

Does the Paleoproterozoic Animikie Basin record the sulfidic ocean transition?

Peir K. Pufahl^{1*}, Eric E. Hiatt², and T. Kurtis Kyser³

¹Department of Earth and Environmental Science, Acadia University, Wolfville, Nova Scotia B4P 2R6, Canada

²Department of Geology, University of Wisconsin, Oshkosh, Wisconsin 54901, USA

³Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario K7L 3N6, Canada

ABSTRACT

The Paleoproterozoic Animikie Basin in the Lake Superior region of North America is the benchmark for understanding one of the most significant changes in seawater chemistry in Earth history—the transition to a sulfidic ocean (ca. 1.84 Ga). This transition marks a dramatic increase in ocean sulfide produced by bacterial reduction of sulfate formed through the oxic chemical weathering of pyrite during the Great Oxidation Event. Such a change is thought to have caused the cessation of widespread iron formation deposition and marks the beginning of a long lull in the evolution of eukaryotes. The feasibility of using the Animikie Basin to understand this transition is re-evaluated by comparing new sulfur isotope data ($\delta^{34}\text{S}_{\text{pyrite}}$) from the Michigamme Formation in northern Michigan, United States, to published results from the correlative Rove Formation in Ontario, Canada. These data suggest that microbial sulfate reduction was restricted to organic-rich environments away from the influence of deltas, which delivered low-sulfate river water to the coast. Sulfur isotope data and the patchiness of sulfate reduction within the Animikie Basin suggest strong lateral and vertical gradients in seawater sulfate concentrations. When viewed in the context of the most recent tectonic and sedimentologic models, these observations are best interpreted as reflecting an evolving basin with restricted water circulation, not open circulation with the global ocean as previously postulated. Thus, the Animikie Basin does not contain an accurate record of open-ocean structure and composition during the onset of sulfidic conditions. What is clear is that marginal seas must be carefully evaluated before they are used to model the global ocean, especially given the rarity of preserved Precambrian deep-sea sediments.

INTRODUCTION

The Paleoproterozoic sulfidic ocean transition is proposed as one of the most significant changes in seawater chemistry in Earth history (Canfield, 1998; Anbar and Knoll, 2002; Poulton et al., 2004). It is thought to be the result of the Great Oxidation Event (Holland, 2006) whereby rising atmospheric oxygen levels ca. 2.4 Ga permitted, for the first time, the widespread oxic chemical weathering of the young continents. Under such conditions, weathering of sulfide minerals produced sulfate that was delivered by rivers to the ocean where it was transformed through bacterial sulfate reduction into sulfide. By ca. 1.84 Ga the flux of sulfate was apparently sufficient to produce enough sulfide to titrate the shallow ocean of dissolved Fe(II), ending the deposition of Superior-type iron formation (Canfield, 1998; Poulton et al., 2004). The sulfidic conditions that supposedly prevailed for nearly a billion years afterwards are generally regarded as causing the observed Mesoproterozoic lull in the evolution of eukaryotes (Anbar and Knoll, 2002).

What is known about the sulfidic ocean transition is largely based on sulfur isotope and iron speciation data (Poulton et al., 2004, 2008; Johnston et al., 2006) from sedimentary rocks in

the Paleoproterozoic Animikie Basin of North America (Fig. 1). The purpose of this paper is to re-evaluate whether the Animikie Basin does in fact record this important oceanographic change using new sedimentologic and sulfur

isotope data within a chronostratigraphic and tectonic framework. Sedimentary pyrite $\delta^{34}\text{S}$ values in the Baraga Group of northern Michigan are compared to published data from the correlative Animikie Group in Ontario (Poulton et al., 2004; Johnston et al., 2006) (Figs. 1 and 2), which has become the benchmark for understanding the transition to sulfidic conditions. Correlation of the Sudbury meteorite impact ejecta horizon (Addison et al., 2005; Pufahl et al., 2007) between these two regions allows, for the first time, direct comparison of data sets.

