Precambrian Research 174 (2009) 337–346

Contents lists available at ScienceDirect

Precambrian Research

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

Distribution of high field strength elements (Y, Zr, REE, Hf, Ta, Th, U) in adjacent magnetite and chert bands and in reference standards *FeR-3* and *FeR-4* from the Temagami iron-formation, Canada, and the redox level of the Neoarchean ocean

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ARTICLE INFO

Article history:
Received 26 January 2009
Received in revised form 10 August 2009
Accepted 27 August 2009

Keywords:
Archean iron-formation
Rare earth elements
Zirconium
Hafnium
Tantalum
Reference standards

ABSTRACT

Adjacent magnetite and chert bands and reference standards *FeR-3* and *FeR-4* from the Neoarchean Temagami iron-formation (IF) show shale-normalized rare earth and yttrium (REY) patterns with low Nd/Yb ratios and positive Eu, Gd and Y anomalies, indicating that they formed as marine chemical sediments. In contrast to previous claims, none of the samples shows any Ce anomaly, indicating the absence of oxidative Ce-REY decoupling and arguing against oxic conditions in the wider vicinity of the Neoarchean "Temagami seabasin". The distribution of Zr, Hf and Ta yields Zr/Hf and Hf/Ta ratios that differ from those of chondrites, average upper continental crust and local shales, suggesting that the Temagami IF is the only case observed so far in which a significant fraction of these elements is non-detrital but sourced from seawater. If Neoarchean seawater was characterized by Zr/Hf and Hf/Ta ratios similar to those of modern seawater these ratios point towards preferential scavenging of Hf over Zr and Ta, as is typical of the modern ocean. Similar to the 2.9 Ga old Mozaan IF in the Pongola Supergroup, South Africa, the Temagami IF shows low Th/U ratios that differ from those of the respective local shales and from that of average upper continental crust. Decoupling of U and Th results from U^{4+} oxidation in the Earth's surface system and fractionated Th/U ratios in these marine chemical sediments are, therefore, at odds with the lack of Ce anomalies. This suggests a different redox-sensitivity of the two paleo-redox-proxies Th–U and Ce-REY and demonstrates that the Temagami IF and the Mozaan IF warrant further study of other paleo-redox-proxies.

1. Introduction

The Temagami iron-formation is a Neoarchean oxide-facies banded iron-formation (IF) in the Temagami greenstone belt, Ontario, Canada. One of the reasons it has attracted the attention of geochemists in the past is that two out of the five international reference standards available for IF (called *FeR-3* and *FeR-4*) have been prepared from Temagami IF material provided by mining operations at Sherman Mine (Abbey et al., 1983). Moreover, a study of the isotopic composition of sulfur in pyrite from oxide-facies Temagami IF suggested an unfractionated and abiogenic sulfur source (Bowins and Crocket, 1994) and recently, the rare earth element (REE) distribution in oxide-facies Temagami IF has been used as supporting evidence of high oxygen levels in the Neoarchean atmosphere–hydrosphere system (Ohmoto et al., 2006).

In a recent review paper on IFs, Ohmoto et al. (2006) published a figure (referenced as "M. Bau, personal communication" (Ohmoto et al., 2006, p. 311)) presenting REE patterns for the Temagami IF, some of which show pronounced negative Ce anomalies. If these data were correct, such negative Ce anomalies indicated oxidative scavenging of Ce and decoupling of redox-sensitive Ce from its redox-*in*sensitive REE neighbors in the Neoarchean Earth's surface system, supporting Ohmoto et al.'s claim of an oxygenated atmosphere–hydrosphere system as early as 2.7 Ga ago. However, the senior author of the present contribution had serious doubts with regard to the analytical quality of these data, since other Temagami samples measured during different analytical runs did not show any Ce depletion. Therefore, he had decided to *not* publish these questionable REE data. To resolve this issue, we (re-)sampled sets of adjacent magnetite and chert bands from the original two hand-specimens for which the disputed data were determined and from an additional hand-specimen, and studied the trace element composition of the Temagami IF, with emphasis on the high field strength elements Zr, Y, REE, Hf, Ta, Th and U.

