Geophysical Research Abstracts
Vol. 16, EGU2014-6037, 2014
EGU General Assembly 2014
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Sulphur bacteria mediated formation of Palaeoproterozoic phosphorites

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Modern phosphorite formation is typically associated with high productivity in upwelling areas where apatite (Ca-phosphate) precipitation is mediated by sulphur oxidising bacteria [1]. They inhabit the oxic/anoxic interface within the upper few centimetres of sediment column, accumulating phosphate in their cells under oxic conditions and releasing it rapidly when conditions become anoxic. Sulphur bacteria are known to live in close association with a consortium of anaerobic methane oxidising archaea and syntrophic sulphate-reducing bacteria.

Paleoproterozoic, c. 2.0 Ga Zaonega Formation in Karelia, Russia contains several P-rich intervals in the upper part of 1500 m thick succession of organic-rich sedimentary rocks interlayered with mafic tuffs and lavas. Apatite in these P-rich intervals forms impure laminae, lenses and round-oval nodules which diameters typically range from 300 to 1000 μm. Individual apatite particles in P-rich laminae and nodules commonly occur as cylinders that are 1-8 μm long and have diameters of 0.5-4 μm. Cross-sections of best preserved cylindrical apatite particles reveal a thin outer rim whereas the internal parts consist of small anhedral elongated crystallites, intergrown with carbonaceous material. During recrystallization the outer rim thickens towards interior and cylinders may attain hexagonal crystal habit, but their size and shape remains largely unchanged [2].

The sizes of Zaonega nodules are similar to giant sulphide-oxidising bacteria known from modern and ancient settings [3, 4]. Individual apatite cylinders and aggregates have shapes and sizes similar to the methanotrophic archaea that inhabit microbial mats in modern seep/vent areas where they operate in close associations with sulphur-oxidising microbial communities [5]. Seep/vent influence during the Zaonega phosphogenesis is indicated by variable, though positive Eu anomaly, expected in magmatically active sedimentary environment experiencing several lava flows. Moreover, P-rich intervals in the Zaonega Formation are found in organic-rich sediments exhibiting strongly negative δ^{13}Corg values (-37 to -34 per mil) which is interpreted to reflect the methanotrophic biomass. We conclude that modern-style phosphogenesis, mediated by sulphide-oxidising bacteria living in consortium with methanotrophs, was established at least 2 Ga ago.

[1] Schulz and Schulz (2005) *Science* **307**, 416-418 [2] Lepland, Joosu, Kirsimäe, Prave, Romashkin, Črne, Martin, Fallick, Somelar, Üpraus, Mänd, Roberts, van Zuilen, Wirth, Schreiber (2014) *Nature geoscience* **7,** 20-24 [3] Bailey, Joye, Kalanetra, Flood, and Corsetti (2007) *Nature* **445**, 198-201 [4] Schulz, Brinkhoff, Ferdelman, Marine, Teske and Jorgensen (1999) *Science* **284**, 493-495 [5] Knittel, Losekann, Boetius, Kort and Amann (2005) *Applied and Environmental Microbiology* **71**, 467-479.