

# Sedimentary phosphate and associated fossil bacteria in a Paleoproterozoic tidal flat in the 1.85 Ga Michigamme Formation, Michigan, USA



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## ABSTRACT

Phosphorus is a nutrient fundamental to life and when it precipitates in modern environments bacteria are intimately involved in its release, concentration, and mineralization. Preserved fossil bacteria in phosphate crusts and grains from the ca. 1850 million-year-old Bijiki Iron Formation Member of the Michigamme Formation, Michigan provide insight into the longevity and nature of this relationship. The Michigamme Formation accumulated near the end of the Earth's initial phosphogenic episode (ca. 2.2 and 1.8 Ga) to produce one of the first granular phosphorites. Phosphatic lithofacies consist of fine- to medium-sand-sized francolite peloids concentrated on bedding surfaces in peritidal facies. Granular beds are up to 2 cm thick and peloids are often partially to completely replaced by dolomite and chert. The grains contain organic matter and pyrite framboids that suggest bacterial breakdown of organic matter and bacterial sulfate reduction.

The peritidal nature of phosphorite in the Michigamme Formation is in sharp contrast to Phanerozoic phosphogenic environments in deeper coastal upwelling settings. Peritidal settings were well suited for phosphogenesis under the very low oxygen and low dissolved sulfate levels of the Paleoproterozoic as cyanobacteria produced oxygen in shallow water and evaporation led to increased sulfate concentrations. Such concomitant processes helped establish focused redox interfaces in the sediment that chemosynthetic bacterial communities (sulfur oxidizers, reducers, forms that concentrate P, and possibly iron oxidizers) could exploit. Phosphate released from organic matter by heterotrophic bacteria and Fe-redox pumping was further concentrated by these chemotrophs; a process that forms late Neoproterozoic to Phanerozoic phosphorites but on a much larger scale.

This early example of a granular phosphorite demonstrates that, like their Phanerozoic counterparts, Paleoproterozoic phosphorites are the concentrated indirectly biomineralized products of bacterial communities. But unlike younger analogs, which accumulated across subtidal shelves and shelf margins, these ancient deposits formed only in tidal flat settings where phosphogenic redox processes could be established in the sediment. From this early beginning, the zone of phosphogenesis likely migrated into deeper water settings as oxygen and sulfate levels rose, expanding the zone of chemosynthetic bacterial and associated phosphogenesis across the shelf.

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## 1. Introduction

Phosphorus (P) is critical in organic molecules involved in metabolism (ATP) and cell replication (DNA; e.g. Filippelli, 2008). Phosphorus is strongly bound to oxygen at the Earth's surface and in the lithosphere forming phosphate ( $\text{PO}_4^{3-}$ ) and is a bioessential nutrient

that limits biologic activity in the oceans on geologic time scales (e.g. Froelich et al., 1982; Pasek and Lauretta, 2005; Filippelli, 2008). Phosphate is removed from the oceans by sedimentation of organic molecules and bound to iron-oxyhydroxide particles (e.g. Föllmi, 1996). Organic matter contains up to a few weight percent P that is very efficiently returned to seawater under anoxic conditions (Froelich et al., 1982). It is, however, effectively bound by iron-oxyhydroxide particles and as the authigenic mineral francolite at or just below the sediment–water interface when the overlying water is oxygenated to form the chemically complex carbonate–fluorapatite mineral francolite  $\{\text{Ca}_{10-x-y-z}\text{Na}_x\text{Mg}_y(\text{PO}_4)_6 - x(\text{CO}_3)_x - y - z(\text{CO}_3\text{F})_y(\text{SO}_4)_z(\text{F}_2)\}$  (e.g. Nathan, 1984).