Since available reference data (Govindaraju, 1994) suggest that at least IF-standard *FeR-3* is very low in detrital aluminosilicates, it might serve as a good complementary standard to *IF-G*, the most widely used IF reference material from Isua, Greenland. However,

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doi:10.1016/j.precamres.2009.08.007

for many trace elements recommended values are either not available or ill-defined, and we, therefore, measured the concentrations of 30 trace elements to enlarge and improve the data base, in particular for the high field strength elements Zr, Y, REE, Hf, Ta, Th and U.

The new REE data from this study for the Temagami IF bear no evidence of Ce oxidation in an oxygenated Neoarchean atmosphere–hydrosphere system. These data are supported by the trace element distribution in the *FeR-3* and *FeR-4* reference standards. We also show that the Temagami IF is characterized (i) by Th/U ratios that differ strongly from the Th/U ratio of average upper continental crust and local shale, which suggests oxidative mobilization of U in the source area of dissolved U in the “Temagami seabasin”, and (ii) by Zr/Hf and Hf/Ta ratios which indicate that at least a significant fraction of Hf is not detrital but derived from ambient Neoarchean seawater and that similar to the situation in the modern ocean, Hf is preferentially removed from seawater relative to Zr and Ta during IF sedimentation.

2. Geological background

The Temagami IF is part of the Temagami greenstone belt, Ontario, Canada, which is comprised of one metasedimentary and four metavolcanic units. All specimens studied (including the controversial samples *TM1* and *TM2*) have been taken within several meters distance from each other from a roadcut along Highway 11 and consist of oxide-facies banded iron-formation composed of magnetite and ferruginous chert bands with very minor hematite. The IF occurs at the top of the uppermost metavolcanic unit and is associated with turbiditic shales and greywackes, all of which have been metamorphosed at lower greenschist facies conditions (see Bennett, 1978; Fyon and Cole, 1989, for details). While the exact paleo-waterdepth at which the Temagami IF was deposited is not known, its association with turbiditic shales argues against shallow waterdepth. Rhyolite flows within the sequence yield a U–Pb zircon age of 2736 Ma (Bowins and Heaman, 1991), suggesting a Neoarchean age for the Temagami IF.

3. Analytical

In three individual hand-specimens (*TM1*, *TM2* and *TM3*) successive chert and magnetite bands of between 5 and 12 mm thickness were microdrilled (3.5 cm lateral distance between *A* and *B* samples in *TM1*), producing 13–15 mm long microcores with a diameter of 3 mm. While hand-specimens *TM1* and *TM2* are the same as those from which the samples presented in Ohmoto et al. (2006) were taken, *TM3* is an additional hand-specimen studied to enlarge the data base on adjacent chert and magnetite bands.

All samples were digested under pressure at high-temperature ($T > 160\,^\circ C$) using ultrapure HF and $HClO_4$ acids. After digestion and HF-$HClO_4$ evaporation the samples were diluted in 0.5 molar HCl, producing clear solutions that were analyzed immediately for trace elements (to avoid the potential precipitation of Zr, Hf and/or Ta compounds) using inductively couple plasma mass spectrometry (ICPMS) following the procedures of Dulski (2001) and Alexander (2008). Major elements were determined using a Spectro Ciros Vision inductively couple plasma optical emission spectrometer. The same analytical protocols were followed for *FeR-3* and *FeR-4*. Note that Nb concentrations could not be determined due to strong interference of $FeCl^+$ analyte species on monoisotopic Nb (for details see Alexander, 2008).

