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Diagenetic reddening of Early Eocene paleosols on King George Island, Antarctica

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ABSTRACT

The objective of this study was to determine if the Early Eocene paleosols on King George Island, Maritime Antarctica, have acquired their reddish color during the paleopedogenesis, by burial diagenesis and/or by heating of a covering lava flow. We used micromorphology, diffuse reflectance spectroscopy, X-ray diffraction, and mineral magnetic properties to identify the iron oxides in these paleosols. These are weakly/moderately developed paleosols formed on a basaltic tephra under a cool humid paleoclimate, therefore, prone to ferrihydrite and goethite rather than hematite formation. However, the iron oxide assembly was dominated by maghemite and hematite. Nevertheless, the large grain size and high crystallinity of hematites suggested they are rather diagenetic than pedogenic.

The clustering, content, and distribution of hematites (finely dispersed on the groundmass; coating/replacing primary minerals and as mottles and/or nodules) rather than their crystal size were responsible for the color differences. These properties were likely the result of past pedogenesis processes (forming originally ferrihydrite) linked with paleodrainage conditions. Heating by the covering lava flow affected the magnetic properties of two profiles but without affecting their color. Taken together, all these results suggest that the burial reddening took place by dehydration and transformation of ferrihydrite to hematite. Our findings highlight the importance of detailed mineralogical analysis to identify iron oxides present in reddish paleosols because identification based solely on morphology (e.g. yellowish color, gradual horizon transitions) can lead to misinterpretation of paleoenvironmental conditions.

1. Introduction

The color is one of the most important soil properties because it is a reliable indicator of the pedoenvironment (Cornell and Schwertmann, 2003). Reddish pigmentation in soils is usually due to hematite (α-Fe_2O_3), which is more frequently found in well-drained soils of tropical regions undergoing seasonal droughts, whereas goethite (α-FeOOH) becomes more abundant in soils of cool temperate areas or soils that remain moist throughout the year (Cornell and Schwertmann, 2003; Schwertmann and Taylor, 1989).

Despite reddish soils being most common in warmer regions, the paleoenvironmental interpretation of reddish paleosols must be made with extreme care because of a possible diagenetic reddening that could have been caused by the dehydration of iron oxyhydroxides (e.g. goethite) to hematite (Retallack, 1991; Van Houten, 1973). This effect has to be considered in this context when a reddish paleosol (especially pre-Quaternary paleosols) has no other characteristic features of paleotropical/semi-arid and/or long-term weathering (e.g. strong chemical weathering, saprolite profiles, concretions).

Although the diagenetic reddening of paleosols is a well-known process, the persistence of goethite in Cretaceous paleosols (Porter et al., 1998; Vacca et al., 2012) and Eocene paleosols (Kraus and Hasiotis, 2006; PiPujol and Buurman, 1994) have raised some questions about the ubiquity of this process. Additionally, there is little information about the diagenetic conditions under which dehydration takes place, e.g. if there is a need for high temperatures for goethite

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dehydration to hematite.

Heating experiments have suggested that goethite is converted to hematite at temperatures higher than 300 °C (Gialanella et al., 2010; Gualtieri and Venturelli, 1999). For some Chinese red beds, conversion of goethite to hematite required diagenetic temperatures higher than 150 °C (Jiang et al., 2015) and > 105 °C for Triassic sandstones in Denmark (Weibel, 1999).

Another pathway for paleosol reddening, regardless of its age and climate, is due to heating by a lava flow. The heating due to the emplacement of a lava flow can result in dehydration of iron hydroxides to hematite (Lange et al., 2002; Srivastava et al., 2015). On the other hand, the effects of heating are usually limited on the top few centimeters because of the thermal isolation properties of soils (Sheldon, 2003; Solleiro-Rebolledo et al., 2016).

Previous research described a set of three reddish weakly to moderately developed volcanic paleosols that were covered by a lava flow on King George Island (KGI), Maritime Antarctica (Spinola et al., 2017b). These paleosols were formed during the greenhouse period of the Early Eocene. This was a period when Antarctica was ice-free and covered by rainforests similar to those in southern Chile, and was considered the best modern analogue environment (Francis and Poole, 2002; Poole et al., 2003). Soils formed under similar environments (i.e. cool and humid climate with volcanic parent material) are usually Andosols with brownish/yellowish colors having ferrihydrite ($Fe_5HO_8 \cdot 4\ H_2O$) and goethite (α-FeOOH) as the main iron hydroxides (Shoji et al., 1993; Ugolini and Dahlgren, 2002). Therefore, the reddish color of the investigated KGI paleosols is in apparent disagreement with volcanic soils formed under a cool humid paleoenvironment.

The objective of this study was to characterize the iron oxides that impart reddish colors to the KGI paleosols and to determine their genesis: pedogenic, diagenetic, and/or heating by a lava flow. Our hypothesis was that the red colors of the KGI paleosols are the result of burial reddening because these paleosols were moderately developed under a cool humid climate, not prone to hematite formation. Our second hypothesis was that the horizons in contact with the lava flow were not substantially affected by heating because they are not redder than the deeper horizons. To test these hypotheses, we combined a set of techniques, such as X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), magnetic susceptibility, selective iron extraction (dithionite-citrate-bicarbonate, ammonium oxalate and dissolution with H_2SO_4), and microscopic techniques to characterize the iron oxides in KGI paleosols and understand their genesis.