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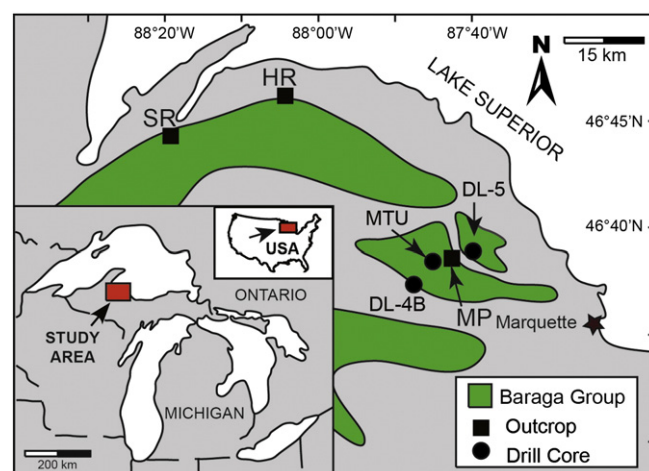
Large economically important sedimentary phosphorite deposits are formed almost entirely of authigenic francolite and generally contain ca. 40 wt.%  $P_2O_5$ ; this is twice the 18 wt.%  $P_2O_5$  minimum to be considered a true phosphorite (e.g. Glenn et al., 1994). These giant phosphorites are related to major phosphogenic events that are interpreted as reflecting a change in the biogeochemical cycling of P (e.g. Föllmi, 1996). Most phosphogenic episodes are Phanerozoic phenomena with only one occurring prior to the “fully oxygenated Earth” of the Late Neoproterozoic (Nelson et al., 2010; Pufahl, 2010; Pufahl and Hiatt, 2012; Bailey et al., 2013). This initial phosphogenic pulse is Paleoproterozoic in age (2.2 to 1.8 Ga) and produced “phosphorites” that contain much less than 18 wt.%  $P_2O_5$  (Pufahl, 2010 and references therein).

Cenozoic phosphorites accumulated across an array of shelf environments, but formed primarily under oxygen-minimum zones in organic-rich sediments deposited beneath zones of oceanic upwelling (e.g. Garrison and Kastner, 1990). Large Paleozoic and Mesozoic phosphorites are epeiric sea deposits reflecting phosphogenesis across a broad depositional spectrum that includes shallow subtidal settings (e.g. Hiatt and Budd, 2001, 2003; Pufahl et al., 2003).

Bacteria have long been interpreted to have facilitated phosphate mineralization and to play a role in phosphogenesis (Berger, 1911; Cayeux, 1936; Gallardo, 1977; Soudry and Champetier, 1983; Williams and Reimers, 1983; Soudry and Lewy, 1988; Nathan et al., 1993; Krajewski et al., 1994; Lamboy, 1994; Reimers et al., 1996; Schulz et al., 1999; Schulz and Schulz, 2005; Arning et al., 2009; Goldhammer et al., 2010; Berndmeyer et al., 2012; Crosby and Bailey, 2012; Edwards et al., 2012; Bailey et al., 2013). Fossil bacteria have been observed in many ancient phosphorites (e.g. Soudry and Champetier, 1983; Glenn and Arthur, 1988; Rao and Nair, 1988; Soudry and Lewy, 1988; Nathan et al., 1993; Krajewski et al., 1994; Lamboy, 1994; Reimers et al., 1996; Bailey et al., 2007; Arning et al., 2009; Berndmeyer et al., 2012). In the modern, bacteria are intimately involved in the biogeochemical cycling of P (e.g. Schulz and Schulz, 2005; Goldhammer et al., 2010), suggesting that such processes played a fundamental role in the co-evolution of the geosphere and biosphere (e.g. Pufahl and Hiatt, 2012). Bacteria break down sedimentary organic matter and release phosphate, create redox gradients that also liberate phosphate sorbed onto Fe-(oxyhydr)oxide particles, and concentrate polyphosphate compounds inside their cells, all of which lead to francolite precipitation and the potential encapsulation of the bacteria (e.g. Soudry and Champetier, 1983; Krajewski et al., 1994; Schulz et al., 1999; Schulz and Schulz, 2005; Konhauser, 2007; Arning et al., 2009; Goldhammer et al., 2010).