GEOLOGIC HISTORY OF THE ANIMIKIE BASIN

The Animikie Basin is interpreted to have been a backarc basin (Hemming et al., 1995; Van Wyck and Johnson, 1997) that evolved into a foreland basin during the Penokean orogeny (Hoffman, 1987; Southwick and Morey, 1991; Hemming et al., 1995; Ojakangas et al., 2001). Initial flooding of the Animikie backarc produced extensive siliciclastic tidal deposits. As sea level continued to rise, Superior-type iron formation accumulated when upwelling introduced anoxic, iron-rich, bottom water into photosynthetically oxygenated shelf environments (Pufahl, 1996;

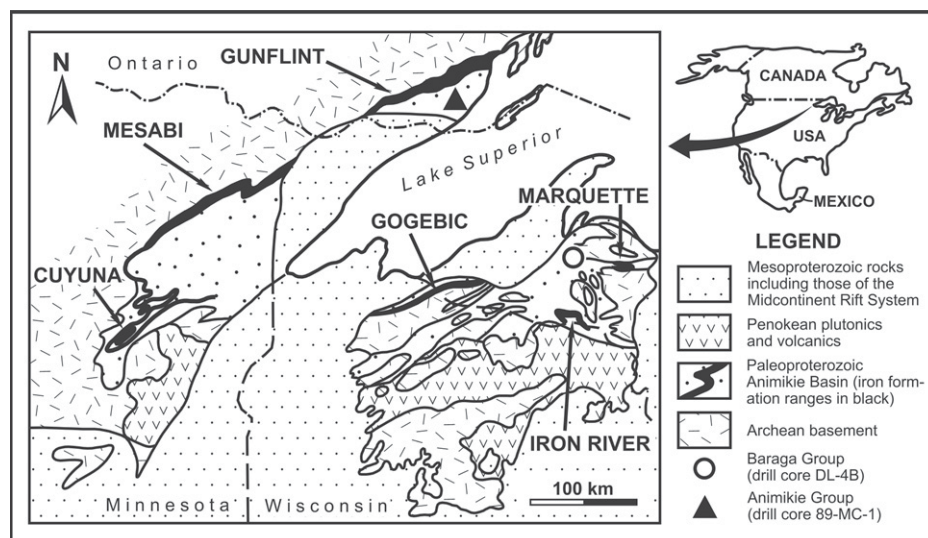


Figure 1. General geology of the Lake Superior region of North America with location of drill cores DL-4B and 89-MC-1. Baraga Group sulfur isotope data are from drill core DL-4B. Animikie Group data are from drill core 89-MC-1 and are published in Poulton et al. (2004) and Johnston et al. (2006). Drill cores DL-4B and 89-MC-1 were ~100 km apart prior to Mesoproterozoic rifting.

*E-mail: peir.pufahl@acadiau.ca.

