Precambrian Research 270 (2015) 165–180

Contents lists available at ScienceDirect

Precambrian Research

journal homepage: www.elsevier.com/locate/precamres

# Geochemistry of the Krivoy Rog Banded Iron Formation, Ukraine, and the impact of peak episodes of increased global magmatic activity on the trace element composition of Precambrian seawater

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ARTICLE INFO

*Article history:*
Received 3 April 2015
Received in revised form 12 August 2015
Accepted 12 September 2015
Available online 25 September 2015

*Keywords:*
Krivoy Rog
Archean
BIF
Seawater
Mantle plume
REE

ABSTRACT

Pure Superior-type Banded Iron Formation (BIF) samples from the Krivoy Rog Supergroup (Ukraine) are excellent archives of ambient Early Precambrian seawater. They show low concentrations of incompatible elements such as Zr, Hf, and Th, and shale-normalized Rare Earths and Yttrium ($REY_{SN}$) patterns similar to those of modern seawater, i.e. heavy $REY_{SN}$ enriched patterns with positive $La_{SN}$, $Gd_{SN}$ and $Y_{SN}$ anomalies. Lack of $Ce_{SN}$ and presence of positive $Eu_{SN}$ anomalies indicate REY contributions to anoxic ferruginous seawater from high-temperature hydrothermal fluids.

The depositional age of the Krivoy Rog BIF is ill-defined, but a Late Archean to Paleoproterozoic age has been suggested based on U–Pb zircon ages for units stratigraphically above and below the BIF. We determined Sm–Nd isotopic compositions of pure and impure samples from the Krivoy Rog BIF, which yield an errorchron with an apparent age of 2406 ± 350 Ma (MSWD 15), that falls within this broad age range. All pure BIF samples show chondrite-normalized (subscript $_{CN}$) REY patterns with strong positive $Eu_{CN}$ anomalies that are typical for Archean but rather rare and much less pronounced in Proterozoic BIFs. Associated schists also show Archean – rather than post-Archean-style REY distributions. The REY geochemistry of both, chemical and epiclastic sediments, therefore, is more consistent with a Late Archean rather than a post-Archean depositional age of the Krivoy Rog Supergroup.

Initial εNd values of impure BIFs and of associated schist reveal variable contributions from TTGs less radiogenic in Nd and a more radiogenic component possibly comprised of basement amphibolites or mafic volcanics of the stratigraphically underlying New Krivoy Rog Group. The purest Krivoy Rog BIF, representing *local* Krivoy Rog seawater, displays an $\varepsilon Nd_{2.60\,Ga}$ value of −2.3. This value is less radiogenic than impure Krivoy Rog BIFs or other near-contemporaneous Neoarchean pure chemical sediments. To preserve this specific local isotopic fingerprint in anoxic Archean seawater, the Krivoy Rog BIF must have been deposited in an isolated sea basin with limited exchange with ferruginous deep-waters of the open ocean.

A compilation of REY data for high-purity Precambrian BIFs reveals that $Eu_{CN}/Eu^*_{CN}$ ratios of Precambrian seawater follow a general global evolution curve, that shows specific peaks which reflect times of increased high-temperature hydrothermal REY input into seawater. Following declining $Eu_{CN}/Eu_{CN}$ ratios from the Eoarchean to the Mesoarchean, the ratios suddenly rise at 2.7 Ga and reach a maximum at 2.6 Ga, indicating an increased flux of high-temperature hydrothermal REY to Neoarchean seawater, which supports the hypothesis that times of widespread BIF deposition coincided with periods of intense submarine hydrothermal activity, probably triggered by major mantle plume events. This association is supported by a strong increase of the $\varepsilon Nd_{(t)}$ values of pure seawater archives at 2.7–2.6 Ga, which reflects an increased flux of mantle Nd into seawater. These results suggest that Eu-REY systematics (and potentially εNd systematics) are robust tools to indentify episodes of enhanced mantle plume activity.



