ARTICLE IN PRESS

Planetary and Space Science xx (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Planetary and Space Science

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

Spectral analysis of Deccan intrabasaltic bole beds: Implications for the formation and alteration of phyllosilicates on Mars

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ARTICLE INFO

Keywords:
Mars
Mineralogy
Deccan Volcanic Province
Mawrth Vallis
Chemical weathering

ABSTRACT

To fully understand phyllosilicates on Mars, it is beneficial to study analog deposits on Earth. One attractive candidate for martian phyllosilicates is the intrabasaltic bole beds (palaeosols) from the Deccan Volcanic Province of India. Eleven samples from the upper-layer red Deccan bole beds and underlying yellow and green Deccan bole beds were analyzed by X-ray diffraction (XRD), near-infrared (1.0–2.5 μm) and mid-infrared (5–15 μm) reflectance spectroscopy. Analysis of the bole beds indicated that the red boles are composed of a mixture of montmorillonite and hematite, yellow boles contain vermiculite and minor montmorillonite and green boles are composed mainly of nontronite (smectite) and celadonite (mica). While the bole beds are all chemically similar to each other and to the underlying basalt from which they were weathered, they are mineralogically different. This suggests transformation from one mineral to the next without ion transfer or loss which could be indicative of a limited-water environment. In fact, celadonite can transform into smectites (such as montmorillonite), often with vermiculite as an intermediate step. This not only explains the stratigraphy and mineralogy of the Deccan bole beds but may also explain the layered phyllosilicates identified in various, global locations on Mars. The transition observed in the Deccan bole beds suggests an evolution of the alteration process from deuteric alteration to low-temperature weathering, likely due to changes in temperature, in a closed system (no significant ion transfer) as evidenced by the minerals' similar chemistry. Thus, the Deccan bole beds are a good analog for the phyllosilicates layers on Mars and by studying the chemistry, mineralogy and spectral properties of the Deccan bole beds, we can link their formation and alteration processes to those of martian phyllosilicates. This will provide a clearer understanding of the environmental conditions on Mars at the time of the phyllosilicates' formation and hence during Mars' earliest history.

1. Introduction

Phyllosilicates were first identified on Mars by the Observatoire pour la Mineralogie, l'Eau, les Glaces et l'Activite (OMEGA) spectrometer on board Mars Express (Poulet et al., 2005) and later confirmed by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on Mars Reconnaissance Orbiter (MRO) (Bishop et al., 2008a; Mustard et al., 2008). These minerals have been found in the oldest Noachian terrains, such as Meridiani Planum (Wiseman et al., 2008), Mawrth Vallis (Bishop et al., 2008a) and Nili Fossae (Ehlmann et al., 2008), in various geologic settings, including in association with lava flows (Poulet et al., 2005) and in the central peaks and ejecta of impact craters (Mangold et al., 2007). The most abundant phyllosilicates observed so far are smectites such as nontronite (Fe^{3+}) or saponite (Mg) and montmorillonite (Al) and vermiculite (Fe^{2+}) (Carter et al., 2013), whose exact origins remain unclear. Some studies suggest these phyllosilicates are the result of weathering of basaltic material (Michalski and Noe Dobrea, 2007) under neutral to alkaline conditions while a recent study by Peretyazhko et al. (2016) demonstrated that they can form from the weathering of basalt in slightly acidic (pH ~4) conditions. Other formation processes include surface (Poulet et al., 2005) or subsurface (Ehlmann et al., 2011) hydrothermalism resulting from volcanic activity or meteoritic impacts (Fairen et al., 2010; Schwenzer and Kring, 2009).