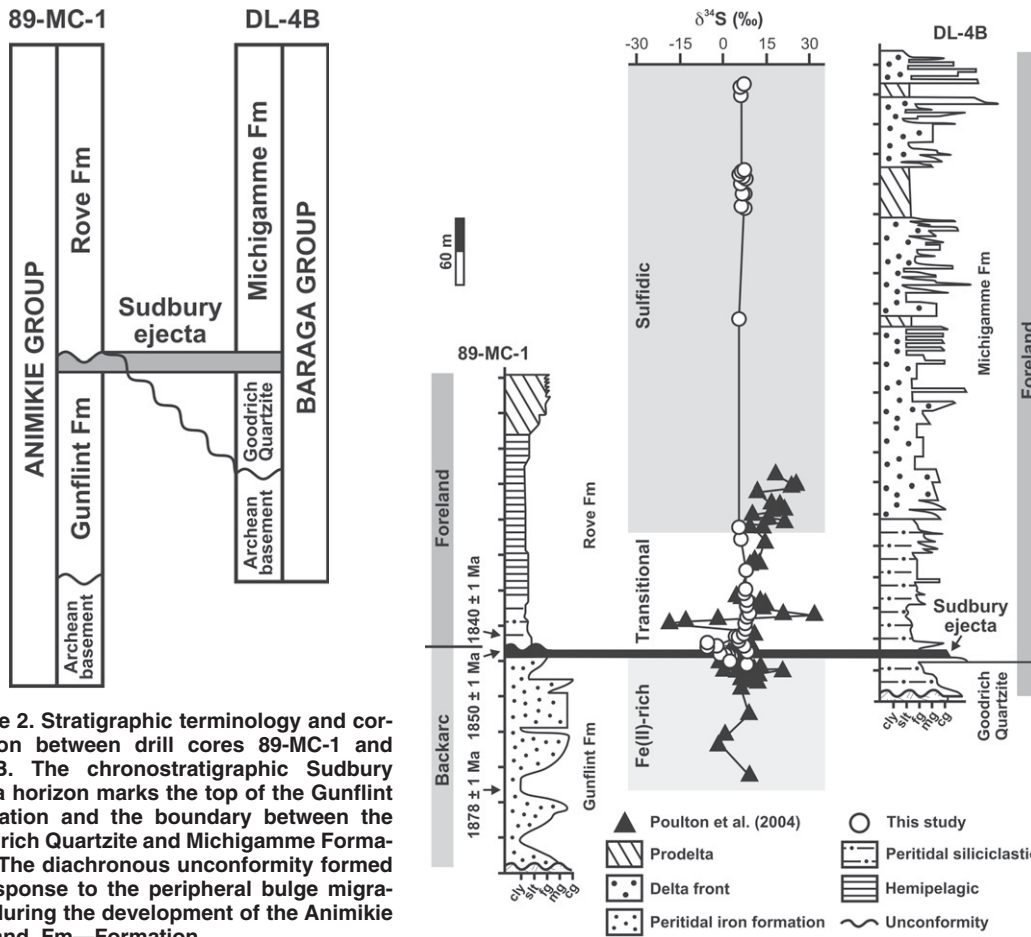


Figure 2. Stratigraphic terminology and correlation between drill cores 89-MC-1 and DL-4B. The chronostratigraphic Sudbury ejecta horizon marks the top of the Gunflint Formation and the boundary between the Goodrich Quartzite and Michigamme Formation. The diachronous unconformity formed in response to the peripheral bulge migration during the development of the Animikie foreland. Fm—Formation.

Figure 3. $\delta^{34}\text{S}$ data plotted against backarc and foreland deposits of the Animikie and Baraga Groups. The 1850 ± 1 Ma Sudbury impact ejecta horizon provides a chronostratigraphic reference. Pyrite occurs only in organic-rich peritidal, hemipelagic, and prodelta lithofacies. Backarc fill is dominantly Superior-type iron formation. Foreland sediments consist primarily of hemipelagites interbedded with prograding delta complexes (Johnston et al., 2006; Nelson et al., 2010). Stages in the development of a sulfidic ocean are those of Poulton et al. (2004). The width of the lithologic columns reflects relative grain size (cly—clay; silt—silt; fg—fine-grained sand; mg—medium-grained sand; cg—coarse-grained sand).

Pufahl and Fralick, 2004). Zircons from interbedded tuffs confirm a depositional age of 1878 ± 1 Ma (Fig. 3) (Fralick et al., 2002). Deposition of chemical sediments ceased with the change from a backarc to foreland basin (Johnston et al., 2006). The development of a peripheral bulge created a diachronous, regional unconformity (Hoffman, 1987; Johnston et al., 2006). During this time, a meteorite impacted ~ 650 km to the east near present-day Sudbury, Ontario, at 1850 ± 1 Ma (Krogh et al., 1984) and produced ejecta that blanketed the Animikie Basin (Figs. 2 and 3) (Addison et al., 2005; Pufahl et al., 2007). After ejecta emplacement, a thick succession of tidal deposits, deltaic sediments, and hemipelagites was deposited in the newly formed foreland basin (Fig. 3). A U-Pb age from zircons in a tuff near the base of this succession indicates sedimentation began at ca. 1840 Ma (Kissin et al., 2003). Sedimentary rocks of the Animikie Basin were rifted apart in the Mesoproterozoic during development of the Midcontinent Rift System ca. 1100 Ma (Heaman et al., 2007).