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http://dx.doi.org/10.1016/j.precamres.2015.09.015
0301-9268/

## 1. Introduction

Banded Iron Formations (BIFs) are iron- and silicon-rich chemical sediments which directly precipitated from ferrous iron-rich Precambrian seawater and, therefore, may provide detailed insights into the physico-chemistry of the early oceans. The Late Archean to Early Proterozoic Krivoy Rog BIF, Central Ukraine, hosts one of the world's most important Fe ore deposits, but has only attracted limited attention in past research. The Krivoy Rog Supergroup comprises seven cycles of clastic and chemical sediments with a total thickness of up to 1400 m (Belevtsev et al., 1983) and a lateral extent of 120 km × 10 km. Drastic sea level changes of the "Krivoy Rog sea" in the tectonically unstable, restricted Krivoy Rog trough characterized the depositional environment (Belevtsev et al., 1983; Kulik, 1991; Kulik and Korzhnev, 1997). Post-depositional lower greenschist- to amphibolite-facies tectono-metamorphic events and supergene weathering eventually produced the economically important iron ores of the Krivoy Rog area (Kulik and Korzhnev, 1997) from a BIF precursor. While mining companies focus on high-grade ores, only the pristine BIFs, i.e. chemical sediments the pristine composition of which has not been modified by syn- and/or post-depositional processes, are archives of proxies that allow evaluating ancient seawater characteristics. Rare Earths and Yttrium (REY) are such proxies that combined with data for selected particle-reactive trace elements such as Zr, Hf, and Th are also powerful tools to distinguish between pure BIFs and those "contaminated" by detrital aluminosilicates and/or post-depositional overprint (e.g., Bau, 1993). Only pure Precambrian chemical sediments show (with the exception of redox-sensitive REY) REY distributions similar to those of modern seawater and may be used as prime archives to evaluate the chemical composition of ancient seawater (e.g., Bau and Dulski, 1996; Planavsky et al., 2010). Typical modern seawater-style $REY_{SN}$ features are small positive $La_{SN}$ and $Gd_{SN}$ anomalies, super-chondritic Y/Ho ratios ($Y/Ho_{chondrite}$ = 26.22 after Pack et al., 2007) and enrichment of heavy REY (HREY) relative to light REY (LREY) (e.g. Elderfield and Greaves, 1982; Bau et al., 1995; Alibo and Nozaki, 1999).

As BIFs are often associated with volcanogenic units, U–Pb age determinations of zircons in these clastic units are the most common and precise method to define depositional ages of BIFs. Unfortunately, the Krivoy Rog BIF is a Superior-type BIF, i.e. the chemical sediments are intercalated with epiclastic sedimentary units, show large vertical and horizontal extents and presumably were deposited during marine transgressions onto "shallow" marine platforms (e.g. Gross, 1965; Trendall, 1968; Beukes, 1983). The lack of intercalated igneous or pyroclastic rocks in the BIF sequence, therefore, prevents the determination of precise igneous U–Pb ages. The U–Pb ages of epiclastic zircons in over- and underlying units only allow bracketing the BIF depositional age to between ~2700 Ma and ~2080 Ma (Shcherbak et al., 1989). Long-lived radioactive decay systems such as the Sm–Nd and the Lu–Hf isotope systems are potential candidates to determine the depositional age of the Krivoy Rog BIFs, as it has rather successfully been done in a few other Early Precambrian BIFs (Alibert and McCulloch, 1993; Viehmann et al., 2013). Based on precise determinations of depositional ages, initial Nd isotopic compositions of pure chemical sediments may also unravel the source(s) of dissolved REY in ancient seawater. The divergence of Sm–Nd isotope compositions in the Earth's mantle and continental crust began with the first differentiation between the early mantle and the continental crust during the Hadean. Therefore, initial Nd isotope characteristics may be used as a tool to determine the relative importance of hydrothermal REY input with mantle-like Nd isotope composition derived from oceanic crust and terrigenous REY input from continental run-off, dust or pore waters into the oceans (e.g., Miller and OíNions, 1985; Jacobsen and Pimentel-Klose, 1988; Bau et al., 1997b; Frei and Polat, 2007; Alexander et al., 2008, 2009; Viehmann et al., 2013; see Frank (2002) and references therein, for a detailed overview on modern seawater).

