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Mineral magnetic and diffuse reflectance spectroscopy characteristics of the Deccan volcanic bole beds: Implications to genesis and transformations of iron oxides

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ABSTRACT

Deccan volcanic bole beds are important indicators of paleoenvironmental conditions during Cretaceous–Tertiary volcanism. However, little attention has been paid to iron oxide characteristics of these lava flow hosted sediments. Therefore, in order to understand the genesis and transformation of various iron oxides in different colored bole beds, we studied the mineral magnetism and diffuse reflectance spectroscopy (DRS) characteristics of red, brown and green boles that are extensively exposed in the Deccan volcanic province (DVP) of Western India. Mineral magnetism and DRS characteristics indicate hematite (α-Fe_2O_3) as the major iron oxide in all the bole beds with traces of goethite (α-FeOOH) in many. Maghemite (γ-Fe_2O_3) was also present in red boles as well as in few brown and green boles. The higher concentration of magnetic minerals in red boles is due to the neo-formation of fine magnetic minerals produced from heating of the weathered sediments by the overlying lava flow. The increasing concentration of superparamagnetic (SP) fraction (indicated by frequency dependent susceptibility, χ_{fd}) with increased reddening of the bole beds (mean χ_{fd} for green, brown and red boles = ~2.5, 11.1 and 19.3 × 10^{-8} m^3 kg^{-1}, respectively) facilitates the use of χ_{fd} as first order estimate for degree of heating in red boles. The paragenesis of ferrimagnetic and antiferromagnetic minerals in green and brown boles is indicated by good correlation ($R^2 = 0.78$) between hard isothermal remanent magnetization (HIRM) and χ_{fd} suggests that green and brown boles have undergone some pedogenesis. The overall distribution of iron oxides in these bole beds indicate their genesis from incipient weathering of Fe–Mg minerals (e.g. olivine and pyroxenes) under humid conditions leading to the formation of ferrihydrite and goethite as precursors. Partial to complete heating resulted into oxidation of precursors and titanomagnetite to maghemite as the intermediate transformation phase and hematite as end product. The green, brown and red boles thus represent the transitional baking environments under various hydrous–anhydrous conditions and pedogenic processes. The genesis and transformation of various iron oxides in DVP bole beds may have significant implications for the characterization of such interflow sediments/paleosols from other igneous provinces (e.g. Israel, Karoo Flood Basalt, South Africa and Columbia River Basalt, USA). Further, complex genesis of the iron oxides in the DVP bole beds also envisages a great scope to study them as Martian analogues apart from their significance to paleoenvironment and demands more advanced rock magnetic and spectroscopic approaches.

1. Introduction

The inter-basaltic/interflow sediment units commonly termed as "*bole beds*" are significant markers of hiatus in pulsate phases of Deccan volcanism encompassing the Cretaceous–Tertiary (K–T) period (Widdowson et al., 1997; Ghosh et al., 2006; Chenet et al., 2008; Srivastava et al., 2012). These bole beds trapped into two successive lava flows typically occur in wide range of colors from red, brown and green (Inamdar and Kumar, 1994) with varied thicknesses (~0.10 to 1 m) in the form of strata, lensoid shapes and as pocket fillings in the Western Deccan Province (WDP) (Walker, 1999; Chenet et al., 2008; Srivastava et al., 2012). Whereas ~4 to 6 m thick bole beds are common in the Eastern Deccan Province (EDP) (Shrivastava et al., 2012) and ~3 to 7.5 m thick bole beds are reported from the NE part of the Deccan Province (Inamdar and Kumar, 1994). The common occurrences of such interflow sediments/paleosols have also been reported from other igneous provinces e.g. Golan Heights, Israel (Singer and Ben-Dor, 1987; Singer et al., 1994); Argentina (Tabor et al., 2004); Columbia River Basalt, USA (Sheldon, 2003; Takeuchi et al., 2007; Thomson et al., 2014); Canada (Jutras et al., 2012); Karoo Flood Basalt, South Africa (Moulin et al., 2011); Cape Verde, Fogo Island (Marques et al., 2014); North Atlantic Igneous Province (Walker et al., 2013); and Eastern Taiwan (Song and Lo, 2002).