Based on studies of Phanerozoic phosphorites chemosynthetic bacteria seem to be integral; they create and maintain chemical gradients in sediment that indirectly facilitates phosphogenesis (e.g. Schulz et al., 1999; Schulz and Schulz, 2005; Konhauser, 2007; Arning et al., 2009; Goldhammer et al., 2010; Bailey et al., 2013). Mat-forming, sulfur-oxidizing bacteria, such as *Thioploca* sp. and *Beggiatoa* sp. thrive in modern phosphogenic environments and exploit oxidation gradients at, or just beneath, the seafloor and provide an important link between the nitrogen, sulfur, phosphorus, and carbon cycles (Gallardo, 1977; Jørgensen and Revsbech, 1983; Larkin and Strohl, 1983; Fossing et al., 1995; Bailey et al., 2013).

It is not clear whether bacteria played similar roles throughout the majority of Earth history before the oceans became fully oxygenated. To test this hypothesis, we conducted a holistic study that incorporated sedimentology, stratigraphy, microbial ecology, micro-beam techniques, taphonomy, and paragenesis to understand diagenesis and environmental significance of granular phosphorite from the Paleoproterozoic Bijiki Iron Formation Member of the Michigamme Formation, Michigan, because it contains exquisitely preserved phosphatized filamentous bacteria that are coeval with silicified fossil microbial communities in the well-studied Gunflint Formation (Figs. 1, 2; Cannon and Klasner, 1976; Nelson et al., 2010; Papineau, 2010). Both accumulated in the Animikie



**Fig. 1.** Map of study area with general Baraga Group belt, Upper Peninsula, Michigan, and outcrop (HR = Huron River, SR = Slate River, and MP = Mulligan Plains) and drill core (DNR-MTU, DL-4B and DL-5) locations. Inset shows general location (modified from Nelson et al., 2010).

Basin of the Lake Superior region, North America and have precise depositional ages (Fig. 1; Hoffman, 1988; Morey and Southwick, 1995; Ojakangas et al., 2001).

The purpose of this study is to (1) to understand the relationship between bacteria and phosphogenesis in granular phosphorite; and (2) to assess the taphonomic processes that led to the preservation of possible heterotrophic and chemosynthetic bacteria. The exceptional preservation of filamentous bacterial communities observed in this study of the Bijiki Iron Formation provides a window into the nature of Paleoproterozoic phosphogenesis and the biogeochemical cycling of P during the Paleoproterozoic.

## 2. Geologic setting

The Bijiki Iron Formation Member is located along the southern margin of Lake Superior in the Upper Peninsula of Michigan (Fig. 1). It is one of three members near the base of the Michigamme Formation, which rests conformably on the Goodrich Quartzite (Fig. 2). The Goodrich Quartzite is in disconformable contact with Archean basement rocks. Together, the Goodrich Quartzite and Michigamme Formation constitute the Baraga Group, which in turn belongs to the Marquette Range Supergroup. The Baraga Group accumulated during an overall marine transgression (Ojakangas, 1994) in the Animikie Basin, one of many depocenters along the margin of the Paleoproterozoic supercontinent Columbia (Cannon and Gair, 1970; Barovich et al., 1989; Morey and Southwick, 1995; Ojakangas et al., 2001; Nelson et al., 2010; Meert, 2012).

The Animikie Basin extends from eastern Minnesota to northern Michigan and is bounded to the west by the Gunflint and Mesabi iron ranges, the Gogebic Range to the south, and the Marquette Range to the east (Fig. 1). The geologic history of the Animikie Basin is contentious, but it is generally interpreted to have begun as a passive margin that during the Penokean orogeny developed first into a backarc basin and then a foreland basin with restricted circulation (Larue, 1981; Hoffman, 1988; Hemming et al., 1995; Morey and Southwick, 1995; Van Wyck and Johnson, 1997; Ojakangas et al., 2001; Schulz and Cannon, 2007; Pufahl et al., 2010). The Penokean orogeny marks the collision of an island arc with the Superior Province and subsequent subduction-related crustal thickening between ca. 1875 and 1835 Ma (Ojakangas et al., 2001; Schneider et al., 2002; Schulz and Cannon, 2007).

The Baraga Group is composed of iron formation, quartz sandstone, quartzite, turbidite-to-deltaic deposits, and phosphate-bearing chert-carbonate horizons (Mancuso et al., 1975; Cannon and Klasner, 1976;

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