Although the Animikie Basin experienced numerous changes in relative sea level throughout its history (Pufahl, 1996; Nelson et al., 2010), it is generally regarded as having been well connected to the open ocean (Poulton et al.,

2004; Johnston et al., 2006). Such an interpretation is based on the presence of iron formation in the backarc phase and tidal deposits in both the backarc and foreland fills (Pufahl, 1996; Nelson et al., 2010). The rare-earth-element and Nd isotopic compositions of iron formation are consistent with an open-ocean, hydrothermal iron source (Derry and Jacobsen, 1990). The occurrence of tidal deposits is commonly cited as the best evidence for unrestricted circulation (Johnston et al., 2006).

PYRITE AND SULFUR ISOTOPE DATA

Pyrite analyzed in this study is from drill core DL-4B (Fig. 1), which penetrates the Goodrich Quartzite and Michigamme Formation of the Baraga Group in the Upper Peninsula of Michigan (Fig. 2). The Goodrich Quartzite records tidal and shoreface deposition over Archean basement (Nelson et al., 2010). The Michigamme Formation consists of progradational delta deposits interbedded with fine-grained shelf sediments (Nelson et al., 2010). Our interpretation of lithofacies associations in drill core and outcrop show that pyrite is abundant only in organic-rich peritidal and prodelta deposits (Fig. 3) (Nelson et al., 2010). The lack of pyrite in organic-rich delta front sedimentary rocks is

interpreted to reflect higher accumulation rates and input of river water that was low in sulfate (e.g., Canfield and Teske, 1996; Holland, 2006). All pyrite samples are from disseminated pyrite to best represent a synsedimentary precipitate (Raiswell, 1982; Schieber, 2002). Its fine-grained and dispersed nature suggests initial precipitation as framboidal pyrite at or just beneath the seafloor (e.g., Schieber, 2002). Such authigenic pyrite differs from observed overgrowths, replacements, and large euhedral crystals in the rocks that are generally interpreted as late diagenetic or metamorphic in origin (Raiswell, 1982; Wagner and Boyce, 2006).

Sulfur isotope measurements ($\delta^{34}\text{S}$; Table DR1 in the GSA Data Repository¹) in the Baraga Group were made on pyrite using a Carlo Erba NCS 2500 elemental analyzer coupled to a Finnigan MAT 252 mass spectrometer with a Finnigan MAT ConFlo 11. Samples were hand-picked using tweezers under a dissecting microscope. Sulfur isotope values are reported in the

¹GSA Data Repository item 2010176, Table DR1 (Animikie sulfur isotope data), is available online at www.geosociety.org/pubs/ft2010.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

delta (δ) notation in units of per mil (‰) relative to the standard V-CDT (Vienna Canyon Diablo Troilite). Replicate $\delta^{34}\text{S}$ sample analyses are reproducible to $\pm 0.3\%$.

Pyritiferous lithofacies also occur in the Gunflint and Rove Formations of the Animikie Group in northwestern Ontario (Figs. 1 and 2). It is pyrite in these rocks from drill core 89-MC-1 (Fig. 3) that has been analyzed by Poulton et al. (2004) and Johnston et al. (2006). The Gunflint Formation is a granular iron formation deposited in shallow, wave-agitated settings (Pufahl, 1996). Pyrite is rare in these chemical sediments and is limited to fine-grained, organic-rich lithofacies. Like the Michigamme Formation, the overlying Rove Formation records delta lobe progradation and abandonment in nearshore and middle shelf environments (Johnston et al., 2006). As in the Michigamme Formation, pyrite also occurs in organic-rich lithofacies away from prograding deltas. Prior to the development of the Midcontinent Rift System, pyritiferous facies in cores 89-MC-1 and DL-4B were ~100 km apart and belonged to the same delta system.

