Negative Ce Anomaly in the Banded Iron Formation and Associated Clastic Rocks of the Sirsi Shelf Region, Southern India: Inferences on the Fluid-Rock Alteration Event during the Pan-African Orogeny

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Abstract

Banded Iron Formations (BIFs) are archives of Precambrian seawater composition. Presence or absence of negative Ce anomaly (Ce/Ce*) in BIFs has been widely used to understand paleo-redox conditions on the Earth's surface in the Precambrian. However, whether the extremely negative Ce anomaly associated with the BIFs reflects a primarily depositional signature or not has been questioned and it has been suggested that such signatures could also arise from secondary alterations.1 We report elemental and Nd isotopic data for BIFs and associated clastic rocks from the Sirsi region in southern India. Major and trace element compositions of these BIFs were measured using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, X series II) while Nd isotope ratio (143Nd/144Nd) measurements were performed using a Thermal Ionization Mass Spectrometer (TIMS, Triton Plus), both at the Centre for Earth Sciences (CEaS), Indian Institute of Science Bangalore, India. The BIF samples are sub-divided into two groups based on their REE+Y (REY) compositions. The group-1 BIFs show seawater-like REY pattern with HREE enrichment over LREEs and super-chondritic Y/Ho (41-52). These BIF samples also lack significant negative Ce anomalies. In contrast, group-2 BIFs show high LREE/HREE enrichment, negative Ce anomaly, and sub-chondritic Y/Ho. Very high values of La/Yb in the group-2 BIFs cannot be explained by simple two-component mixing of basement rock (Dharwar TTG) and pristine Sirsi BIFs. Instead, fluid-rock alteration by LREE enriched, and Ce depleted fluid could explain the observed REY variations. We further utilized Sm-Nd isotope systematics to calculate the timing of this alteration event. These BIFs show lowest RSD (%) in their initial 143Nd/144Nd composition around 0.6 Ga, which we consider as the time of alteration event which affected the Sm/Nd of these rocks. The timing of alteration event coincides with the Pan-African orogeny which had regionally affected the Greater Dharwar Craton. The associated red shales are also characterized by high LREE/HREE ratios and negative Ce anomalies. These shales also show very high Chemical Index of Alteration (CIA) values (83-99) suggesting high degree of chemical weathering. [1] Bonnand et al, (2020) Earth and Planetary Science Letters

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1. Introduction

- Banded Iron Formations (BIFs) are archives of Precambrian seawater
- Shale normalized REY (REE+Y) pattern, specifically presence or absence of Ce anomaly in the BIFs have been used to infer paleo-redox condition of the Precambrian ocean-atmosphere system
- This study focuses on the geochemistry and Nd isotope composition of BIFs and associated clastic rocks of the Sirsi shelf region, southern India (Fig.1)

➢ Do the BIFs preserve REY signature of Precambrian water-mass?
➢ What are the effects of post-depositional modifications on the REY signature of BIFs?

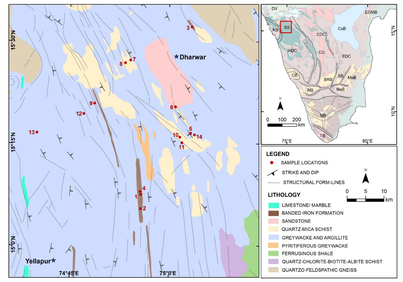
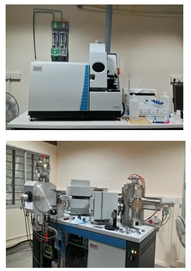


Fig. 1. A generalized geological map of the Sirsi shelf region of the southern India study area (after Ishwar-Kumar et al., 2013) showing the sample locations

This study presents geochemical and Nd isotope data of banded iron formations and clastic sedimentary rocks from the Sirsi shelf region, southern India

2. Analytical techniques



- Elemental concentrations were measured using Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Thermo Scientific, X Series II) at the Centre for Earth Sciences (CEaS), IISc.
- Nd isotopic ratios were measured using a Thermal Ionization Mass Spectrometer (TIMS, Triton Plus) at CEaS, IISc following established protocols.[10]

3. Results and Discussion

BIFs from the Sirsi region, Southern India

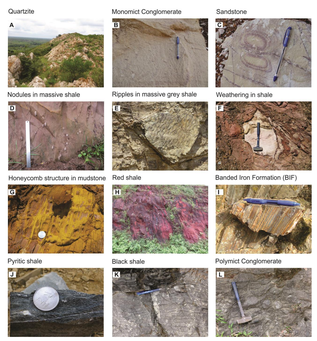


Fig.2. Representative field occurrence of BIFs and Clastic rocks from the Sirsi region, Southern India