In order to better understand phyllosilicate formation on Mars, it is beneficial to study analog materials on Earth. One potential analog for martian phyllosilicates is the intrabasaltic bole beds from the Deccan Volcanic Province (DVP) of India. These bole beds have been the

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http://dx.doi.org/10.1016/j.pss.2016.11.008
Received 30 May 2016; Received in revised form 22 November 2016; Accepted 24 November 2016

Please cite this article as: Craig, P., Planetary and Space Science (2016), http://dx.doi.org/10.1016/j.pss.2016.11.008

primary focus of several studies investigating terrestrial palaeoenviroments (Ghosh et al., 1995, 2001, 2006; Fürish et al., 2005; Sayyed and Hundekari, 2006; Sheldon and Tabor, 2009) and can give insight into the environmental conditions prevailing during their formation. The boles' geochemistry shows they are composed mainly of smectites (Greenberger et al., 2012; Ghosh et al., 2006; Roy et al., 2001) and were formed by the chemical weathering of basalts (Wilkins et al., 1994). While the mineralogy of each bole bed is different from each other and of the underlying basalt from which they formed, their chemistries are very similar, especially within the bole beds themselves. This implies that significant ion transfer did not occur during the formation and/or alteration of the bole beds. In fact, isochemical (closed-system) weathering has been suggested to occur on Mars based both on orbital spectroscopy (Ehlmann et al., 2011) and rover data (Ming et al., 2008). This study investigates the mineralogy and spectral properties of the Deccan bole beds and compares them to those of the phyllosilicates identified in Mawrth Vallis, Mars, in an effort to link terrestrial formation processes with those that occurred on Mars.

2. Sample description and analytical techniques

2.1. Source region and sample description

The Deccan Volcanic Province (popularly known as Deccan Traps) is one of the largest continental flood basalt plains in the world, covering about 500,000 km^2 of western and central India. These basaltic flows are generally tholeiitic in composition (containing plagioclase feldspar, clinopyroxene, iron ore and glass, but with little or no olivine) and exceed 2 km thickness in the western regions (Ghosh et al., 2006). The Deccan Traps are made up of several basaltic lava flows frequently showing the presence of bole beds sandwiched between two successive lava flows which range in thickness from 20 to 50 cm (Sayyed and Hundekari, 2006) and vary in color of different shades of red, green, brown, purple or grey.

While there still exists debate on the origin of these soils, chemical and weathering characteristics indicate they are the weathering product of the respective underlying basaltic flow (Ghosh et al., 2006; Roy et al., 2001; Sayyed and Hundekari, 2006; Wilkins et al., 1994). Further supporting this idea is the bole beds' physical setting in association with the basaltic flows. The bole beds show sharp contact with overlying flows yet an intermixing with underlying flows, indicating a gradual transition from the underlying flow to the bole beds. This suggests they are the weathering product of the underlying basalts and were covered by subsequent flows (Fig. 1).

Additionally, the bole beds have been grouped by their general color – red or green. Red bole beds typically contain higher amounts of Fe^{3+} while green bole beds contain more Fe^{2+}. Sometimes, red and green bole beds occur alone. However, in some instances, both red and green bole beds are present. When this is the case, the red bole beds are found on top of the green bole beds, indicating that the red bole beds are younger than the green ones. This suggests either a later deposition event or that the red bole beds could be an alteration product of the green bole beds. Here, we explore the latter of these two cases by investigating the mineralogy, chemistry and spectral properties of both red and green bole beds and relate these formation and alteration processes to similar stratigraphies identified on Mars.

2.2. Analytical techniques

Each sample's color was precisely categorized using Munsell soil color charts (Munsell, 1954). Samples' mineralogy was analyzed by X-ray diffraction (XRD) at the Wadia Institute of Himalayan Geology, India, with a CuK$_\alpha$ anode, a voltage of 45 kV, an intensity of 40 mA and a 0.5° divergence slit. The 2θ range was 4–65° with a step size of 0.017° and the time per step was 16.24 s.