Published sulfur isotopic data from the Animikie Group are from disseminated pyrite, pyrite-replaced iron carbonates, and pyrite crystals associated with mafic pyroclasts (Poulton et al., 2004; Johnston et al., 2006). These data were interpreted to record the change from anoxic, Fe(II)-rich seawater to a sulfidic (H_2S) ocean via a transitional stage of fluctuating water column and pore water conditions (Fig. 3) (Poulton et al., 2004; Johnston et al., 2006). This interpretation is based on $\delta^{34}\text{S}$ values that gradually increase from $8.4\% \pm 5.4\%$ in the Gunflint Formation to $17.2\% \pm 5.1\%$ in the Rove Formation (Fig. 3) (Poulton et al., 2004). Isotope values through the Fe(II)-rich, iron formation-producing stage have been interpreted to reflect pyrite precipitation from low-sulfate bottom and pore waters (Canfield, 2001; Shen et al., 2003; Johnston et al., 2006). Such low sulfate concentrations likely resulted in sulfate-limited, bacterial sulfate reduction and the observed $\delta^{34}\text{S}$ values, which are very close to the predicted $\delta^{34}\text{S}$ value for seawater during this stage (Johnston et al., 2006). The rapid consumption of pore water sulfate is postulated to have produced pyrite with an isotopic composition similar to that of seawater sulfate (Carrigan and Cameron, 1991; Anbar and Knoll, 2002, and references therein). Sulfur isotopic fractionation during bacterial sulfate reduction, however, is strongly affected by environmental conditions (Strauss, 2003).

The higher $\delta^{34}\text{S}$ values that typify the sulfidic ocean stage are interpreted to reflect pyrite precipitation beneath a euxinic water column that experienced continuous and significant sulfide loss through time (Johnston et al., 2006). Sulfide loss is postulated to have occurred via

pyrite precipitation and seasonal upwelling, which might have ventilated vast quantities of hydrogen sulfide to the atmosphere (Johnston et al., 2006). The greater variability in $\delta^{34}\text{S}$ values during the transitional stage has been attributed to rapid fluctuations in seawater composition during the change to a sulfidic ocean (Poulton et al., 2004; Johnston et al., 2006). Based on the stratigraphic position and ages of the Sudbury ejecta horizon (Krogh et al., 1984) and a tuffaceous layer (Kissin et al., 2003) near the base of this isotopic shift (Figs. 2 and 3), the onset of sulfidic conditions postdates the unconformity between the Gunflint and Rove Formations by no more than ~10 m.y., not 40 m.y. as previously assumed (Johnston et al., 2006).

The observed trend in Animikie Group $\delta^{34}\text{S}$ data (Poulton et al., 2004; Johnston et al., 2006) is not recognized in the Baraga Group (Fig. 3); the stratigraphic change to progressively higher $\delta^{34}\text{S}$ values is absent. The $\delta^{34}\text{S}$ values in the Michigamme Formation are also lower and less variable than those from the time-equivalent Rove Formation (Fig. 3). The average $\delta^{34}\text{S}$ value in the Michigamme Formation is $6.3\% \pm 1.0\%$, which is closer to the mean value in the Gunflint Formation. $\delta^{34}\text{S}$ values from samples taken near the Sudbury ejecta layer are more variable. The average value through this 9 m interval is $0.1\% \pm 4.7\%$ (Fig. 3).

Baraga Group data are less variable than published data from the Animikie Group. Such a relationship likely reflects the fact that only disseminated pyrite was sampled, whereas data from the Animikie Group include analyses of diagenetic and metamorphic pyrite (Poulton et al., 2004). The greater variability in Baraga Group $\delta^{34}\text{S}$ values near the Sudbury ejecta horizon is interpreted to reflect diagenetic alteration. This intensely carbonate-altered layer was apparently a conduit for diagenetic and metamorphic fluid migration because of its coarse and poorly sorted nature (Pufahl et al., 2007).