Here we present a comprehensive trace element data set for all seven alternating clastic and chemical sedimentary cycles of the Late Archean to Early Proterozoic Krivoy Rog Supergroup. Trace element compositions and chondrite- and shale-normalized (subscript $_{CN}$ and $_{SN}$, respectively) REY patterns allow us to discriminate between pure and impure BIF samples. The position of the Krivoy Rog BIF relative to the evolution curve of the $Eu_{CN}$ anomaly of BIFs throughout the Precambrian (compiled from more than 700 published REY data sets of Precambrian pure BIFs) and a Sm–Nd errorchron confirm the published wide range of the possible depositional age of the Krivoy Rog Supergroup, but shift the *preferred* depositional age to the Late Archean. Initial Nd isotope compositions of selected pure BIF, impure BIF and schist samples provide detailed insights into the provenance of the detritus co-deposited with the BIFs and into the origin of REY in the *local* Krivoy Rog seawater. The initial $\varepsilon$Nd values of pure Krivoy Rog BIFs are discussed with respect to a *global* compilation of other Archean pure BIFs to evaluate the evolution of the Nd isotopic composition of Archean seawater and, therefore, unravel the source(s) of REY and the mechanisms triggering BIF deposition in the Archean oceans.

## 2. Geological overview

The Krivoy Rog (also known as Kryvyi Rih) basin is located in the western part of the Archean to Proterozoic Middle Dnieper granite–greenstone terrain of the Ukrainian Shield, Central Ukraine (Fig. 1). Low grade metamorphic units of the Konka and Belozerka Supergroup are surrounded by the high-grade, 3.2–3.1 Ga old Aulian Gneiss basement complex which consists of tonalitic gneisses, amphibolites and intruded tonalitic-trondhjemitic granodiorites (TTGs). The Konka and the Belozerka Supergroup are comprised of metavolcanics, rare metasediments and various intruded TTGs which yield U–Pb zircon ages between 3120 ± 10 Ma and 2815 ± 15 Ma (Shcherbak et al., 1989; Samsonov and Chernyshev, 1996; Bibikova et al., 2010, and references therein). The stratigraphically younger Late Archean to Lower Proterozoic greenschist- to amphibolite-facies Krivoy Rog Supergroup is divided into five subgroups (after Belevtsev and Belevtsev, 1981; Belevtsev et al., 1983 and summarized in Kulik and Korzhnev, 1997; Fig. 1).

Lowermost Latovka metasandstones–quartzites and younger metatholeiites and metaandesites of the New Krivoy Rog Group (1) are discordantly separated from the older Archean basement and the younger Skelevat Group (2) which is composed of metasedimentary units, including metaconglomerates, metasandstones, phyllitic schists, and talc schists. Uranium–Pb zircon ages of Skelevat siliciclastics yield 3000–2700 Ma (Shcherbak et al., 1989), providing the maximum ages of the Krivoy Rog Supergroup and the overlying chemo-clastic Saxagan Group (also translated as Sakssagan, (3), respectively. Up to seven alternating Superior-type BIF (f) and ferruginous schist (s) units (named from base to top as 1f–1s, 2f–2s, etc.) reach a thickness of up to 1400 m and indicate a cycle of transgression–regression periods of the Krivoy Rog sea during the deposition of the Krivoy Rog Supergroup (Kulik, 1991). The Fe content of the lower sequences is less than 40%, while upper Saxagan Group BIF horizons may contain up to 65% Fe (Mboudou et al., 2012), probably triggered by post-depositional supergene Fe-ore upgrade. Mboudou et al. (2012) and Belevtsev and Belyaev (1989) report greenschist facies metamorphic conditions in the lower part of the Saxagan BIF stratigraphy which increase to amphibolite facies in the upper part of the sequence and are probably related to a