Fourier Transform Infrared (FT-IR) reflectance spectra were taken of each sample using a Nicolet 6700 Smart Diffuse Spectrometer with dry N$_2$ purge gas. Near-infrared (NIR) spectra were recorded with an attached CeramOptec optical probe (Gavin and Chevier, 2010) in reflectance mode in the 4000–10,000 cm^{-1} (1.0–2.5 μm) range with 2 cm^{-1} resolution. Samples were placed in a ceramic tube under a flow of dry N$_2$ on a hot plate at 120 °C for two hours before each spectrum was recorded. Heating to ~120 °C removed any adsorbed water (Morris et al., 2010) but not interlayer water, which has been shown to be retained by smectites up to ~500–600 °C (Gavin and Chevrier, 2010; Che and Glotch, 2012) The optical probe was inserted into a small hole drilled into the top of the tube and the sample's spectrum was recorded. This ensured the removal of any atmospheric or adsorbed water on the sample. The configuration consisted of a quartz-halogen IR source, a CaF$_2$ beamsplitter, and a TECP detector. A background spectrum was taken using KBr powder under the same measurement protocol as the samples. This technique was used on all Deccan bole bed samples and on the nontronite and montmorillonite samples to which they were compared (see Section 4).

Mid-infrared (MIR) spectra were recorded using the spectrometer without the optical probe under ambient conditions in the range 670–2000 cm^{-1} (5–15 μm). For this spectral range, we used an IR source, a KBr beamsplitter, and a DTGS detector. Background spectra using a gold coated emery tape were taken before each sample's spectrum was recorded. Each NIR and MIR spectrum was normalized to the maximum value for consistent comparison.

3. Results

3.1. Color

The samples were categorized by their general color: red, yellow or green. Each sample's color was precisely categorized using Munsell soil color charts (Table 1) (Munsell, 1954).

Red samples ranged from reddish brown 2.5YR 5/4 (e.g., Sample E) to various shades of red 10R 5/8 (e.g., Sample F). Yellow samples were either pale yellow 2.5Y 7/4 (Sample EG) or light olive brown 2.5Y 5/4 (Sample HG). Green samples were pale olive 5Y 6/3 (Sample B) and olive 5Y 5/3 (Sample D). Previous studies suggest that the red samples' color is due to their iron oxide content and green samples' color is due to their chlorite content (Ghosh et al., 2006).

3.2. Mineralogy

XRD patterns of each sample contained a large peak at 2θ values ~5° (Fig. 2), as previously reported by Roy et al. (2001), similar to that of smectites. All NIR spectra exhibited bands at 1.4 and 1.9 μm (Fig. 3) similar to those in phyllosilicate minerals which represent the OH stretching overtones of both structural OH and molecular H$_2$O, and the H-O-H stretching of molecular water most commonly observed as interlayer water, respectively (Bishop et al., 2008b, 2002a, 2002b). This supports previous studies that the bole beds are mainly composed of phyllosilicates (Ghosh et al., 2006; Roy et al., 2001). Spectra of every sample also contained bands in the 2.2–2.4 μm range, representing the cation-hydroxyl (OH) bond. Table 2 gives the exact positions of the bands identified in each sample's NIR spectrum. MIR spectra of all samples contained bands at 6.1 and ~8.5 μm (1639 and 1176 cm^{-1}) (Fig. 4) representative of H$_2$O bending and SiO$_2$, respectively (Bishop et al., 2008b), as well as a peak at ~9.5 μm (1053 cm^{-1}) indicating the Si(Al, Fe)O$_4$ vibrations (Bishop et al., 2008b), and are characteristic to MIR spectra of phyllosilicate minerals such as nontronite, montmorillonite, and celadonite (Bishop et al., 2008b; Gavin and Chevier, 2010).

3.2.1. Red bole samples

XRD patterns of red samples showed evidence for the smectite montmorillonite [$(Na, Ca)_{0.3}(Al, Mg)_2Si_4O_{10}(OH)_2{\cdot}nH_2O$] by the large 001 peak at 2θ = 5.7° (15.5 Å) and several others in addition to iron