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Late Miocene-Pliocene coastal acid sulphate system in southeastern Australia and implications for genetic mechanisms of iron oxide induration

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ABSTRACT

Ferricrete – sediment cemented by iron oxides and hydroxides – is common in subaerial weathering environments around the world. Formed under alternating oxidising and reducing conditions, ferricretes record pedogenetic processes of translocation and concentration of iron and trace elements in the soil. Given their stability and high preservation potential, ferricretes can provide insights to ancient soil forming and weathering processes.

In this study the key processes controlling ferricrete geochemistry in a Neogene strandplain are identified and interpreted in the context of a coastal acid sulphate weathering system. Textural and geochemical variations in sediment indurated by hematite and goethite represent a record of in situ induration, erosion, and reworking. This development took place within an environment of fluctuating pH and Eh and subaerial wetting and drying cycles. We distinguished depositional and post-depositional processes based on the results of whole rock geochemistry, hyperspectral mineralogy, and major and trace element maps of petrographic thin sections. The ferricretes have three morphological types: flat-lying indurations, concentric pisoliths, and rounded nodules with fragmented internal textures. Successive laminae of Fe-oxides and hydroxides in all morphological types of ferricrete have variable Fe, Al, and Si abundances, reflecting cyclic precipitation and groundwater chemistry changes. Episodic wetting and drying of near coastal sediments was superimposed on a long-term trend of marine regression and local tectonic uplift (from ~7 Ma to present). This resulted in the diachronous exposure of relatively reduced shoreline sediments and concomitant acid production due to ferrolysis and the oxidation of biogenic sulphide. Local landform variations contributed to a wide variety of pedogenic processes and subsequent ferricrete formation. Acid sulphate weathering recorded by these indurated sediments is similar to conditions that are observed at present in the shallow water estuary of the Lower Lakes, near the mouth of the Murray River.

1. Introduction

Indurations, coatings, and crusts formed by iron (oxyhydr)oxides in sediments and weathered rocks – here referred to as ferricretes – are common features in a variety of environments from soils (Dawson et al., 1985; Gasparatos et al., 2004; Singh and Gilkes, 1992; Singh and Gilkes, 1996), sediments and saprolite (Beauvais and Tardy, 1993; Bourman, 1993; Butt, 1985), to caves (Frierdich and Catalano, 2012), as well as freshwater and marine environments (Banjeree et al., 1999; Hickey et al., 2008; Manceau et al., 2014; Schwertmann and Taylor, 1989). Ferricretes and similar materials, such as ferromanganese crusts, form in climates ranging from semi-arid to tropical (Bourman, 2010; Löhr et al., 2010; Macumber, 1991), and at different of stages in the geological record (Anand and Verrall, 2011; Firman, 1994; Milnes et al., 1985). Formed by alternating oxidation and reduction, the properties of ferricretes and related weathering products record the pedogenic environment in which they were formed (Gasparatos, 2012).

The two fundamental end-members of formation are in situ accumulation of goethite and hematite (collectively referred to as Fe-oxides in this study) (for example, Beauvais and Roquin (1996)) and disaggregated, transported ferricretes (for example, Bourman (1993)). Increasingly, studies are recognising the importance of several stages of formation, including transportation, erosion, and further alteration of indurated sediments (Löhr et al., 2010; Milnes et al., 1985; Thorne

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et al., 2014). Much of our understanding of ferricretes and ferromanganese crusts has come from relatively modern products, particularly for their role in acid mine drainage (Hickey et al., 2008), metal and metalloid contamination (Contin et al., 2007; Contin et al., 2008; Gasparatos, 2012; McKenzie, 1980), and potential as geochemical sample media (Butt et al., 2000; Chao and Theobald, 1976; Spinks et al., 2017). Given the geochemical stability of Fe-oxides and their resistance to physical degradation in terrestrial environments, ferricrete can be potentially preserved for considerable time in the landscape and reflect ancient pedogenic processes and subsequent reworking.