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The Deccan volcanic bole beds comprise earthy, clayey or silty material and are variously described for its origin and post-depositional alterations (Walker, 1999; Wilkins et al., 1994; Widdowson et al., 1997; Ghosh et al., 2006; Sayyed and Hundekari, 2006; Srivastava et al., 2012). Wilkins et al. (1994) described the bole beds as weathering product of basalt admixed with volcanic ash. Widdowson et al. (1997) suggested two different types of bole beds: (1) sparolitic boles from sub-aerial in situ weathering of basalt flow and (2) pyroclastic boles from extensive ash fallout deposits. The green boles have been considered as equivalent of andosols (Ghosh et al., 2006), whereas hydrothermal deuteric alteration of lava flow is suggested for the genesis of red boles (Gérard et al., 2006; Chenet et al., 2008). The baking of weathered basaltic sediments from overlying flow is commonly addressed for red color of the bole beds (Walker, 1999; Srivastava et al., 2012). Gavin et al. (2011) suggested that baking of these weathered Deccan phyllosilicates might have taken place at ~400 to 500 °C. However, the presence of zeolites in few sparolitic boles suggested low-grade temperature alterations (Greenberger et al., 2012). The detrital transportation, deposition and reworking of weathered sediments following trapping from upper lava flow are suggested based on their field appearances and magnetic mineralogy by Srivastava et al. (2012).

The different colored bole beds show variations in clay mineralogy such as the green boles comprise nontronite and celadonite; red boles contain montmorillonite; and yellow boles are enriched in vermiculite and montmorillonite (Gavin et al., 2011, 2012). The magnetic signatures have also shown a clear relation with color such as decreasing order of mean magnetic susceptibility from red to brown boles and minimum for green boles (Srivastava et al., 2012). The iron oxides in bole beds are mainly represented by hematite, goethite and maghemite (Ghosh et al., 2006; Sayyed and Hundekari, 2006; Gavin et al., 2010; Greenberger et al., 2012; Srivastava et al., 2012). However no detailed work is available on the relationship of magnetic domain size and concentration of iron oxides in different colored bole beds, which is essential to understand their genesis and the effect of heating from overlying lava flow. Therefore, considering the global significance of bole beds as: (I) paleoenvironment indicators during the Cretaceous–Tertiary volcanism (Ghosh et al., 2006; Sayyed and Hundekari, 2006; Shrivastava et al., 2012; Sayyed, 2013); (II) for estimation of time and duration of volcanic eruptions (Chenet et al., 2008, 2009; Shrivastava et al., 2012); and (III) as close analogue for heated Martian soils and sediments (Gavin et al., 2010; Greenberger et al., 2012), we attempt to characterize the iron oxides of these bole beds using mineral magnetism and DRS techniques.

2. Study area

The occurrence of bole beds in Deccan volcanic province is ubiquitous although their synchronicity is not yet established. Notably high frequency of bole bed occurrence has been reported from Nasik area (Deshmukh, 1988) and Pune district (Widdowson et al., 1997) in the Western Maharashtra. The area around Pune City, Ahmed Nagar and Satara (Patan) district of Maharashtra shows some of the fresh exposures due to road cutting displaying a variety of bole bed occurrences. For the present study, we selected 16 samples from the 12 profiles including samples from new as well as from few previously studied profiles by Srivastava et al. (2012). The details on field characters including lateral dimensions, contact relationships and macro-morphology are given in Srivastava et al. (2012) and are not reproduced here for brevity.

Figs. 1 and 2 show sampling locations and field occurrences of the bole beds trapped in upper compact basalt and the lower weathered basalt with sharp and gradational contacts, respectively. The small scale prismatic jointing structure resulting from the loss of fluids due to baking by overlying lava flow (e.g. Walker, 1999; Sarkar et al., 2000) is observed amongst some of the boles. The new Katraj Ghat section shows a unique appearance of bole bed with lateral transition from brown to red bole and further red to grayish brown bole. These lateral transitions within the single bole horizon depict a unique interplay of color and mineralogy. Samples from the transition zones are termed as transitional bole samples. The transitional bole samples are brown in color and are discussed here under the brown boles category. The terminology of 'transitional bole' is used only to represent their magnetic and DRS characteristic correlation with unique field occurrence (for details see Fig. 9).