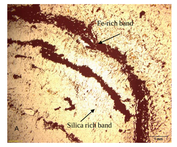


Fig. 3. Representative photo-micrograph of Sirsi BIFs

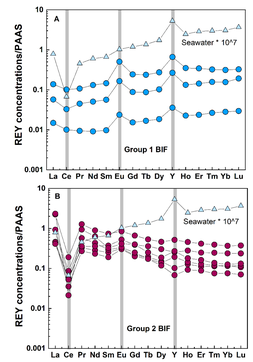


Fig.4. Post-Archean Australian Shale (PAAS) normalized REY pattern of Sirsi BIFs. Sirsi BIFs have been sub-divided into two groups based on their PAAS normalized REY pattern

Do REY signature of Sirsi BIFs reflects composition of Precambrian water-mass?

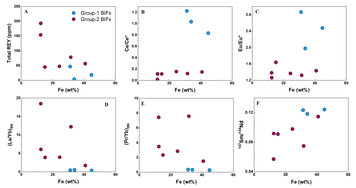


Fig.5. The Sirsi BIFs (group-1 and 2) show compositional variation in terms of their Fe concentration and elemental ratios

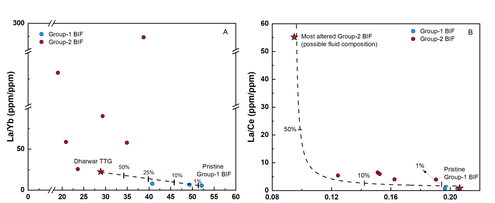


Fig. 7: (A) Plot of La/Yb vs. Y/Ho (A) of BIFs from the Sirsi region. Extremely high La/Yb ratio (>50) of group-2 BIFs cannot be explained by physical mixing between Archean TTGs derived ions and seawater. (B) Plot of La/Ce vs. Sm/Nd of Sirsi Group-1 and Group-2 BIFs showing two-component mixing. One end-member is pristine group-1 Sirsi BIF. Another end-member is LREE enriched and Ce depleted fluid which has altered the Sirsi BIFs. The mixing calculation suggests Group-2 BIFs have been affected by alteration due to later fluid addition.

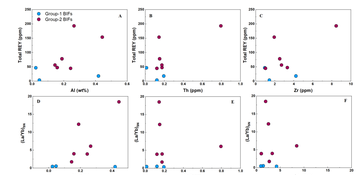


Fig.6. The Sirsi BIFs show low Al, Th, and Zr concentration suggesting minimal detrital contribution

- The group-1 Sirsi BIFs record REY signature of Precambrian water-mass
- REY signature of the group-2 BIFs can be explained by alteration by a fluid with high LREE/HREE ratio and depleted Ce

Timeline of the weathering event

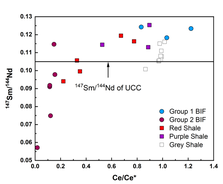


Fig. 8: In plot of $^{147}Sm/^{144}Nd$ vs. Ce/Ce the Group-2 BIFs and clastic rocks show fractionated Sm/Nd ratio compared to upper continental crust which most likely reflects secondary alteration.*

- The RSD (%) calculated show lowest value around 0.6 Ga ago suggesting timing of the weathering event
- This timeline is similar to the Pan-African Orogeny that had affected the Greater Dharwar Craton

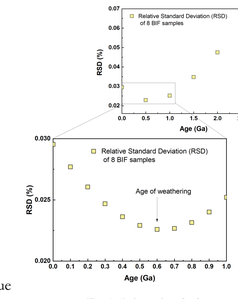


Fig. 9: Relative Standard Deviation (% RSD) of 8 Sirsi BIF samples. The RSD (%) is lowest around 0.6 Ga ago which has been considered as the age of weathering event which altered composition of Sirsi BIFs

Weathering signature from associated clastic rocks from the Sirsi region

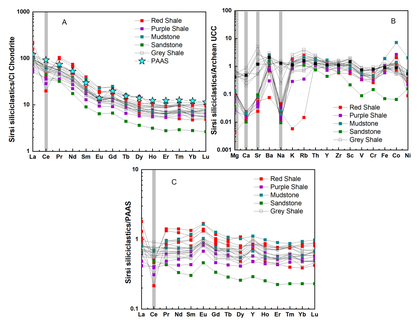


Fig. 10: (A) Chondrite normalized REE pattern of the Sirsi siliciclastic rocks (data from Taylor and McLennan, 1985. (B) Archean UCC normalized multi-element plot of the Sirsi siliciclastics. Note the red and purple shales are showing depletion in fluid mobile elements (i.e., Mg, Ca, Na, and Sr) (Archean UCC data taken from Taylor and McLennan, 1985) (C) PAAS normalized (Pourmond et al., 2012) REY (REE+Y) pattern of the Sirsi siliciclastic rocks

