represent the remains of a new microorganism that appeared and disappeared with the PETM sheds some light upon the ecological response to biogeochemical changes that occurred during this warming event. The abundance of fossil magnetotactic bacteria on the Atlantic Coastal Plain during the PETM could be explained by enhanced production, enhanced preservation, or both. The presence of novel magnetofossils, however, argues that changes in growth conditions are a major part

of the explanation. Considering that other bacterial magnetofossils are present (although less abundant) and well-preserved in sediments below and above the PETM clay, as well as in a sand lens within the PETM clay [Kopp et al., 2007], suggests that the new magnetofossils are unlikely to be a preservation artefact. We conclude, therefore, that the development of a thick suboxic zone with high iron bioavailability – a product of dramatic changes in weathering and sedimentation patterns driven by severe global warming - resulted in diversification of magnetite-forming organisms, likely including eukaryotes.

In this study we extended the search for these new magnetofossils [Schumann et al. 2008] to other PETM locations of the Atlantic margin and to a possible modern analog environment. High surface productivity with low-organic carbon density sediments and meter-scale sedimentary suboxic zones are provided by tropical shelves fed by energetic river systems, such as the Amazon. We investigated several magnetic extracts of samples taken from the meter-scale suboxic zones of the Amazon delta system.

Sluijs A, Brinkhuis H, Schouten S, Bohaty SM, John CM, Zachos JC, Reichert GJ, Damste JSS, Crouch EM, Dickens GR. 2007. Environmental precursors to rapid light carbon injection at the Palaeocene/Eocene boundary. *Nature* 450:1218-1221.

Kopp RE, Raub TD, Schumann D, Vali H, Smirnov AV, Kirschvink JL 2007. Magnetofossil spike during the Paleocene-Eocene thermal maximum: Ferromagnetic resonance, rock magnetic, and electron microscopy evidence from Ancora, New Jersey, United States. *Paleoceanography*, doi:10.1029/2007pa001473.

Lipper PC, Zachos JC 2007. A biogenic origin for anomalous fine-grained magnetic material at the Paleocene-Eocene boundary at Wilson Lake, New Jersey. *Paleoceanography*, doi:10.1029/2007pa001471.

Schumann D, Raub TD, Kopp RE, Guerquin-Kern JL, Wu TD, Rouiller I, Smirnov AV, Sears K, Lücken U, Tikoo SM, Hesse R, Kirschvink JL, Vali H 2008. Gigantism in unique biogenic magnetite at the Paleocene-Eocene Thermal Maximum. *PNAS*, 105:17648–17653.