

Suboxic deep seawater in the late Paleoproterozoic: Evidence from hematitic chert and iron formation related to seafloor-hydrothermal sulfide deposits, central Arizona, USA

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Abstract

A current model for the evolution of Proterozoic deep seawater composition involves a change from anoxic sulfide-free to sulfidic conditions 1.8 Ga. In an earlier model the deep ocean became oxic at that time. Both models are based on the secular distribution of banded iron formation (BIF) in shallow marine sequences. We here present a new model based on rare earth elements, especially redox-sensitive Ce, in hydrothermal silica–iron oxide sediments from deeper-water, open-marine settings related to volcanogenic massive sulfide (VMS) deposits. In contrast to Archean, Paleozoic, and modern hydrothermal iron oxide sediments, 1.74 to 1.71 Ga hematitic chert (jasper) and iron formation in central Arizona, USA, show moderate positive to small negative Ce anomalies, suggesting that the redox state of the deep ocean then was at a transitional, suboxic state with low concentrations of dissolved O₂ but no H₂S. The presence of jasper and/or iron formation related to VMS deposits in other volcanosedimentary sequences ca. 1.79–1.69 Ga, 1.40 Ga, and 1.24 Ga also reflects oxygenated and not sulfidic deep ocean waters during these time periods. Suboxic conditions in the deep ocean are consistent with the lack of shallow-marine BIF ~ 1.8 to 0.8 Ga, and likely limited nutrient concentrations in seawater and, consequently, may have constrained biological evolution.

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1. Introduction

Atmospheric oxygen levels rose twice in the Proterozoic Eon, between 2.47 and 2.32 Ga [1] and after 0.8 Ga [2]. The intervening time period is marked by moderate levels of atmospheric oxygen and a substantial

terrestrial sulfate flux to the ocean due to oxidative continental weathering. The redox state of the deep ocean during this interval is still debated. Holland [3] used the disappearance of banded iron formation (BIF) in shallow-marine settings ca. 1.8 Ga to argue that the deep ocean was fully oxygenated after the rise of atmospheric oxygen, whereas Canfield [4] suggested it was anoxic and sulfidic (euxinic) based on three-box modeling of the oxygen content of deep ocean water and

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on sulfur isotope data for sedimentary sulfides. The two models are based on the assumption that insoluble iron oxyhydroxides or iron sulfides, respectively, formed in the deep ocean and prevented the transport of dissolved iron of seafloor-hydrothermal origin to shallow-marine settings.

The sulfidic deep ocean model has found increasing support from recent studies of S and Mo isotopes, Fe speciation, and biomarkers in late Paleoproterozoic and Mesoproterozoic sedimentary successions of North America and northern Australia [5–11]. Biomarker studies [11] suggest that sulfidic conditions extended even into the photic zone. This model has critical implications for biological evolution because under sulfidic conditions, some trace metals (e.g., Fe, Mo, and Cu) are efficiently scavenged with precipitating sulfides to sediments, leaving seawater depleted in elements that are essential for enzymes involved in the biological nitrogen cycle [12]. Because eukaryotes cope poorly with N-limitation and would be particularly affected by these conditions, the ca. 1 b.y. biological stasis in their evolution ca. 1.8 to 0.8 Ga has generally been interpreted [12] as reflecting deep-ocean sulfidic conditions; alternatively, this stasis might reflect intrinsic evolutionary conservatism in the absence of natural selection imposed by later animals [13].

Most geochemical arguments for marine sulfidic conditions during the late Paleoproterozoic and Mesoproterozoic are based on studies of sedimentary sequences that were deposited in intracratonic settings, including S isotope data for sedimentary sulfate and sulfide minerals that are consistent with low seawater sulfate contents [4]. Significantly, direct indicators of such conditions in deep-water, clearly open-marine settings during this time period are lacking. Molybdenum isotope data [10] potentially constrain Mo burial in oxic versus suboxic/sulfidic settings and, consequently, ocean redox conditions. However, Mo isotope data do not distinguish between sulfidic and suboxic deep-water conditions [10,14]; suboxic waters have low concentrations of dissolved O₂ (<5 μmol/l [15] in contrast to typical values of 150–200 μmol/l in modern oxygenated deep oceans), but no H₂S. Rare earth elements (REE), and specifically Ce anomalies, in chemical sediments like BIF and phosphorites can provide important constraints on the redox state of seawater, but such sediments are rare in open-marine sequences between 1.8 and 0.8 Ga.

Some deep-ocean volcanogenic massive sulfide (VMS) deposits of Paleoproterozoic and Mesoproterozoic age have related chemical sediments including extensive beds of hematitic chert (jasper) and hematitic

iron formation that can provide a window into the redox state of the deep ocean during this time period. Recent studies [16,17] show that such laterally persistent jasper formed from silica–iron gels that precipitated largely from the non-buoyant parts of submarine-hydrothermal plumes, due to the oxidation of dissolved hydrothermal ferrous iron (Fe²⁺) to insoluble ferric iron (Fe³⁺) oxyhydroxide that promoted flocculation of seawater-derived amorphous silica. The formation of such hematite-rich seafloor deposits implies that the redox state of ambient seawater was at or above the oxidation state of ferrous iron. VMS-related hematitic iron formations also likely formed by the precipitation of iron oxyhydroxide particles from submarine-hydrothermal plumes [18]. The setting of these volcanic-hosted, deep-water “Algoma-type” iron formations [19] is distinctly different from that of the sediment-hosted, “Superior-type” BIFs, which consist mainly of interlayered chert and iron oxides in shallow-water sedimentary sequences [19].

In this paper we investigate the geochemistry of late Paleoproterozoic jasper and iron formation in the Jerome mining district of Arizona, with a focus on redox-sensitive Ce. These data are used for testing current models for the existence of sulfidic deep seawater during the Proterozoic, and for introducing a new model that argues for suboxic conditions in the deep part of the late Paleoproterozoic ocean.

2. The Paleoproterozoic Jerome mining district of Arizona

Jasper and iron formation form beds that are spatially and temporally related to seafloor VMS deposits within a late Paleoproterozoic submarine volcanosedimentary sequence of oceanic arc affinity in the Jerome mining district of central Arizona (Figs. 1 and 2) [22,23,27]. This sequence comprises a 1.0 to 2.5-km thick succession of submarine volcanic and volcanoclastic rocks. Basal strata consist of the Shea Basalt together with andesite, dacite, and rhyolite, which are overlain by rhyolite flows and domes of the Deception Rhyolite, rhyolite flows, domes, breccias, and tuffs of the Cleopatra Rhyolite, and an upper unit of volcanoclastic turbidites and minor rhyolites of the Grapevine Gulch Formation. A U–Pb age of 1738.5±0.5 Ma has been determined recently by S.A. Bowring on igneous zircons from the upper part of the Cleopatra Rhyolite (see Supplementary Table 1, Supplementary Fig. 1). Jasper and iron formation occur along the contact of the Shea Basalt and the Deception Rhyolite, and along the base of and interbedded with the Cleopatra Rhyolite, where jasper locally forms rip-up clasts within volcanoclastic

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