Reconstructing diagenetic mineral reactions from silicified horizons of the Paleoproterozoic Biwabik Iron Formation, Minnesota

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ABSTRACT

Primary phases in iron-rich chemical sedimentary rocks are important archives of seawater geochemistry throughout the Precambrian. The record of seawater chemistry, however, is obscured by post-depositional changes that occur during diagenesis, metamorphism, and modern weathering. Recent studies have identified silica-cemented horizons in some Archean and Paleoproterozoic iron formations that may preserve reduced, texturally early mineral phases, which may inform interpretations of oxygen dynamics preceding atmospheric oxygen accumulation before the ~2.3 Ga Great Oxidation Event (GOE). However, fewer investigations focus on silica-cemented horizons in Paleoproterozoic iron formation deposited after the GOE, a period where oxygen levels are poorly constrained. Here, we present petrographic observations, scanning electron microscopy, electron microprobe analysis, and Raman spectroscopy of iron mineral phases preserved within silica-cemented horizons of the ~1.9 Ga Biwabik Iron Formation (Minnesota, U.S.A.) to constrain texturally early iron formation mineralogy from this crucial post-GOE interval. Based on textural relationships, the iron silicate greenalite is identified as the earliest-forming iron silicate mineral preserved within silica-cemented horizons. The magnesium- and aluminum-rich iron silicates chamosite and stilpnomelane are preserved proximal to fine-grained, non-silicified horizons, suggesting local geochemical exchange during early diagenesis. The presence of well preserved, early-forming silicates containing predominantly ferrous iron may indicate reducing conditions at the sediment-water interface during deposition of the Biwabik Iron Formation. More definitively, future studies using iron silicate mineralogy as seawater geochemistry proxies should consider preservation by silica cementation, in addition to the effects of local geochemical exchange during diagenesis.

Keywords: Silicification, silica cementation, diagenesis, chamosite, greenalite

INTRODUCTION

Chemical sedimentary rocks, such as iron formations, archive geochemical conditions of marine environments throughout Earth history. Iron formations are iron and silica-rich chemical sedimentary rocks deposited throughout the Precambrian sedimentary record, notable for providing a record of marine (bio)geochemistry across the Archean-Proterozoic transition and the initial rise of atmospheric oxygen concentrations during the ~2.2–2.4 Ga Great Oxidation Event (GOE) (Lyons et al. 2014; Gumsley et al. 2017; Poulton et al. 2021). Primary authigenic phases preserved in iron formations are of interest because they may record critical chemical information about the water column. Here, primary phases are defined as the earliest forming minerals that reflect geochemical conditions of the fluid at their time of precipitation. Following deposition, primary phases experience processes that alter and overprint original geochemical signatures including early and late diagenesis, burial, metasomatism and metamorphism, and modern weathering during fluid permeation and surface exposure (Klein 2005; Albut et al. 2018). Deciphering the mineralization histories and distinguishing these later secondary and tertiary mineral phases from primary phases is crucial for elucidating original geochemical information that can be linked to the depositing fluid and original depositional conditions.

Cementation by silica during early diagenesis may aid in mineral preservation by encapsulating precursor sediments near the time of silica precipitation, preventing subsequent major cation exchange and mineral transformations (Simonson 1987). Favorably, throughout most of the Precambrian, the lack of silica biomineral sinks likely resulted in high-seawater silica concentrations at or above saturation (e.g., Siever 1992; Maliva et al. 2005), evidenced in part by deposition of abundant Si-rich chemical sedimentary rocks and widespread silicification (e.g., Brengman et al. 2020). Recent studies of silica-cemented horizons in iron formation identified iron silicate inclusions, specifically Fe(II)-rich greenalite, and interpreted these minerals as primary precipitates reflective of anoxic depositional conditions (Rasmussen et al. 2013; Johnson et al. 2018; Muhling and Rasmussen 2020; Rasmussen et al. 2021 and references therein). The presence of putative primary greenalite within these silica-cemented horizons, when