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Re–Os depositional age for black shales from the Kaimur Group, Upper Vindhyan, India

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ABSTRACT

Proterozoic sedimentary deposits from the Vindhyan Supergroup, central India are excellent archives of paleo-environmental conditions. Meaningful interpretation of these geological signatures and their global correlation requires depositional age information for the sediments, data on which are limited for the Upper Vindhyan sediments. In this work, Re–Os isotopic study of the Bijaigarh shale, Kaimur Group from the Upper Vindhyan has been carried out to infer their depositional age and paleo-hydrological conditions. The Re–Os isochron for the Bijaigarh shale, a lagoonal deposit with an open ocean connection, provides a depositional age of 1210 ± 52 Ma (Model 3; MSWD = 69; n = 15; 2σ). This age for the Kaimur Group is younger by ~400 Ma than the underlying Semri Group (age ~1600 Ma), confirming existence of a long sedimentary hiatus between the two groups. The isochron-derived initial $^{187}Os/^{188}Os$ (Os_i) ratio for these shales (~0.6) is higher than those reported for Mesoproterozoic marine shales (~0.3) from other global margins. Os_i ratios of shales could be regulated by regional paleo-hydrological conditions; osmium mass balance calculations for the restricted basin of the Bijaigarh shale show that a minor increase in freshwater influx (as low as ~2.4% *i.e.* salinity change by ~0.8 psu) to the euxinic deep water of the basin is sufficient to elevate Os_i ratio from 0.3 (marine value) to ~0.6 (Os_i ratio of the lagoonal shale). In contrast to lagoonal shales, the Os_i ratios of marine shales seem to mimic the seawater $^{187}Os/^{188}Os$ during their deposition period. Compilation of marine Os_i ratios shows coarse synchrony between temporal changes in Os_i during the Proterozoic eon and the atmospheric oxygen level, pointing to the dominant role of oxidative continental weathering on paleo seawater $^{187}Os/^{188}Os$ ratio.

1. Introduction

The Vindhyan Supergroup is the largest among the *Purana* basins (Proterozoic sedimentary basins) in the Indian subcontinent (Kale and Phansalkar, 1991). This sedimentary basin, comprising about 4000 m of unmetamorphosed and undeformed sediments, preserves signatures of paleo-environmental conditions for a large fraction (~1800–900 Ma) of the Proterozoic eon with good time resolution (Deb et al., 2002; Ray, 2006; Malone et al., 2008; Gopalan et al., 2013). Studies on these sediments have provided insights into the evolutionary history of complex life on the Earth (Azmi, 1998; Seilacher et al., 1998; Azmi et al., 2008; Bengston et al., 2009), exogenic processes (*i.e.* glaciations; Kumar et al., 2002; Ray et al., 2003), and formation and growth of various continental landmasses (Gregory et al., 2006; Malone et al., 2008). This basin, in particular, received significant global attention following the discovery of "Cambrian-like" small shelly fossils in the Lower Vindhyan sequences (Azmi, 1998; Seilacher et al., 1998) of Paleoproterozoic age (Kumar et al., 2001; Rasmussen et al., 2002; Ray et al., 2002, 2003; Bengston et al., 2009). Further, paleo-magnetic properties of the Upper Vindhyan sediments have provided information on the breakup of Rodinia, separation of East Gondwanaland, and the Apparent Polar Wander (APW) path of the continental blocks of India (Gregory et al., 2006; Malone et al., 2008). Global correlation of these important results requires information on chronology of the Vindhyan sediments. Depositional ages for the Lower Vindhyan sediments (~1800–1600 Ma) are now well constrained through a number of radiometric ages (Kumar et al., 2001; Rasmussen et al., 2002; Ray et al., 2002, 2003; Sarangi et al., 2004; Bengston et al., 2009), mostly based on the U–Pb and Pb–Pb dating techniques. In contrast, sediments from the Upper Vindhyan (Kaimur, Rewa and Bhander) lack good chronological control (Ray, 2006 and references therein).

