



## Trace element behavior in moderately weathered boles from the Deccan volcanic province: Implications for paleoenvironment

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### ABSTRACT

The present study examines the behavior of trace elements in moderately weathered boles of three different colors (i.e., red, brown and green) from the Deccan Traps in order to understand paleoenvironmental conditions during periods of quiescence between successive eruptions of Deccan flood volcanism (DFV). The minimal (< 40%) losses/gains of trace elements, including rare earth elements (REE), in the brown and red boles indicate their low mobility either due to limited release from primary minerals and/or due to sorption on secondary clay minerals and Fe-Mn oxides under near neutral pH (~5.5 to 8) conditions. The green bole shows a greater loss of trace elements, on average ~40–70%, including the REE and the typically immobile elements V and Zr. The low concentrations of V and Zr in the green bole are in accordance with low Ti and high SiO<sub>2</sub>, K<sub>2</sub>O and Rb concentrations that suggest addition of petrogenetically evolved volcanic ash (e.g., andesitic composition) compared to the lower flow basalt.

A negative Ce anomaly and enrichment of the light REE (LREE) in the green bole indicate precipitation of soluble trivalent LREE desorbed from Fe-Mn oxide surfaces preferentially to insoluble oxidized tetravalent Ce. This is interpreted to indicate more reducing conditions at depth, with Fe-Mn oxides in a more oxidized upper saprolite/soil horizon were eroded prior to trapping of the green bole by the upper lava flow. The light red bole, weathered under a more pervasively oxidative environment, shows loss of Mn oxides that might have initially scavenged cerianite leading to a negative Ce anomaly preserved in the residual bole. Positive Ce anomalies in the dark red and brown boles, are consistent with their gain and negligible loss of Mn, respectively, indicating Ce precipitation on the Mn oxide surfaces relative to the other trivalent LREE in an oxidizing environment. Overall, the boles show weathering signatures suggestive of near neutral pH conditions and locally changing redox, some of which may have largely escaped post-eruptive acidic precipitation possibly due to the transport of acidic gases into the upper atmosphere (stratosphere) under arid conditions.

### 1. Introduction

Weathering profiles (soils/laterite and paleosols) developed on basalts throughout the world have been extensively studied to understand (paleo)- environmental conditions (Babechuk et al., 2014; Ghosh et al., 2006; Hill et al., 2000; Ma et al., 2007; Nesbitt and Wilson, 1992; Óskarsson et al., 2012; Sheldon, 2003; Spinola et al., 2017; Tabor et al., 2004). Trace elements including rare earth elements (REE) are commonly investigated to understand physico-chemical processes and redox related changes in basalt weathering profiles (Babechuk et al., 2014; Hill et al., 2000; Ma et al., 2007; Nesbitt and Wilson, 1992; Patino et al., 2003; Price et al., 1991; Prudêncio et al., 1993, 1995). Trace elements in basalt are commonly hosted in primary minerals and glassy groundmass. The easily weatherable primary minerals (e.g.,

olivine, plagioclase, pyroxene) release trace elements upon alteration, which can be then further re-distributed in weathering profiles or mobilized into pore waters (Patino et al., 2003). The retention of trace elements in a weathering profile depends on the formation and stability of secondary clays and iron oxyhydroxides (Patino et al., 2003).

The Deccan flood volcanism (DFV) occurred in pulses, and during periods of quiescence the weathering of existing lava flows took place (Chenet et al., 2008; Ghosh et al., 2006; Srivastava et al., 2012, 2016; Widdowson et al., 1997). These weathered basalts became trapped by successive lava flows, and are termed "boles". The term 'bole' is derived from the Latin word "bōlus" meaning reddish brown soft fine clays (lump of earth), and therefore have been commonly used for the inter-basaltic red color clays (Srivastava et al., 2016). The synonymous term used for bole is red ochre (Hradil et al., 2003). However, boles in the

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**Table 1**

Summary of the mineral compositions, plagioclase index of alteration (PIA) and genesis of the studied different colored boles after Srivastava et al. (2018). The addition of volcanic ashes in boles is relative based on percentage additions in potassium and rubidium concentration.

Bole type	Minerals	PIA	Genesis	Volcanic ash
Green bole	Nontronite and Celadonite	78	Hydrothermal alteration	High additions
Brown bole	Fe-smectite (/nontronite) and Montmorillonite	76	Hydrothermal alteration of Al clays	High additions
Dark red bole	Montmorillonite, Hematite and Quartz	81	Leaching in oxidative environment and subaerial heating	Low additions
Light red bole	Montmorillonite and Hematite	77	Leaching in oxidative environment and subaerial heating	Low additions only in top sample

Deccan Traps occur in a wide range of colors with red being the most abundant and green being rare (Ghosh et al., 2006; Srivastava et al., 2012, 2015). The deposition of volcanic ash (/pyroclastic material) in these boles during subaerial exposures has also been reported (Ghosh et al., 2006; Schoene et al., 2015; Srivastava et al., 2018; Widdowson et al., 1997).