IMPLICATIONS

When viewed in the context of recent tectonic models, the new sulfur isotope, sedimentologic, and paleoceanographic data presented in this study indicate that circulation within the Animikie Basin was not only more variable than previously surmised, but also restricted, especially during the foreland phase of basin development. The absence of a trend toward increasing $\delta^{34}\text{S}$ values through the Baraga Group is interpreted to reflect the influx of low-sulfate river water along the coast of the Animikie foreland. Such freshening would have created pronounced lateral gradients in seawater sulfate around deltas and caused sulfate-limited, bacterial sulfate reduction within these environments. This process produced $\delta^{34}\text{S}$ values similar to those in the Gunflint Formation (Fig. 3). The

lack of large variations in the Baraga Group suggests that seawater in delta-influenced settings had sulfate concentrations of less than $200 \mu\text{M}$, the minimum required to produce large fractionations (Habicht et al., 2002).

We agree that the large fractionations that typify the Rove Formation may reflect bacterial sulfate reduction under conditions of continuous sulfide loss (Johnston et al., 2006). These conditions, however, were not ubiquitous throughout the Animikie foreland and probably occurred only where organic-rich lithofacies accumulated away from major deltas. Sulfate concentrations in these settings were probably over $200 \mu\text{M}$ but less than 2.4 mM , which is thought to be the concentration of Mesoproterozoic seawater (Poulton et al., 2004).

Depth stratification in sulfate concentrations likely occurred in some areas (Poulton et al., 2008). Stratified water masses typically develop in backarc and foreland basins because water generally flows in restricted, closed current systems that are unlike those of the open ocean (Beck et al., 1998; Itaki et al., 2004; Khim et al., 2008). Vertical stratification even develops in backarc and foreland basins with tides (Odamaki, 1989; Bhattacharya and Willis, 2001; Itaki et al., 2004), suggesting that the cited evidence for tidal deposits in the Animikie Basin is not a reliable indicator of unrestricted flow. Bathymetric isolation is exacerbated in backarc and foreland basins during sea level lowstands, when further restriction creates an even more strongly stratified water mass (Khim et al., 2008). Because sedimentologic evidence indicates that sea level fluctuated during the evolution of the Animikie Basin (Pufahl, 1996; Nelson et al., 2010), any vertical stratification in sulfate concentrations that may have existed is interpreted to have been the result of restricted circulation.

We concur that sufficient connectivity existed early in the history of the Animikie Basin to produce upwelling-related iron formation. Once the area had evolved into a foreland basin, however, circulation is interpreted to have become restricted enough to produce seawater compositions that primarily reflect local environmental factors. This is also supported by the observed increase in previously published $\delta^{34}\text{S}$ values through the Rove Formation (Fig. 3) (Poulton et al., 2004). Although this trend has been interpreted to record progressive hydrogen sulfide loss in an open system, box models of the surface sulfur cycle underestimate the amount of hydrogen sulfide lost without invoking upwelling (Johnston et al., 2006). Because the sedimentology of the foreland fill does not support an upwelling interpretation, it is more plausible that this trend reflects hydrogen sulfide loss in a restricted basin through pyrite precipitation and subsequent sequestration in the sediment.

CONCLUSIONS

Results from this study question the usefulness of pyrite in Animikie Basin sedimentary rocks as a proxy for evolving global ocean chemistry. These observations support recent tectonic models that suggest the Animikie Basin became increasingly isolated with time as it evolved from a backarc to a foreland basin marked by widespread deltaic deposition. When viewed in this context, it becomes clear that the interpreted “global” shift to sulfidic conditions approximately coincides with the onset of restricted circulation. Thus, the observed change in pyrite $\delta^{34}\text{S}$ values is primarily the result of local environmental factors. The interpreted patchiness in sulfate reduction around paleodeltas and the likelihood that the Animikie Basin was strongly depth-stratified suggests sluggish circulation in a restricted sea, not open circulation as previously proposed. Consequently, the Animikie Basin should not be used as a benchmark for understanding the sulfidic ocean transition. What the Animikie Basin provides is information on the circulation in an evolving, Paleoproterozoic marginal sea. Studies in other Paleoproterozoic basins are required to clarify the timing and nature of this important oceanographic change.

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