Anomalies in the REE_{SN} patterns (subscript “SN”: normalized to post-Archean Australian Shale, *PAAS*, from McLennan, 1989) are quantified (Tables 1 and 2) as REE_{SN}/REE^*_{SN}, with $Ce^*_{SN} = 0.5La_{SN} + 0.5Pr_{SN}$, $Pr^*_{SN} = 0.5Ce_{SN} + 0.5Nd_{SN}$, $Eu^*_{SN} = 0.67Sm_{SN} + 0.33Tb_{SN}$, and $Gd^*_{SN} = 0.33Sm_{SN} + 0.67Tb_{SN}$. Using local Temagami shale (*SMS-8* in Table 2) or “Average Archean Mudstone” (*AAM*; Taylor and McLennan, 1985) for normalization does not significantly change the REY_{SN} patterns, except that it reduces Eu_N/Eu^*_N ratios by 25 and 35%, respectively, – which, however, does not remove the positive Eu anomalies. To simplify comparison with published REE patterns for other IFs we, therefore, normalized to post-Archean Australian Shale, despite the undisputedly Archean age of the Temagami IF.

Whenever reference is made to the composition of the average upper continental crust, we refer to the compilation by Rudnick and Gao (2003) with Zr/Hf of 36, Hf/Ta of 5.9, Zr/Ta of 214, and Th/U of 3.9. For chondrites we use the data of Anders and Grevesse (1989) with Zr/Hf of 38, Hf/Ta of 7.3, and Th/U of 3.6; Weyer et al. (2002) suggested chondritic Zr/Hf and Hf/Ta ratios which are somewhat lower, but that this does not alter the interpretation of our data.

4. Results

4.1. Reference standards FeR-3 and FeR-4

Concentration data and trace element ratios for *FeR-3* and *FeR-4* are given in Table 1 together with literature data for comparison (compiled reference values from Govindaraju, 1994, and high-quality ICPMS data from Dulski, 2001). Where comparison to literature data is possible (Table 1), our results (with the exception of Rb in *FeR-3*) are in close agreement with data from Dulski (2001), but in several cases (e.g., for Y, Zr, Ba, and Hf in *FeR-3*) do not confirm the reference values compiled by Govindaraju (1994), highlighting the need for an improved data base. The same can be seen for elements which are usually measured as major elements using X-ray fluorescence methods but that occur in IFs at trace levels, such as K and Na.

Compared to *FeR-3*, *FeR-4* shows considerably higher concentrations of elements such as Ti, Rb, Zr, Cs, Ba, light REE (LREE), Hf, Ta, and Th, i.e., of elements which in chemical sediments are typically associated with detrital aluminosilicates (e.g., Bau, 1993). Shale-normalized REY patterns (REY: rare earths and yttrium; Y inserted between Dy and Ho according to its ionic radius) show positive La, Eu and Y anomalies and sample *FeR-3* is slightly depleted in LREE (Fig. 1). The Gd_{SN}/Gd^*_{SN} ratios below unity (Table 1) are anomalous for Precambrian IFs (see Temagami microcore samples in Table 2 and Fig. 2, for example), but are also present in the data of Dulski (2001) and result from unusually high Sm concentrations and not from unusually low Gd concentrations. Compared to the microcore samples from the Temagami IF (Table 2), the standards (*FeR-3* in particular) also show high Nd/Pr ratios due to unusually high Nd levels. The high Sm/Nd ratios of *FeR-3* and *FeR-4* (0.33 and 0.28, respectively) relative to the microcore samples (0.17–0.23) suggest that the Nd isotopic composition of the two reference standards might not be representative of that of the Temagami IF.

While *FeR-4* shows a Zr/Hf ratio of 36, detritus-poor *FeR-3* displays a much higher Zr/Hf ratio of 54. The Hf/Ta and Zr/Ta ratios are 1.9 and 105 in *FeR-3* and 5.9 and 213 in *FeR-4*. Average upper continental crust is characterized by Zr/Hf, Hf/Ta, and Zr/Ta ratios that are similar to those of *FeR-4*.

Both standards show a low Th/U ratio (*FeR-3*: 0.14; *FeR-4*: 0.82) when compared to the Th/U ratio of 4.5 of local shale (*SMS-8*) and 3.9 of average upper continental crust.

4.2. Temagami IF microcore samples

Major and trace element concentrations in the 21 microcore samples (Table 2) reflect the bimodal mineralogical composition of the sample set, i.e., the chert bands (Fe: 2.6–9.4%) show lower concentrations than the magnetite bands (35.9–56.6%). All samples are