In the present study, we analyze the trace elements in four well developed bole profiles of three different colors i.e., red (dark = 10R-3/6 and light = 10R-4/8), brown (5YR-4/4) and green (5G-6/2) to understand paleoenvironmental conditions during successive eruptions of DFV. The detailed information on mineralogy and major element chemistry of these boles is given in Srivastava et al. (2018). A summary of mineralogy, plagioclase weathering index (PIA), and mode of genesis is reproduced in Table 1. The PIA of all the different colored boles show consistent and moderate degrees of chemical weathering. The different colored boles, however, show distinct mineralogy with the red bole being dominated by montmorillonite and hematite, the brown bole by Fe-smectite and montmorillonite, and the green bole by nontronite and celadonite (Table 1). Further, distinct origins have been suggested for different colored boles, i.e., (1) leaching under an oxidative environment at near neutral pH (~5.5 to 8) conditions for the red bole; (2) hydrothermal alteration of volcanic ash admixed with altered basalts in a reducing environment for the green bole; and (3) hydrothermal alteration of Al clays (i.e., montmorillonite) for the brown bole. The different colored boles, therefore, provide an ideal natural laboratory to study the trace element behavior in moderately weathered profiles developed under distinct alteration conditions. Further, only a limited number of studies on trace element characteristics of boles have been carried out (Ghosh et al., 2006; Sayyed et al., 2014; Widdowson et al., 1997) to date, despite the potential of these data to reveal new insights into the paleoenvironment during volcanism.

## 2. Study area and sample description

The Deccan volcanic province (DVP) covering an area of ~500,000 km<sup>2</sup> across central and western India, is one of the largest areas of continental flood basalt. The samples for this study were collected from four well-developed bole profiles representing red, brown and green colors from Ahmednagar, Satara and Pune districts of Maharashtra (Figs. 1 and 2). The red bole samples were collected from two profiles showing distinct Munsell notations: (1) 10R-3/6 representing dark red (DG-3-RB) bole (~78 cm thick) exposed in Dive Ghat section, Pune district, and (2) 10R-4/8 representing light red (SBH-RB) bole (~70 cm thick) exposed on Satara-Bengaluru highway, Satara district (Fig. 2c and d). The green (A-GB) bole (Munsell notation = 5G-6/2) of ~68 cm thickness is exposed in a quarry section in Ahmednagar district, and a brown (DG-2-BB) bole (Munsell notation = 5YR-4/4) of ~130 cm thickness is exposed in Dive Ghat section, Pune district (Fig. 2a and b). Boles show variable thickness over their lateral extent. The green and brown bole profiles show ~2 to 5 cm thick reactive surfaces at the contact with the upper lava flow. The reactive surface represents hydrothermally altered sole of the upper lava flow, which has formed from its own last liquid water fraction (Chenet et al., 2008) and/or upon contact with the underlying hydrous substrate (/hydrous bole) (Srivastava et al., 2012). Chemostratigraphically, the

host basalts of all the bole profiles fall in the Poladpur formation of the Wai Subgroup.

Twenty samples from four bole profiles including upper and lower flow basalts, and reactive surfaces were collected. Boles do not show any distinguishable features with depth and represent a single strata or unit; therefore, we collected bole samples as upper, middle and/or lower boles to understand depth-wise geochemical variations.

## 3. Methodology

The trace element analysis of whole rock powdered (~200 mesh size) samples of basalts, boles and reactive surfaces were carried out using a pressed powder technique. The pressed pellets were prepared using 4–5 drops of polyvinyl alcohol as a binding agent, and were analyzed by standard Wavelength Dispersive X-ray Fluorescence (WD-XRF) using a Bruker S8 Tiger Sequential X-ray spectrometer with an end window 4 kW Rh anode tube (60 kV, 170 mA) at Wadia Institute of Himalayan Geology (WIHG), Dehradun. The precision and accuracy of the sample preparation and instrumental performance were checked using several international reference standards of basic composition, e.g., BIR-1, BHVO-1, PCC-1, JB-1a, JP-1 and MB-H (WIHG) for basalts, and soils and sediment reference standards e.g., SO-1, GSS-1, GSS-4, GSS-7, GXR-2, GXR-5, SCO-1, SGR-1, SDO-1, GSD-9, GSD-10 and BX-N for boles. A modified Lucas-Tooth and Pyne (1964) intensity based matrix correction model was used to derive the calibration coefficients. The accuracy of measurement for trace elements is < 12%, based on comparison with the certified/working values of the reference materials (except MB-H) from Govindaraju (1994). The MB-H sample is an in-house metabasic reference material of the WIHG and working values of which can be found in Rathi et al. (1994). The precision in terms of maximum observed relative standard deviation (RSD) (1σ) on repeated measurements of the reference standards is < 1.5%. The minimum detection limit for the studied trace elements using XRF measurement on a Bruker S8 Tiger X-ray spectrometer is ~5 mg/kg.

Rare earth elements + U were analyzed by a solution method on a PerkinElmer SCIEX ELAN DRC-e inductively coupled plasma mass spectrometer (ICPMS) at WIHG, Dehradun. The samples were digested using an open acid digestion method (Khanna et al., 2009). A 100 mg powdered (~200 mesh) sample was digested with 10 ml of HF-HNO<sub>3</sub> mixture (2:1) in open Teflon crucibles on a hot plate. This process was repeated 3 to 4 times with evaporation to incipient dryness for complete digestion. This was followed by two treatments of HClO<sub>4</sub> (~2 ml) and further evaporation to complete dryness. This dried mass was dissolved in 10 ml of 20% HNO<sub>3</sub> and a final volume was made up to 100 ml using distilled water. The standards BHVO-1 and JB-1a were digested under same conditions for calibration. A batch including blank, standards and seven samples were made and measured. After measurement of each batch of samples, the instrument was recalibrated to nullify the drift, if any, induced during analysis. The results of standards BHVO-1 and JB-1a along with the certified values are given in Table 2. The accuracy and precision for the rare earth elements varies from 1% to 10% and 1% to 9% RSD, respectively.

The trace element and REE data were examined using a mass balance calculation. The elemental mass balance is calculated as the percent change of an element relative to the least weathered parent rock

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