Available reports on the chronology of the Upper Vindhyan sediments are inconsistent and the suggested ages vary unrealistically from the Mesoproterozoic to the Ordovician (Gregory et al., 2006; Ray, 2006; Azmi et al., 2008 and references therein). Depositional age for the uppermost (Bhander) Group has recently been constrained based on Pb–Pb dating of three distinct carbonate horizons (Gopalan et al., 2013) at ~900 Ma, consistent with that proposed earlier from the U–Pb ages of detrital zircons and paleo-magnetic data (Malone et al., 2008). This direct and reliable age constraint for the Bhander Group

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(~900 Ma; Gopalan et al., 2013) overruled earlier inferred relatively younger age (~600 Ma) for the Group based on comparison of global strontium and carbon isotopic curves (Kumar et al., 2002; Ray et al., 2003), less precise Pb–Pb dating of carbonates (650 ± 770 Ma; Ray et al., 2003), magnetostratigraphy (McElhinny et al., 1978), and occurrence of Ediacaran fossils (De, 2003, 2006; Azmi et al., 2008).

In contrast to the Bhander Group, its underlying Rewa and Kaimur Groups in the Upper Vindhyan lack direct and reliable depositional age constraints. Information on the chronology of the Kaimur Group is crucial to understand the evolutionary history of the Vindhyan, in particular to assign age for the initiation of sedimentation in the Upper Vindhyan and to place a time constraint for the sedimentary hiatus between the Lower and Upper Vindhyan. The present study is an attempt to constrain the depositional age for the Kaimur Group using the Re–Os geochronometer (Ravizza and Turekian, 1989). Prior to this work, only a minimum age limit for the Group was available through radiometric dating of the Majhgawan kimberlite pipe that cuts across the basin at the top of the Kaimur Group (Auden, 1933; Crawford and Compston, 1970; Kumar et al., 1993; Gregory et al., 2006 and references therein). Although the reported ages (mainly based on Rb–Sr, K–Ar and Ar–Ar) for this kimberlite pipe vary widely between 1630 ± 353 and 947 ± 30 Ma, majority of them cluster around 1050 Ma (Gregory et al., 2006 and references therein). This younger age limit (1050 Ma) is contrastingly higher than the K–Ar age (910 ± 39 Ma; Vinogradov et al., 1964; Tugarinov et al., 1965) reported for the authigenic gluconites from the group. Although the exact cause for this age inconsistency is not known, the underestimated K–Ar age can be attributed to post-depositional mobilization of Ar from sediments.

Depositional ages for the Vindhyan sediments are by and large constrained through Pb–Pb or U–Pb dating of carbonates present in the basin (Ray, 2006). These dating approaches could not be employed for the sandstone-dominated Kaimur Group, which is carbonate-free. Further, effort to date the Upper Vindhyan sediments through U–Pb dating of zircons from volcanoclastic sediments was not successful (Malone et al., 2008). In this context, occurrence of a black shale (Bijaigarh shale) sequence in the Kaimur Group (Singh, 1980) provided an opportunity to employ the Re–Os chronometer to determine the depositional age for the group. Re and Os in black shale are mainly hydrogenous/authigenic in nature and hence radiogenic growth of ^{187}Os through β-decay of ^{187}Re provides a reliable measure of depositional age for the shales (Ravizza and Turekian, 1989; Cohen et al., 1999; Singh et al., 1999; Selby and Creaser, 2005; Kendall et al., 2009a; Yang et al., 2009; Rooney et al., 2010; Georgiev et al., 2011; Tripathy et al., 2014a).