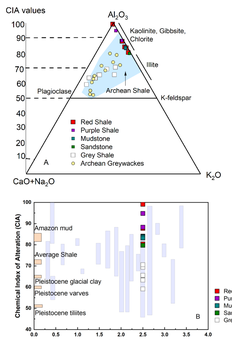


Fig. 11.(A) In the A-CN-K plot the Sirsi red shales plot near the Al_2O_3 apex and show high CIA values. (B) The Sirsi red shales show high CIA values compared to contemporaneous shales (data from Bindeman et al., 2015)

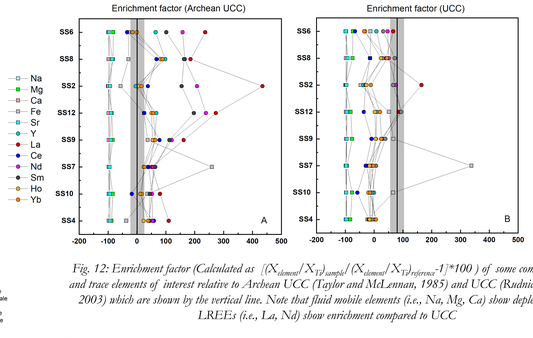


Fig. 12: Enrichment factor (Calculated as $[(X_{element}/X_Y)_{sample}/(X_{element}/X_Y)_{reference}-1]*100$) of some common major and trace elements of interest relative to Archean UCC (Taylor and McLennan, 1985) and UCC (Rudnick and Gao, 2003) which are shown by the vertical line. Note that fluid mobile elements (i.e., Na, Mg, Ca) show depletion while LREEs (i.e., La, Nd) show enrichment compared to UCC

- The Sirsi red shales show high Chemical Index of Alteration suggesting intense chemical weathering
- These shales also show depletion in fluid-mobile elements (i.e., Na, Mg, Ca)
- These shales show high enrichment factors for LREEs (i.e., La, Nd) and depletion in Ce which could explain observed very high La/Yb, La.Ce ratio and negative Ce anomaly

Source of REY in the pristine BIF

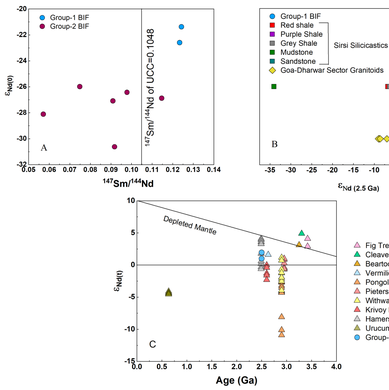


Fig. 13: The plot of (A) $\varepsilon_{Nd(0)}$ vs. $^{147}Sm/^{144}Nd$ of Sirsi group-1and group-2 BIFs suggest variation observed in the present-day Nd isotopic composition is controlled by their Sm/Nd ratio. (B) The $\varepsilon_{Nd(0)}$ of pristine Sirsi group-1 calculated at 2.5 Ga, along with associated clastic sedimentary rocks from the Sirsi Shelf region and Granitoids of the Goa-Dharwar Sector. (C) The $\varepsilon_{Nd(2.5\,Ga)}$ of pristine group-1 Sirsi BIFs plotted along with global Precambrian BIFs

- Nd isotope composition of pristine group-1 BIF is similar to contemporaneous BIFs
- Nd isotope composition of group-1 BIFs suggest REY contribution from hydrothermal sources

4. Conclusion

➢ The REY composition of the Sirsi group-1 and group-2 BIFs show variation in terms of LREE/HREE enrichment, Ce anomaly, and Y/Ho ratio. The group-1 Sirsi BIFs record pristine water -mass composition

➢ The timing of alteration is calculated as to be 0.6 Ga ago, which is contemporaneous with Pan-African orogeny. The Chemical Index of Alteration (CIA) in the associated Sirsi shales ranges from 59-99, which suggests extreme chemical weathering. Hence, a wide scale disturbance due to Pan-African orogeny possibly responsible for such extreme alteration event

➢ Extremely negative Ce anomaly observed in the group-2 BIFs does not represent an 'oxygen oasis'. Instead, REY composition of the Sirsi group-2 BIFs can be explained by fluid-rock alteration event.

References: 1. Taylor and McLennan 1985, 2. Pourmond et al., 2012, 3. Rudnick and Gao 2003, 4. Bindeman et al., 2015