The Loxton-Parilla Sands in the western Murray Basin are a laterally extensive strandplain of predominantly marginal marine and minor fluvial sediments covering 140,000 km^2 of southeastern Australia (Fig. 1). Strandplains are important settings to study paleogeography and sedimentology because they record the prolonged interaction of fluvial and marine processes (Dunbar et al., 1992). The unit is a semi-confined aquifer and preserves a textural and mineralogical record of protracted syn- and post-depositional weathering processes during the Late Cenozoic. The stratigraphy and depositional setting of the Loxton-Parilla Sands have been the subject of a number of studies (Bowler et al., 2006; Brown and Stephenson, 1991; Miranda et al., 2009; Paine et al., 2004; Robson and Webb, 2011; Roy et al., 2000), as has the modern hydrogeology (Barnett, 1980; Berens et al., 2009; Brown and Radke, 1989; Brown and Stephenson, 1991; Cartwright et al., 2007; Cartwright et al., 2010; Macumber, 1991). The significance of depositional and post-depositional geochemical processes in this system has not been addressed in depth. Though the Loxton-Parilla Sands were deposited in marginal marine and fluvial environments and are predominantly quartz sand, there are marked variations in the morphology and geochemistry of weathering materials in the upper parts of the unit.

The indurated weathering profile in the Loxton-Parilla Sands has often been discussed as a separate stratigraphic unit. Named the Karoonda Surface by Firman (1975) and the Karoonda Regolith by Kotsonis (1995) it has been regarded as a chronostratigraphic marker, implying it was formed in a single continuous event that was initiated well after deposition of the unit. The accumulation of Fe-oxide in the unit has been interpreted as the result of periods of increased weathering triggered by temporally discrete shifts in climate (Bowler et al., 2006; Kotsonis, 1995; Miranda et al., 2009). Alternative scenarios of syn-depositional and ongoing geochemical processes have not been strongly considered. Integrating whole rock geochemistry with

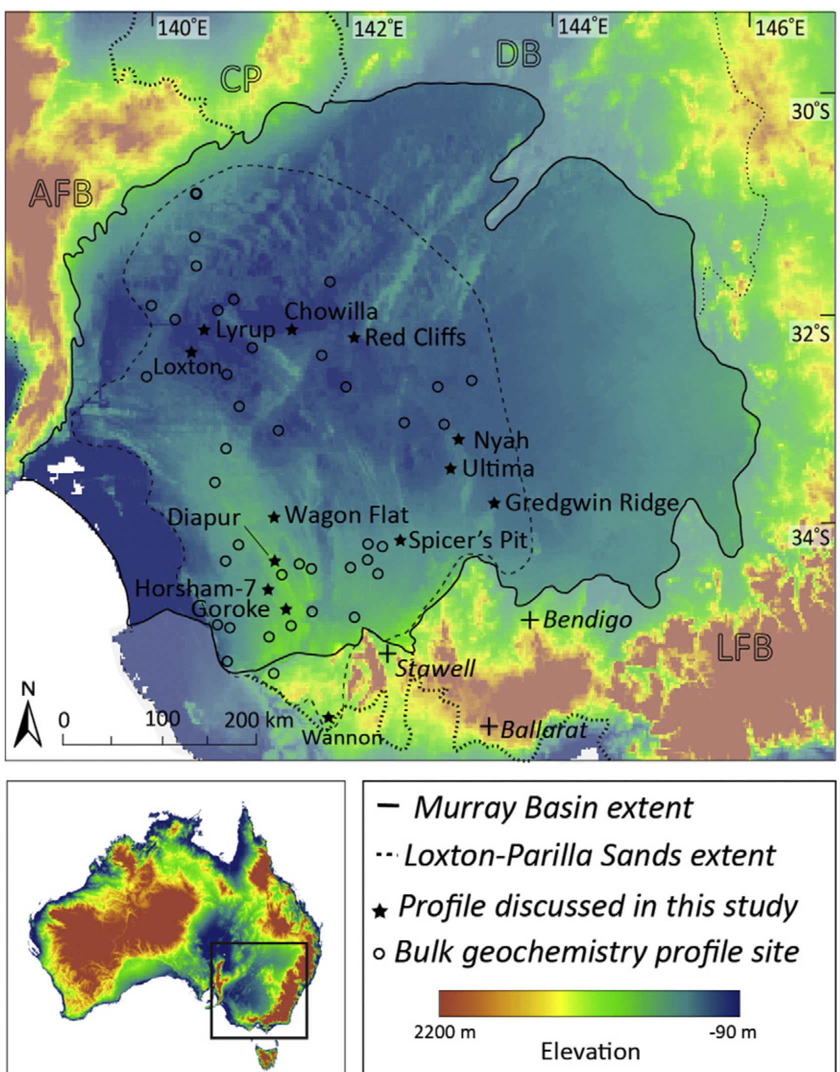

Fig. 1. Study location and extent of the Loxton-Parilla Sands in the Murray Basin, southeast Australia, and locations of profiles discussed in this study. The basin is bordered by geological terranes: AFB – Adelaide Fold Belt, CP – Curnamona Province, LFB – Lachlan Fold Belt, DB – Darling Basin.