2. Geology of the Vindhyan Supergroup

The Vindhyan Supergroup, a Proterozoic sedimentary sequence, is exposed over an area of ~100,000 km^2 in Central India and a significant part of this Supergroup is concealed below the Deccan traps and the Ganga alluvium (Venkatachala et al., 1996; Gopalan et al., 2013). This Supergroup is bounded by the Great Boundary Fault in the west and the Narmada–Son lineament in the south (Fig. 1). Sedimentary archives from this Supergroup are mostly undeformed and unmetamorphosed. These sediments are exposed in two outcrop areas, western (Rajasthan) and eastern (Son valley) regions. The present study is carried out in the Son valley exposure. The Supergroup overlies the Bundelkhand granite massif (2.5 Ga; Azmi et al., 2008) and is sub-sectioned into Lower and Upper sections (Fig. 2). The litho-units of the Lower Vindhyan (Semri Group) are dominated by carbonates and shales along with sandstones and volcaniclastic units (Ramakrishnan and Vaidyanadhan, 2008). The Upper Vindhyan comprises of three groups, *viz*. Kaimur, Rewa and Bhander Groups. The Kaimur Group, the lower section of the Upper Vindhyan, is composed of sandstone, shales, and conglomerates. Occurrence of a sedimentary hiatus at the Semri–Kaimur junction has been inferred through sedimentological evidence (Prakash and Dalela, 1982). Proper time assignment for this gap, however, has not been possible due to lack of precise chronological information on the Kaimur Group (Ray, 2006 and references therein; Fig. 2). A kimberlite pipe (Majhgawan) cross-cuts the Semri and the Kaimur Groups and is currently exposed within the Kaimur sandstones. Sediments from the Kaimur Group are mostly terrigenous clastics and their depositional environment varies from tidal flat to lagoonal facies. The Bijaigarh shale from this group is a lagoonal deposit with an open ocean connection (Singh, 1980). Black shale and pyrite samples analyzed during this study belong to this shale sequence from the Upper Vindhyan. The provenance of sediments for the Bijaigarh shale is not well constrained; available studies point to various possible sources, *e.g.* Banded Gneissic Complex, Bundelkhand Granites, Bijawar Group, Chotanagpur Gneiss Complex (CGC) and Mahakoshal Group (Bose et al., 2001; Chakrabarti et al., 2007; Paikray et al., 2008; Mishra and Sen, 2010). A recent study based on U–Pb and Hf isotopes invoked the possibility of a supply of Vindhyan sediments from the Aravalli region (Turner et al., 2014).

The Kaimur Group is followed by the Rewa and the Bhander Groups of the Upper Vindhyan (Fig. 2). The Rewa Group is dominated by shales and sandstones with presence of red shale, limestone, barite, and glauconite siltstone indicating its lagoonal deposition. The Bhander Group is mainly a sandstone–shale–sandstone–stromatolitic limestone sequence, deposited in a tidal flat–lagoon environment (Bose et al., 2001; Ramakrishnan and Vaidyanadhan, 2008).

3. Sampling and analytical methods

A suite of black shales and a few pyrite samples were collected for this study from the Bijaigarh shale of the Kaimur Group (Fig. 3). In order to minimize the influence of surficial weathering, the samples were collected from the underground PPCL pyrite mine at Amjhore, in the Rohtas area, about 30 km south of Dehri-on-Sone (Fig. 1). The Amjhore pyrites associated with black shales exhibit syndepositional features and are sedimentary in origin (Nair and Ray, 1977). A pyrite-rich layer approximately one half meter thick is sandwiched between two black shale layers (Fig. 3). These sediments were deposited in gradually changing (stable to unstable) shelf water conditions. These beds generally maintain a horizontal orientation and have abundant idiomorphic pyrite crystals, with typical sizes varying between 50 and 80 μm (Nair and Ray, 1984). The shale and pyrite samples for this study were collected within a distance of ~2 m vertically (Fig. 3) and few tens of meters horizontally. In hand specimen, the collected shales are well-indurated, black, and have fine laminations with disseminated pyrite of varying sizes (few mm).

About 100 g of the shale and pyrite samples were powdered (to 100 μm size) using an agate mortar and pestle. Splits of these homogenized samples were used for both elemental and isotopic analyses. Total nitrogen (TN) and carbon concentrations of the samples were measured using a CN analyzer, whereas inorganic carbon contents of the samples were analyzed using a UIC coulometer (Tripathy et al., 2014b). Total organic carbon (TOC) contents of the samples were estimated from the difference between the total and inorganic carbon concentrations. Re–Os elemental and isotopic analyses were carried out following the procedure of Tripathy et al. (2013). About 1000 mg of the powdered sample, along with a known amount of ^{185}Re and ^{190}Os spikes, were dissolved with inverse aqua regia in a sealed Carius tube at 240 °C for 24 h. This acid digestion releases Re and Os from the shales to the oxidizing solution. Osmium present in the solution was extracted following the solvent (Br_2 liquid) extraction method and the Os fraction was further purified using a micro-distillation approach (Birck et al., 1997). The remaining solution from the solvent extraction was dried and re-dissolved in 0.8 N HNO_3 acid. This solution was passed through an anion-exchange resin (AG 1X-8; 100–200 mesh) to extract and purify Re. Isotopes of Os were measured in their oxide forms (OsO_3) using negative thermal ionization mass spectrometry in ion counting mode; the measured OsO_3 isotopic data were corrected for instrumental mass