2. Methods

2.1. Site description and geological background

The samples were collected on King George Island, South Shetland Islands, Maritime Antarctica. The specific outcrop is located at the Cytadela area of the Ezcurra Inlet in the Admiralty Bay (62° 11.057′S–58° 35.209′W) (Fig. 1).

The outcrop stratigraphically belongs to the Point Thomas Formation, Ezcurra Inlet Group, which comprises a 500 m thick Paleogene (Eocene-Oligocene) volcanic succession (Birkenmajer, 1980; Birkenmajer and Zastawniak, 1989). This formation was deposited during the Arctowski interglacial period (ca 50 to ca 32 Ma), a climostratigraphic unit introduced by Birkenmajer (1988).

Two informal units of the Point Thomas Formation are recognized at the Cytadela outcrop, the Lower Member (LM) and Upper Member (UM) (Birkenmajer, 1980). The LM is a 20–40 m thick regular high-Al flow basalt with a thickness of 1–6 m alternating with pyroclastic deposits. The UM comprises 150–450 m of irregular, lenticular basalt lavas alternating with feldspathic tuff, interbedded with coarse vent breccia and plant–bearing tuff.

13 samples were taken horizon-wise from the paleosols covered by the 6th basalt flow (from bottom to top) in the LM of the schematic field section made by Mozer (2012). Three profiles (P1, P2 and P3) were chosen, which are located with a distance of 60 m between P1 and P2 and of 90 m between P2 and P3 (Fig. 1). The basalts underlying and overlying the paleosols gave $^{40}Ar/^{39}Ar$ ages ranging between 51 and 48 Ma, confirming their Early Eocene age (Spinola et al., 2017a).

2.2. Field and laboratory analyses

The color (dry) of the samples was measured in the field under natural light using the Munsell Color Charts. For the subsequent laboratory analysis 13 paleosol bulk samples were ground to powder using a ball-mill with agate beakers.

2.3. Micromorphological and SEM-EDS analyses

The analyses were made in 9 × 6 cm thin sections and photographed using a polarizing microscope (Zeiss Axio Imager.A2m, Software AxioVision 4.7.2) with plane polarized light (PPL) and crossed polarized light (XPL). Oblique incident light (OIL) was obtained by an external light source with a double-arm swan neckglass fiber light guide. A detailed micromorphological description can be found in Spinola et al. (2017b) mainly using the terminology of Stoops (2003).

The morphology and microchemistry of iron nodules/mottles were determined using a Hitachi TM3030 Plus Scanning electron microscope (SEM) coupled with a Bruker Quantax 70 X-ray microanalysis detector (EDS) on polished uncoated thin sections at the Institute of Mineralogy and Geodynamics, University of Tübingen.

2.4. Diffuse reflectance spectroscopy (DRS)

The detection of goethite and hematite were performed by DRS after Torrent et al. (2007). DR spectra were recorded at a scan rate of 30 nm min^{-1} from 380 to 770 nm in 0.5 nm steps using a Varian Cary 5000 UV–Vis-NIR spectrophotometer equipped with a diffuse reflectance attachment. The samples were heated at different temperatures in a muffle furnace for 2 h at 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and measured after each heating interval. The reason for the heating is to help the identification of goethite, which is unstable at around 300 °C (Gialanella et al., 2010; Gualtieri and Venturelli, 1999) while hematite is rather stable. Thus, the goethite band should disappear after 300 °C, making easier to distinguish between the most intense absorption band of goethite at ~415 nm and a less intense absorption band of hematite at ~423 nm (Scheinost et al., 1998).

The second derivative of the Kubelka–Munk (K–M) remission function within the 380–710 nm range were calculated by using a cubic spline procedure based on segments of 30 data points. The intensities of spectral bands at ~415 nm and ~535 nm are proportional to the concentration of goethite and hematite, respectively (Scheinost et al., 1998). With this technique, it is possible to detect goethite and hematite concentrations of < 0.1%, which is more than one order of magnitude smaller than the detection limit of ordinary X-ray diffraction (Torrent and Barrón, 2002).

The spectra measurements were converted into tristimulus values (X, Y, Z) according to the CIE color system (Commission Internationale de L'Eclairage, 1978). Afterwards, the X, Y, Z values were converted to Munsell hue (H), value (V), and chroma (C) and to L* a* b* color systems (Wyszecki and Stiles, 1982). The L*-axis represents “lightness-darkness”, the a*-axis “redness-greenness”, and the b*-axis “yellowness-blueness”.

2.5. Selective iron extraction

The following extractions were made sequentially. First, the Fe in nanocrystalline compounds, basically ferrihydrite, was extracted by shaking 2.5 g of soil 100 mL 0.2 M acid ammonium oxalate (pH 3) for 4 h in the dark (Schwertmann, 1964) and is named Fe_o.