3. Laboratory methods

3.1. Mineral magnetic analysis

The magnetic susceptibility (κ) of bole samples was measured using a Bartington MS 2B laboratory sensor in two frequencies, i.e. low ($\kappa_{lf} = 0.46$ kHz) and high ($\kappa_{hf} = 4.6$ kHz). The volume susceptibility (κ) was mass normalized and denoted as χ for further interpretations. The frequency dependent susceptibility (χ_{fd}) and the corresponding percentage frequency dependent susceptibility ($\chi_{fd}\%$) were calculated as $\chi_{lf} - \chi_{hf}$ and $[(\chi_{lf} - \chi_{hf}) / \chi_{lf}] \times 100$ (Dearing et al., 1996a). Anhysteretic remanence magnetization (ARM) was grown using a Molspin alternating field demagnetizer at a 100 mT peak field superimposed over a 0.1 mT DC field. The ARM was normalized by DC field to acquire ARM intensity per unit of applied bias field and is represented here as anhysteretic susceptibility (χ_{ARM}) (Verosub and Roberts, 1995). Isothermal remanence magnetization (IRM) was induced using an ASC-IM-10-30 Impulse magnetizer and the remanence was measured on a Minispin fluxgate spinner magnetometer. Saturation isothermal remanent magnetization (SIRM) was measured at a forward field of 1 T considering that most ferrimagnetic minerals are saturated by ~0.3 T (Thompson et al., 1980) whereas antiferromagnetic minerals such as hematite requires 4 to 7 T (France and Oldfield, 2000) and goethite may require 7 to 57 T for saturation (Rochette et al., 2005). The hard isothermal remanent magnetization (HIRM) was calculated using the derivation of $0.5 \times (\mathrm{SIRM} + \mathrm{IRM}_{-300\ \mathrm{mT}})$ where $\mathrm{IRM}_{-300\ \mathrm{mT}}$ is the remanent magnetization measured in a back-field of 300 mT (Thompson and Oldfield, 1986; Liu et al., 2007). The remanent coercivity (B_{CR}) is the reverse DC field required to reduce the SIRM to zero (Thompson et al., 1980). The S-ratio was calculated as $\mathrm{IRM}_{-300\ \mathrm{mT}}/\mathrm{SIRM}$ for the quantitative estimates of the degree of saturation (Thompson and Oldfield, 1986).

The temperature dependent magnetic susceptibility analysis was carried out using a Bartington MS 2WFP sensor. The samples were heated from room temperature to 700 °C for identification of different magnetic minerals in bole beds based on their Curie (T_C)/Néel (T_N) temperature properties.

3.2. Diffuse reflectance spectroscopy (DRS)

The DRS and citrate–bicarbonate–dithionite (CBD) extraction techniques are widely used for qualitative and quantitative estimates of hematite and goethite concentration in natural soils and sediments (Torrent et al., 2006, 2007). The DRS curves for fine grained powdered (<10 μm) sample of bole bed were recorded between 380 and 700 nm in 0.5 nm steps at a scan rate of 30 nm min^{-1}, using a Varian Cary 1E spectrophotometer equipped with a $BaSO_4$-coated integrating sphere 73 mm in diameter (Varian Inc., Palo Alto, California). The second derivative of the Kubelka–Munk (K–M) remission function at each wavelength was calculated by the method of Torrent and Barrón (2003). The intensities of spectral bands at ~425 nm (I_{425}) and ~535 nm (I_{535}) are proportional to the concentration of goethite and hematite, respectively (Scheinost et al., 1998). The mass ratio of hematite (Hm) to goethite (Gt) plus Hm was calculated by the following calibration curve:

$$Y = -0.133 + 2.871X - 1.709X^2 \tag{1}$$

where Y is the Hm/(Hm + Gt) mass ratio and X is the $I_{535}/(I_{425} + I_{535})$ ratio. This calibration curve is based on 22 soil samples from the Mediterranean region where the "true" concentration of the two minerals was